ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 98 (1996) 103-111

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Supporting titanium dioxide photocatalysts on silica gel and hydrophobically modified silica gel

Giuseppe P. Lepore, Lalchan Persaud, Cooper H. Langford *

A110 The University of Calgary, 2500 University Dr. N.W., Calgary, Alta., T2N 1N4, Canada

Received 27 June 1995; accepted 29 September 1995

Abstract

This report describes preparation and characterization of TiO_2 supported on silica gels and modified silica gels. The objective is manipulation of the photocatalytic TiO_2 phase on the support, separately from manipulation of the organic solute adsorption and mass transport characteristics of the support. If the two features can be controlled separately, these systems should become good models for elucidation of mechanistic behavior of supported photocatalysts. TiO_2 characteristics and adsorption of substrates are key variables.

TiO_2 may be anchored on silica gel 100 by hydrolysis of $Ti(OR)_4$ (R=isoprophyl) or heating mixtures of silica gel and TiO_2 crystals (p25). In the first case, TiO_2 penetrates pores of silica gel and forms a phase which is either amorphous or of particle size small enough to give broad lines in powder XRD at angles suggesting anatase. In the second case, anatase particles too large to penetrate pores are anchored on the outer surface. The former method produces a superior photocatalyst. The silica surface can be modified by esterification with octanol to produce a photocatalyst which adsorbs solutes from an aqueous medium in a manner describable by an octanol/water partition coefficient. This modification has little effect on photocatalytic reactivity. A larger particle size silica gel (silica gel 58) produces a photocatalyst with TiO_2 in the interior of the pores which is less active for oxidation of 2,4-dichlorophenol but produces long-lived trapped electron colors in the presence of oxidizable substrates (e.g. propanol). This indicates a way to explore the role of intraparticle diffusion in the larger particles which are attractive for large scale applications.

Keywords: Photocatalysis; Titanium dioxide; Silica gel; Hydrophobic surface; Advanced oxidation process; Wastewater treatment

1. Introduction

In the effort to develop photocatalysts based on TiO_2 for the oxidation of organic wastes in aqueous streams, a great deal of recent effort has been devoted to developing supported TiO_2 catalysts [1-8]. There are two motives. One is simply to immobilize TiO_2 so that it is more readily handled in a reactor than the usual fine powder form of commercial TiO_2. The other is to try to modify the activity of the catalyst. Most of these systems have not yet produced photocatalysts superior to TiO_2 dispersions (see for example, Refs. [6,8]). TiO_2 presents a very polar surface to an aqueous medium. Water is more strongly adsorbed than a typical organic contaminant. One of the key properties of a support may be to provide a hydrophobic surface which adsorbs organics. This report describes a model system which allows manipulation of the hydrophobicity of the support and the distribution and form of the TiO_2 independently. It should prove a useful system for analysis of the factors influencing performance of supported photocatalysts. The system is based on the use of silica gel supports, silica gel 100 (particle diameters 0.06 to 0.20 mm — pore diameter 100 Å) and silica gel 58 (particle diameters 4 to 8 mm — pore diameter 140 Å). These supports may be surface modified by forming silicate esters of alcohols or by reaction with alkyltrichlorosilanes. The modified surface will have distinct and predictable adsorption properties for organic substrates.

2. Experimental

2.1. Apparatus

A Hewlett Packard UV-vis diode array spectrophotometer, (model HP8452) was used for optical absorption measurements, for chemical actinometry experiments, and for the semi-quantitative monitoring of photocatalytic reactions. Substrate concentrations and product yields were monitored with a Varian 5000 Liquid Chromatography instrument coupled with a 100 μl loop injector and a UV-vis variable wave-

---

* Corresponding author. Fax: + 1 403 289 8926.

SSDI 1010-6030(95)04242-3

length detector (set at 228 nm). The unit was interfaced to a Varian CDS 401 data station (Vista Series). A Varian MicroPak MCH-10 reverse phase column (30 cm long × 4 mm i.d. × 0.25 in o.d.) with 10 mm particle size was used. An isocratic elution was performed with a mobile phase mixture of 50% deionized distilled water, 35% methanol (Can LAB, HPLC grade) and 15% acetonitrile (Can LAB, HPLC grade). Aliquot samples were filtered through HVLP 0.45 μm pore size Millipore filters, before analysis.

Surface area and pore volume were determined with a Micrometrics instrument at low temperature using N_2 adsorption. A model 440 Elemental Analyzer (Control Equipment Corporation) was used for carbon and hydrogen determinations and materials for this analysis were weighed on a Cahn Micro balance C-31 (0.1 μg).

Surface characterization was performed with a Kevex scanning electron microscope (Cambridge Stereoscan 250) linked to an Analytical Spectrometer 6100 data processor which gave surface images and semiquantitative elemental measurements by monitoring microprobe X-ray emissions. An XDS 2000 (Scintag Inc) instrument was used to evaluate the X-ray diffraction patterns of various loaded silica supports. The instrument employed a Cu Kα radiation source with the voltage set to −45 kV and the current to 40 mA.

2.2. Photochemical reactors

Two distinct photochemical reactors with different geometry and irradiation arrangements were used. One reactor geometry (System I) was suited to powder samples with particle diameters of less than 1 mm while another (System II) was constructed for materials having diameters 2–8 mm. It modelled dynamic flowthrough reactors. In System I photoreactions were performed in a static, thermostated cylindrical Pyrex cell with 100.0 ml volume. The reactor was covered entirely with aluminum foil leaving an aperture of 3.14 cm^2 exposed to irradiation at the face of the quartz window. The light source was a GPTI 200 Watt Xenon-mercury lamp, powered by a LPS-250 PTI (Photon Technology International) power supply. A 10 cm water filter was placed in front of the reactor to remove IR from the light source. The light incident inside the photoreactor geometry was measured with potassium ferrioxalate actinometry [9]. The radiant intensity was determined to be 5.00 (±0.10) × 10^{17} photons S^{-1}.

The photocatalytic reactions in System II were effected in a vertically mounted Pyrex glass tube, 22 cm long and 8 mm wide, which had a dead volume of 35 ml. A 100.0 ml solution was continuously recirculated in the reactor zone from a 100 ml reservoir. The effluent was periodically monitored in a 1.00 cm flow cell set in the UV–vis spectrophotometer. The absorption spectrum was scanned from 200 to 800 mm. Illumination was carried out in a high intensity Rayonet^{TM} photochemical reactor (The Southern New England Ultraviolet Co. Hamden, CT) equipped with eight 350 nm lamps.

2.3. Stock solutions

Individual stock solutions of organic substrates containing respectively: 1.23 mM 2,4-dichlorophenol (2,4-DCP purchased from Aldrich 99 + %), 294 mM 2-chloro-1,4-hydroquinone (2-CHQ purchased from Aldrich 85%), and 350 mM 2-chloro-1,4-benzoquinone (2-CBQ purchased from Aldrich 95%), were prepared in distilled water. Before preparing solutions of 2-chloro-1,4-hydroquinone and 2-chloro-1,4-benzoquinone, the solids were purified by two successive sublimations.

2.4. Procedures

Titanium dioxide was anchored to a silica support by two separate procedures. One approach involved the treatment of silica gel with known amounts of titanium isopropoxide (Aldrich 97% purity) capable of reacting with silanol groups and also with the hydroxylated surface of TiO_2. The resulting sample was slowly hydrolyzed. Unreacted organic groups were burned away during calcination in air. The other procedure for anchoring titania onto silica was to thermally bind a commercial TiO_2 (p25 Degussa) onto the surface of the silica gel.

2.4.1. Method I

A silica gel 100 (EM Science, 70–230 mesh size) with 100 Å pore size and a 310 m^2 g^{-1} surface area was used to support TiO_2 prepared by the hydrolysis method. A 10 g sample of silica gel was transferred into a 400 ml beaker containing 250 ml hexane (Caledone, spectroscopic grade). The slurry was stirred with known amounts of titanium(IV) isopropoxide (0.1–8.0 grams) added dropwise. The slurry was immediately sonicated for 20 min and then stirred until the hexane evaporated. The dry sample was left to stand overnight to undergo slow hydrolysis in a covered 1.0 l beaker. A 50 ml beaker containing water was enclosed with the sample beaker to keep humidity at a constant level. The powder was then added to 375 ml deionized distilled water with vigorous mixing along with 2.5 ml concentrated nitric acid. The suspension was stirred with heating (80 °C) until most of the water evaporated. The sample was then dried in an oven at 105 °C overnight and afterwards calcinated in a Pyrex tube furnace at 500 °C for 12 h under a constant flow of moist air. The powder was washed with distilled water with vigorous shaking and decanting. Before each decantation, the mixture was allowed to settle for 5 min during which time the larger particles settled at the bottom. The finer silica particles along with suspended TiO_2 powder were decanted. This process removes TiO_2 particles which are not attached firmly to the silica gel. This process was continued until the supernatant was essentially free of suspended particles. The sample was finally washed on a Whatman 541 filter paper, repeatedly until the filtrate was transparent in the 350 nm region of the visible spectrum, where TiO_2 is known to absorb. Samples prepared by this procedure will be designated as {TiO_2/silica} for simplicity.

A coarse silica gel 58 material {Aldrich, 3–13 mesh size} was washed several times with distilled water and dried at 20 °C before the incorporation of titania. This material had a surface area of 300 m^2 g^{-1}, a 140 Å pore diameter, and a pore volume of 1.15 ml g^{-1}. Its particle size ranged from 4 to 8 mm. To a flask containing dry silica gel 58, an excess amount of titanium(IV) isopropoxide was introduced, completely covering the support material. The flask was stoppered and the mixture equilibrated for 24 h. Then, the excess titanium-containing liquid was decanted and the material left to stand for seven days on the lab bench for slow hydrolysis. Afterwards the silica was immersed in distilled water to complete the hydrolysis. The sample was then washed with distilled water and dried overnight in an oven set at 120 °C. The sample was removed from the drying oven and placed in a Pyrex tube furnace to be calcinated at 500 °C. It was noted that the mechanical strength of the modified silica gel 58 was increased by the inclusion of titania. Samples prepared by this method will be designated as {TiO_2/silica 58}.

2.4.2. *Method II*

A commercially available TiO_2 (p25, Degussa) was anchored onto silica gel 100, and silica gel 58. Samples prepared by this method will be designated as {p25 TiO_2/silica} and {p25 TiO_2/silica 58} respectively. The preparation was identical for each of the supports. 3 wt.% TiO_2 to silica gel was employed in successive loadings. A titanium dioxide slurry (pH ~2.5) was sonicated for a 20 min period before introducing the support into the beaker. The entire sample was sonicated for another 20 min. Most of solvent was then evaporated off by heating on a hot plate-stirrer. The sample was then placed in an oven set at 100 °C. The dry powder was then heated at 300 °C. All samples were thoroughly washed and filtered. The cycle was repeated when necessary to increase loading. Silica gel 58 and non-porous glass beads were loaded with p25 TiO in one step in a similar fashion. The non-porous glass beads, 3–4 mm in diameter were etched with 1.4 M NH_4F solution prior to loading. The final TiO_2 contents of silica gel 58 and glass beads were found to be 0.20 wt.% and 0.33 wt.%, respectively by weight increase.

2.5. *Derivatization of titania-support by silylation*

A 5 g sample of modified silica gel 100 (titania loaded) was transferred into a round bottomed two neck flask (50 ml), and evacuated to a pressure of 0.02 Torr. With a glass syringe, toluene was added to the stoppered flask and the slurry was stirred, while maintaining a low pressure. A known weight of octadecyl-trichlorosilane (Aldrich) was reacted with the support for two hours, subsequently excess toluene was removed and humid air was pumped into the flask. Later the sample was washed and filtered with hexane, methanol and acetone to remove unbound silane groups. To remove organic groups from the surface of TiO_2 the material was photolyzed for periods of 3 h in 75:25 methanol-water (employing the entire emission spectrum of the lamp in System I). The sample was then washed, filtered, and dried. After every treatment, the material was examined for its photoactivity and sorption properties using 2,4-dichlorophenol.

2.6. *Derivatization of titania-support by esterification*

The esterification of silica gel was performed by first heating the support at 200 °C to expel residual water which can slow down the esterification process on the support and reduce surface coverage. The hot silica gel was introduced into a 50 ml Teflon tube containing the alcohol reactant (e.g. 95% *n*-octanol, BDH) which was autoclaved at a temperature 20 °C above the boiling point of the alcohol for 12 h. The esterified material was then filtered and washed with hexane, acetone and methanol. The sample was photolyzed in methanol–water (75:25) for a duration of 3 to 4 h to oxidize the esters bound on the surface of TiO_2. The material was then washed, filtered and vacuum dried.

2.7. *Titanium analysis*

Where samples could be dissolved in acid, the estimation of TiO_2 loadings was done by a classical colorimetric method that is highly selective and sensitive to titanium [10]. The procedure involved the dissolution of TiO_2 in acid solution and the formation of an extractable titanium–thiocyanate complex which had a high molar extinction coefficient (4.10×10^{-4} M^{-1} cm^{-1}) in the visible region (422 nm). Several titanium standards were prepared from a stock solution containing 1.291 g of titanium (IV) propoxide (Aldrich, >99% purity) dissolved in a 500 ml volumetric flask using 6 M sulfuric acid. Extraction efficiencies of 99.9% were obtained with several standards and the molar extinction coefficient at 422 nm was determined to be 4.10×10^{-4} M^{-1} cm, in agreement with the value reported by Young and White [10].

Samples were prepared as follows. A weighed sample (0.600–1.000 g) containing TiO_2 or a blank (silica only) was dissolved in a flask containing equal volumes (100 ml) of concentrated sulfuric acid and hydrochloric acid; this was then heated at 80 °C for several days. The samples were regularly sonicated for 30 min periods during dissolution. After dissolution was complete, the solutions were cooled and gradually diluted with 100.0 ml distilled water. Titanium was then complexed with the addition of 4 g of ammonium thiocyanate (Fischer, 99% purity). The complex was extracted with 50.0 ml of 0.050 M tri-*n*-octylophospine oxide (Terochem Laboratories Ltd.) in hexane under vigorous stirring for 20 min followed by a 15 min settling period. Samples were then diluted with hexane and an absorption spectrum taken in a 1.00 cm cell at 422 nm.

3. Results and discussion

3.1. Characterization of modified supports

Silica gel 100 is a porous and hydrated material with 100 Å pore diameters. Since Ti(IV) isopropoxide has a molecular diameter less than 10 Å, it should be feasible to hydrolyze it within the pores. Loading TiO_2 on the support decreases the surface area (BET) of the silica gel (Fig. 1). Pore volume changes were small suggesting that most of the loading is on the outer surface or in thin layers. Calcination of the silica support (without TiO_2) at a temperature of 400 °C (for 8 h) had no major effect on the surface area or pore volume.

X-ray powder diffraction patterns were obtained for TiO_2 modified supports. A sample which contained 0.83 wt.% TiO_2 displayed an X-ray diffraction pattern that was broad and featureless with hardly any sign of TiO_2 crystallinity. The broad reflection at lower angle, corresponds to the amorphous silica gel. Higher TiO_2 loading (2.8 wt.%) samples exhibit broad peaks at angles similar to those for anatase (Fig. 2).

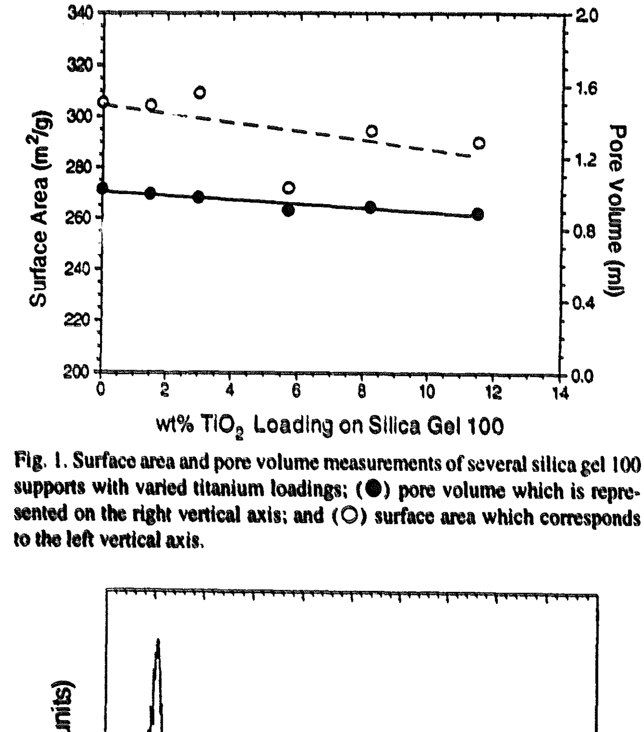

Fig. 1. Surface area and pore volume measurements of several silica gel 100 supports with varied titanium loadings; (●) pore volume which is represented on the right vertical axis; and (○) surface area which corresponds to the left vertical axis.

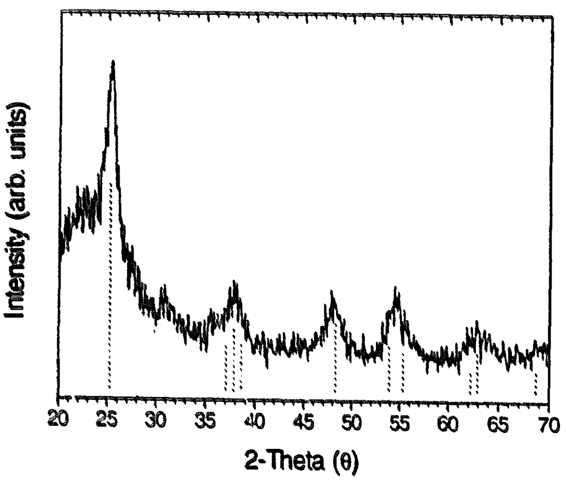

Fig. 2. Powder XRD of a 2.8 wt.% TiO_2 loading on a silica gel 100 support (Method I). Dotted vertical lines represent the TiO_2 anatase pattern.

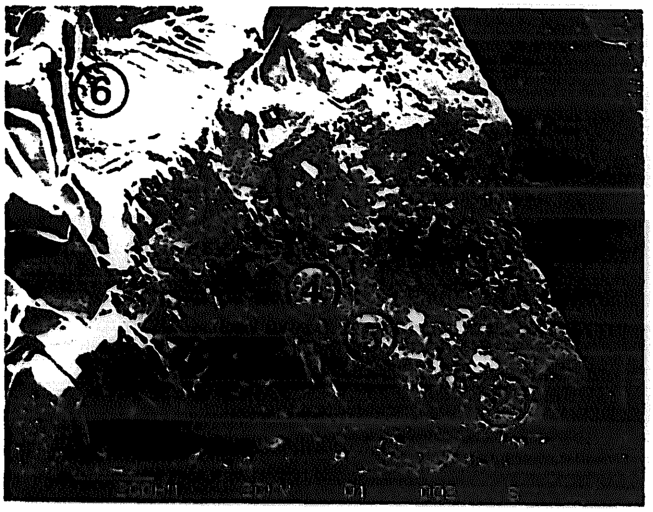

Fig. 3. Scanning electron microscope image of {TiO_2/silica} loaded with 2.5 wt.% TiO_2 prepared by Method I. Elemental composition monitored by X-ray emission spectroscopy; region 1 represents an aggregated fragment of titanium oxide (0.78 Ti/Si ratio), and region 2 corresponds to low titanium loading (0.14 Ti/Si ratio). Intermediate values of the Ti/Si ratio were found at points marked 3 through 6.

The X-ray diffraction pattern of crushed silica gel 58 which incorporated TiO_2 (Method II) also revealed the presence of reflections at angles similar to anatase.

Scanning electron microscopy (SEM) coupled with an emission microprobe furnished a semi-quantitative elemental analysis of the surface using the X-ray emitted by the elements and provided a view of the surface of a TiO_2 modified silica prepared via Method I. Fig. 3 shows a {TiO_2/silica} sample SEM image.

To clarify the features in the photograph, two regions were chosen for microprobe analysis. In Fig. 3, region 1 exhibits a Ti/Si ratio of 0.8 while region 2 gives a Ti/Si ratio of only 0.1. The visible layers assigned to titanium oxide in region 1 are extensively cracked with individual fragments displaying nearly smooth surfaces. Gratzel and co-workers [11] reported similar features in their preparation of thin TiO_2 films on metallic titanium foils. The distribution of titania on the surface of the silica is consistent with the BET analysis (Fig. 1). Elemental composition of the modified surface of several samples prepared by Method I (with 2.5 wt.% TiO_2 loading), showed a similar distribution of titanium, with an approximate Ti/Si ratio of 0.2 on the support surface. The surface roughness of a support is an essential aspect of the anchoring to TiO_2 to the surface of supports. The maximum amounts of titanium are found near the fractures of the support.

In contrast to silica gel 100, titanium loading into silica gel 58, by Method I, resulted in a sample which exhibited nearly a uniform distribution within the pores, decreasing with depth into the structure (Fig. 4). Much more Ti was successfully incorporated. It was possible to slice these large silica particles and study Ti distribution as a function of depth into the particle.

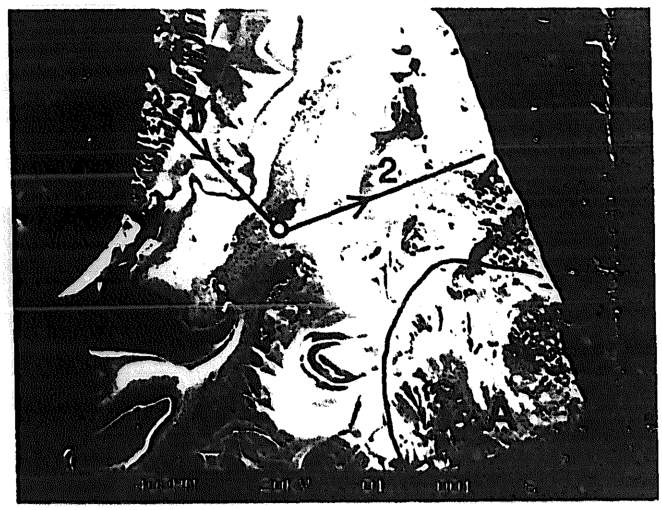

Fig. 4. Scanning electron microscope image of a sliced silica gel {TiO_2/silica 58} particle containing 13 wt.% TiO_2 loading (prepared by Method II); lines show paths taken to illustrate elemental composition (see Fig. 5).

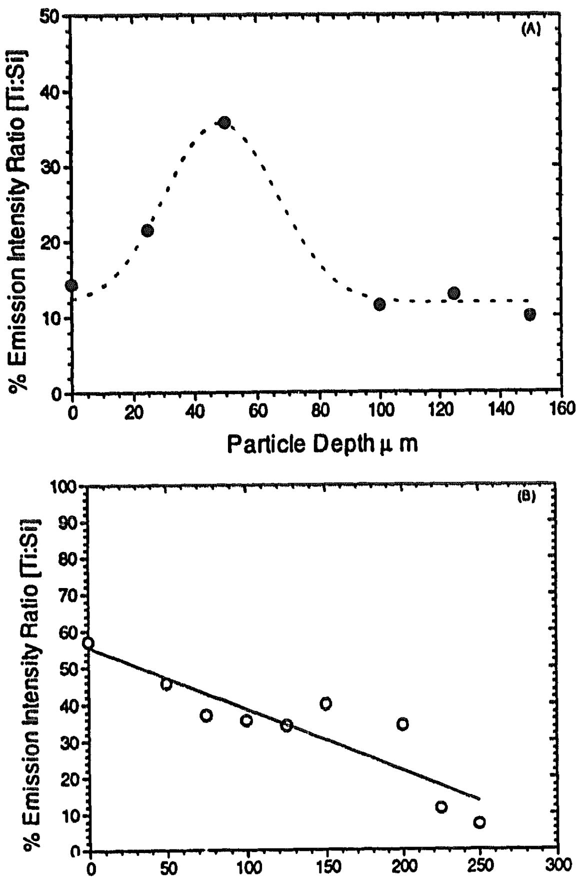

Fig. 5. Semi-quantitative concentration profile of titania vs. particle depth in the slice of the {TiO_2/silica 58} particle taken from Fig. 4. (A) profile taken from path 1 (B) profile of path 2.

A relatively high concentration of TiO_2 was found within the first 50 μm from the surface of the support (Fig. 5). No aggregates of TiO_2 were observed by the SEM technique, suggesting that thin films were indeed produced within the pores. In Fig. 5, a semi-quantitative titanium concentration profile is plotted against depth into the particle. Profiles of TiO_2 content were taken along two separate paths from a sliced silica particle (see Fig. 4). The curves in Figs. 5(A) and (B) suggest heterogeneous pore sizes and organization throughout the support. In Fig. 5(A), a maximum relative concentration on the path is reached at a depth of about 50 μm. The path shown in Fig. 5(B) shows high titanium at the surface which decreased monotonically with depth. The reasons for the different distributions along the two paths is not at all clear, but both show significant TiO_2 penetration.

The accessibility of pores (and partially modified pores) in the TiO_2 loaded sample was examined by mixing the modified silica gel into a methylene chloride solution containing zinc tetraphenylporphyrin (ZnTPP). The area of the metal porphyrin is approximately 165 Å^2 per molecule [12,13] and it displays a strong red color in solution. However, when ZnTPP diffused into the pores of the silica gel, the color of the support turned from white to dark green, suggestive of strong interaction between the metal porphyrin and the interior of the pore structure of the modified silica gel. A slice of the modified silica particle revealed that the dark green color (ZnTPP) was distributed throughout the support. This implies that the pores remain open for substrates to diffuse.

A scanning electron microscopic image of a support with commercial Degussa p25 TiO_2 anchored, prepared via Method II, revealed an intact support with an external scabrous surface that contained fissures. The surface of the silica gel 100 displayed irregular TiO_2 particles that accumulated in clumps and randomly distributed over the silica gel sample.

3.2. Relative photocatalyst activity

Photocatalytic activity in the oxidation of 2,4-dichlorophenol (2,4-DCP) was adopted to screen photochemical activity as a function of TiO_2 loading. {TiO_2/silica} prepared by Method I was examined in reactor System I and the results are summarized in Table 1. The photocatalytic reactions were conducted with 0.300 g of material and monitored after an irradiation time of 120 min for the loss of 2,4-dichlorophenol

Table 1
Relative photoactivity of TiO_2 supported on a silica gel 100

wt.% TiO_2	Loading method	% 2,4-DCP [a] consumed
0.83	I	9
1.5	I	18
2.5	I	29
2.8	I	38
16.7 [b]	p25 – II	23

[a] Result of 2 h irradiation of 319.0 mM 2,4-dichlorophenol solution in reactor I.

[b] It was not possible to fully dissolve p25 anchored to silica gel. The wt.% TiO_2 is that of a physical mixture of p25 and silica gel 100 with the same photoactivity as the anchored sample. We do not know the exact TiO_2 loading of the sample prepared by method II but it is probably close to the reference physical mixtures (see text).

from a 319.0 μM solution. An analysis of TiO$_2$ loadings by the colorimetric technique (10) demonstrates the dependence of photoactivity on TiO$_2$ loading (Table 1).

Thermal treatment to affix a commercial crystalline p25 TiO$_2$ on silica gel (Method II – {p25 TiO$_2$/silica}) was used to obtain an exclusively surface-attached TiO$_2$ for comparison with TiO$_2$ distributed through the support {TiO$_2$/silica}. The p25 anchored onto the silica support must be mainly fastened on the surface and not within the pores of the support since its particle diameter (30 nm) exceeds that of the silica pores (10 nm). As noted above, SEM shows attached aggregates of p25 TiO$_2$ particles randomly distributed over the surface. The metal oxide photocatalyst did remain primarily anatase, after thermal treatment at temperatures below 300 °C. The titanium loading of p25 TiO$_2$ onto silica gel was determined indirectly since dissolving the powders was more difficult than TiO$_2$ films chemically produced on silica. A standard curve was constructed with a series of known amounts of dispersed p25 TiO$_2$ mixed with a fixed mass of silica. Rate constants for the photocatalytic oxidation of 319.0 μM 2,4-DCP (in 100.00 ml aqueous solutions) were then determined, for each separate TiO$_2$ quantity. The measured rate constants were plotted against TiO$_2$ amounts (g) and the value obtained was used to approximate a titanium loading from rate constants that were estimated for samples that had p25 TiO$_2$ bonded onto silica.

It was noted that mixing in the silica gel had no detrimental effect on the photocatalytic activity at TiO$_2$ levels above 8 mg 100 ml^{-1} TiO$_2$. To the extent that this indirect approach gives even a crude measure of loading, {p25 TiO$_2$/silica} appears to be an inferior photocatalytic material when compared with {TiO$_2$/silica} sample (Table 1). Furthermore, supports modified by Method I were found to be more resistant to mechanical attrition.

The large particle silica gel supports (silica 58) were employed to provide a model aimed toward evaluation of consequences for scale up in an industrial process. Batch production of TiO$_2$ modified silica 58 was carried out by Method I. The photocatalytic activity of these modified supports was compared to a reference sample that had commercial p25 TiO$_2$ anchored to non-porous glass beads. For photocatalytic evaluation the titanium loaded supports that had a bead size of 3 to 8 mm where studied in System II. An aqueous solution containing 319.0 μM 2,4-dichlorophenol was recirculated from a 100.00 ml reservoir through a Pyrex cell placed inside a photochemical reactor and the effluent was periodically monitored directly by UV–vis spectrophotometry (at 284 nm) in a 1.00 cm flow cell, and also by HPLC (with 224 nm detection).

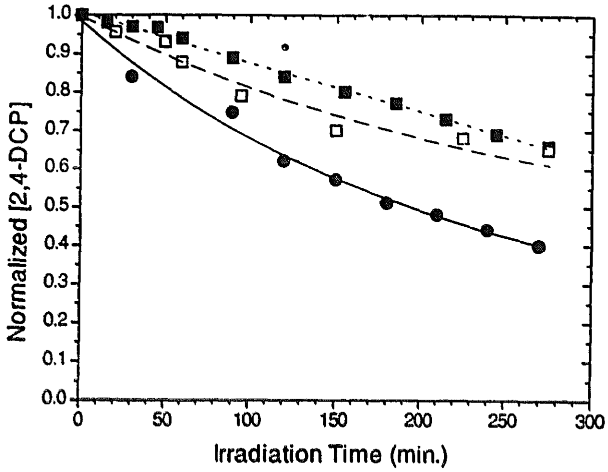

Fig. 6. Photo-oxidation of 319.0 μM 2,4-dichlorophenol aqueous solution by several individual titanium loaded supports (3–8 mm size) in a flow through photoreactor System II. Relative 2,4-dicholorophenol concentrations are shown, (compared with concentration at 5 = 0) (●) 6.00 g etched beads-p25 TiO$_2$ (0.33 wt.% TiO$_2$ loading); (□) 2.90 g {p25 TiO$_2$/silica gel 58} containing a 0.20 wt.% TiO$_2$ loading; and (■) 3.00 g {TiO$_2$/silica gel 58} with a 13 wt.% TiO$_2$ loading. Access to TiO$_2$ inside the larger beads seems limited since silica gel 58 produces a better photocatlyst with a low loading of surface bound p25 particles. It is not unlikely that TiO$_2$ incorporated by method II may not be absorbing all of the incident light at 300 to 350 nm owing to the small particle size formed inside the silica, which may shift the absorption band edge of TiO$_2$ to the blue region of the spectrum. This behavior was pointed out by Yoneyama et al., [25] who studied 50 wt.% TiO$_2$ polycations incorporated in sheet silicates of clay compared with TiO$_2$ suspensions.

The non-porous glass beads appear to have a higher activity in the photocatalytic removal of 2,4-DCP than the remaining supports (see Fig. 6). This may be due primarily to the greater surface area of p25 TiO$_2$ exposed on the surface of the glass beads, since that sample had a lower titanium loading when compared with {TiO$_2$/silica 58}. A non-linear 2,4-DCP disappearance curve was observed after prolonged irradiation. The {p25 TiO$_2$/silica 58} with 0.20 wt.% TiO$_2$ loading displayed similar curvature to that observed for the glass bead reference, appearing at lower conversion owing to lower titanium loading. This tends to suggest a role for product build up on the surface rather than control by reduced solution concentration, since solution concentration effects should not depend upon titanium loading if surface sites release product rapidly. For both materials which had anchored p25 TiO$_2$, the photocatalytic reactions occurred on the surface of the support and not within the pores since pore diameters do not exceed 14 nm and 30 nm p25 particles cannot penetrate (see SEM images. Apparently, photocatalytic activity is strongly influenced by substrate diffusion when large particle supports are used. This was not observed for smaller silica 100 supports (Table 1).

A light yellowish color was detected upon contact of {TiO$_2$/silica 58} with 319.0 μM 2,4-DCP. The solid began to turn darker in color upon band-gap illumination. This suggests that the pores do contain extremely small, large surface area, TiO$_2$ particles that form a charge transfer complex with 2,4-DCP similar to that reported in Ref. [14]. The yellow color was not seen in the other two materials.

When a {TiO$_2$/silica 58} sample prepared by Method I was irradiated in the presence of various organic solutes, including 1-propanol, chloroform and carbon tetrachloride, an intense blue color appeared. The intensity of the color was higher for a sample containing 1-propanol while carbon tetrachloride produced the least intense color. Furthermore, the color appeared throughout the silica support, implying that the support was indeed translucent to irradiation. The color implies build-up of a steady state electron concentration which is not rapidly discharged [15]. This again implies that small particle, thin film TiO_2 has been produced in the interior of the porous silica upon the hydrolysis of titanium(IV) isopropoxide. There may be an advantage to working with transparent supports that incorporate thin films of TiO_2 (i.e. porous silica); the supports can assist in the trapping of light by internal reflection. No blue color was observed in the reference glass bead material or {p25 TiO_2/silica 58}. Upon the addition to the irradiated suspension of {TiO_2/silica 58} of a few drops of 30% H_2O_2 as an electron scavenger, the blue color disappeared rapidly. However, if the solution was exposed to air, the color persisted for several days. If the solution was purged with nitrogen, the blue color persisted for several weeks. The length of time that the excess electrons remain will depend on the diffusion rate of electron acceptors in the solution and into the pore structure of the silica gel. These experiments indicate that diffusion of electron acceptors into the large particles may be overall rate limiting in photocatalytic reactors.

3.2.1. *Support derivatization and photocatalysis*

The aim of this last set of experiments is to render the support hydrophobic to improve substrate adsorption [16]. Two approaches were employed to render TiO_2 modified silica gel organophilic (hydrophobic):esterification and silylation [17]. (Note that a fully organophilic surface might prevent wetting and make the material float).

The adsorption sites in silica gel include silanol groups with single ("free"), vicinal or geminal OH [17,18]. All are capable of reacting with silanes and alcohols. Moreover, the TiO_2 can also be chemically modified, since the photocatalyst contains terminal (Ti^{IV}–OH) and bridging –OH groups (where one OH group bridges two surface vicinal Ti^{IV}; ions) [19] where all the surface –OH groups are accessible for reactions. Therefore, it is imperative that after the derivatization of the TiO_2/silica surface, the material is photolyzed with light energy ≥ band-gap energy of the anchored photocatalyst in a suitable solvent to attempt to remove chemically bonded organic functional groups on TiO_2. Covering of the TiO_2 surface would, no doubt, inhibit photcatalytic activity.

3.2.2. *Consequences of silylations*

A 0.300 g sample of silylated {TiO_2/silica} with 1.8 wt.% TiO_2 which had been photolyzed to uncover TiO_2 by oxidation of attached organic groups was suspended in 100 ml of 319.0 μM 2,4-DCP and equilibrated in the dark in System I. 2.0 ml aliquots were removed, periodically filtered, and monitored (UV–vis spectrophotometer) at 284 nm in a 1.00 cm quartz cell. At the early stages of the solution, 2,4-DCP loss curves are illustrated in Fig. 7. Adsorption from 319.0 μM 2,4-DCP took less than 50 min to reach a dark (light off) equilibrium of 40% 2,4-DCP removed, substantially different from the small dark adsorption in the absence of silylation. However, the sample exhibited poor photocatalytic activity. This is not surprising since the SiO on the TiO_2 surface [18–20] is probably not destroyed by the light treatment and TiO_2 may be blocked by an SiO layer.

3.2.3. *Consequences of alcohol esterification*

The esterification with pure octanol on a {TiO_2/silica} granular powder with a 1.8 wt.% TiO_2 loading, was performed under autoclave conditions, although the process could have been accomplished under high temperature reflux. The esterification was reversed on the TiO_2 surface by the illumination in the presence of alcohol. The dark sorption and

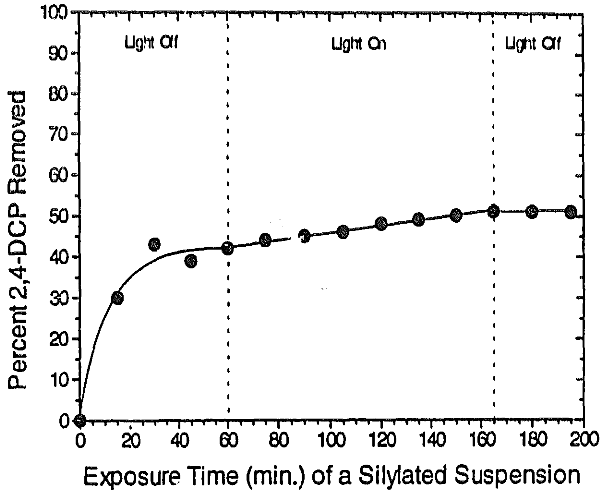

Fig. 7. A time profile of dark sorption and possible photocatalytic reaction of 2,4-dichlorophenol, 319.0 mM in 100.00 ml aqueous suspension containing 0.300 g silylated {TiO_2/silica} (1.8 wt.% TiO_2 loading). The esterification was reversed on the TiO_2 surface by exhaustive illumination open to air. It appears that an SiO layer is left on the photocatalyst, inhibiting activity. The experiment employed photoreaction system I.

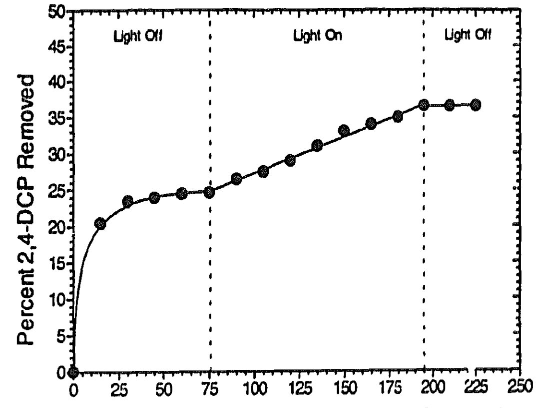

Fig. 8. A time profile of dark sorption and the photocatalytic reaction of 2,4-dichlorophenol, 319.0 mM in 100.00 ml aqueous suspension of 0.300 g of octanol esterified octyl {TiO_2/silica} sample (1.8 wt.% TiO_2 loading). The esterification was reversed on the TiO_2 surface by exhaustive illuminations open to air. The experiment employed photoreactor system I. Note significant photoreactivity. The TiO_2 appears to be accessible.

Table 2
Elemental analysis of esterified support surfaces

Sample analyzed (wt.%) TiO_2	Alkyl FW ($g\,M^{-1}$)	Sample mass (μg)	Percent carbon	Percent hydrogen	Alkyl groups ($M\,g^{-1}$ of support)	[a] 2,4-DCP adsorbed (%)
[b] Silica gel		1957.7	0	0.090	0	<5
TiO_2/Silica–CH_3 [c] (0.13%)	15.04	1423.6	0.56	0.14	5×10^{-4}	<5
TiO_2/Silica–C_4H_9 [c] (0.13%)	57.11	2096.7	3.40	0.60	6.6×10^{-4}	~5
TiO_2/Silica–PC_8H_{17} [c] (1.8%)		3464.3	6.63	1.24	5×10^{-4}	25
p25/Silica–C_8H_{17} [d] (6.2%)	113.2	2478.2	7.00	1.18	6.6×10^{-4}	26

[a] 316.0 μM 2,4-DCP solution was equilibrated with sample material for 60 min;
[b] silica gel 100 was heated at 500°C;
[c] titanium loaded by Method I;
[d] titanium loaded by method II.

the photocatalytic activity of this octyl {TiO_2/silica} toward a 319.0 μM 2,4-DCP is shown in Fig. 8. The equilibrium dark sorption of 2,4-DCP was about 23%. The photocatalytic activity was greater than that observed for silylated {TiO_2/silica}, as expected.

A parallel sample prepared by esterifying a {p25 TiO_2/silica} with octanol displayed dark adsorption similar to that of octyl {TiO_2/silica} where TiO_2 is dispersed and in the particle interior. However, it was less photocatalytically active. The intimate mixing of the small TiO_2 particles and hydrophobic surfaces may be beneficial. Several other esterified samples were prepared with alkyl groups CH_3 and n-C_4H_9 — as well as n-C_8H_{12}–. The ester loadings are shown in Table 2, which reports results of C, H analysis. Similar levels of esterification were achieved as long as silica gel 100 remained the support. As might be expected, adsorption of 2,4-DCP from the test solution in the dark decreased with the decrease of alkyl chain lengths. There are precedents in the literature of chromatographic supports [21]. The higher ester loading on the {p25 TiO_2/silica} may again reflect the surface bonding of p25 particles as compared to the penetration into pores of TiO_2 prepared by hydrolysis.

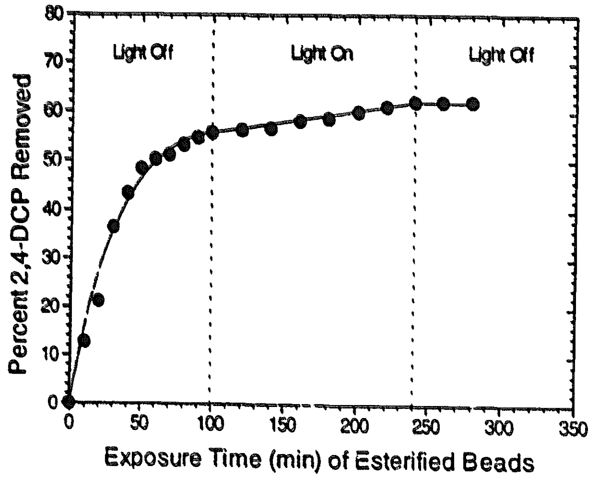

Fig. 9. Time profile of dark sorption and the photocatalytic consumption of 2,4-DCP from a 319.0 mM 2,4-dichlorophenol aqueous solution. The reaction employed a dynamic photoreactor (system II). A solution of 100.00 ml was recirculated in a cell containing 3.00 coarse octyl-{TiO_2/silica 58} sample which had a 13 wt.% TiO_2 loading, freed of ester by extensive illumination.

A 3.00 g sample of a TiO_2 loaded silica gel 58 (Method I) esterified with n-octanol, was used to study the sorption behaviour of coarse silica beads toward 319.0 μM 2,4-DCP in reactor System II. The percentage of 2,4-DCP removed in the dark approached a maximum of 55% after a circulation time of 100 min (Fig. 9). When the photoreactor lamps were turned on, the photocatalytic reaction proceeded only slowly. A supplemental photoactivity test was performed on the beads in the photoreactor. A 3.0 M propanol solution was added to the 100.00 ml reservoir. If the TiO_2 is photoactive, a blue color should appear. After 15 min a blue color had appeared and became intense on prolonged irradiation. Thus the coarse octyl-{TiO_2/silica 58} support (13 wt.% TiO_2 loading) was indeed photo-active. Low conversion of 2,4-DCP may signal that most of the substrate is retained in the octanol "phase" unavailable to TiO_2. We test the concept of octanol phase below.

3.3. *Estimates of 2,4-DCP adsorption from octanol/water particoefficients*

It is expected that "adsorption" is the dominant adsorption mechanism for short chain hydrocarbons, whereas solute "phase partition" would dominate for longer chains [22]. The distinction between the two sorption processes lies in how the solutes interact with the bonded organic phase. In solute adsorption, the solute forms a monomolecular layer on the bonded organic phase and with the exposed surface of {TiO_2/silica}. In solute partition, the substrate becomes fully embedded within the bonded phase ("dissolved in") rather than adsorbed onto the surface of the support or hydrocarbon chain. This partition model is, of course, described in bulk phase separations between the commonly used octanol and water phases [23]. If partition occurs with octyl {TiO_2/silica} it should be possible to predict adsorption in the dark from the partition coefficient, or the reverse, to calculate the partition coefficient from dark adsorptions. Since it displayed large sorption, a sample of octyl-{p25 TiO_2/silica} powder that had 6.2 wt.% TiO_2 is used to estimate an octanol/water partition coefficient value (P_{oct}) for 2,4-DCP. Two values of P_{oct} for 2,4-DCP are reported in the literature [23]; an experimentally determined $\log P_{oct} = 3.16$ and a thermodynamically calculated value of $\log P_{oct} = 2.93$.

A plot of 2,4-DCP concentration sorbed onto the support against 2,4-DCP remaining in solution gave a linear relation for a concentration range from 25.0 to 320.0 mM. The slope gave a value of $\log P_{oct} = 3.04 \pm 0.06$, within the literature range. Solute partition appears to be the dominant process on the octanol esterified supports.

4. Conclusion

The work has shown that TiO_2 may be supported in porous silica (silica gel 100) as a phase which is either amorphous or of small enough particle size to give only wide lines in XRD powder patterns. In this form it is a superior photocatalyst to TiO_2 crystals (p25) anchored on the surface of silica gel. The photocatalyst can be made a better adsorbent for removal of a contaminant from an aqueous medium by alcohol esterification of the silica gel surface. This esterification has little effect on photocatalytic activity. The adsorption characteristics of an octanol esterified surface are similar to an octanol phase.

If a larger particle silica (silica gel 58) is used, hydrolytically formed TiO_2 can reach the particle interior. Activity for oxidation of 2,4-dichlophenol is reduced, but photoactivity is demonstrated by generation of long-lived trapped electron color.

The series of samples illustrates opportunities to tune TiO_2 structure, adsorptivity toward organic solutes, and pore diffusion characteristics as semi-independent variables. This provides a suite of tools for investigation of mechanisms on supported photocatalysts [24].

References

[1] D.F. Ollis, in M. Schiavello (ed.), *Photoelectrochemistry, Photocatalysis and Photoreactors*, Reidel, Dordrecht, 1985, p. 663.

[2] G.P. Lepore, B.C. Pant and C.H. Langford, *Can. J. Chem.*, *71* (1993) 2051.

[3] N. Serpone, E. Borgarello, R. Harris, P. Cahill, M. Borgarello and E. Pelizzetti, *Sol. Energy Mater.*, *14* (1986) 121.

[4] R.W. Matthews, *Australian Patent Application, Canberra, Australia*, 22 July 1986.

[5] R.W. Matthews, M. Abdullah, G.K.-C. Low, *Anal. Chim. Acta.*, *223* (1990) 171.

[6] R.W. Matthews, *Solar Energy*, *38* (1987) 405.

[7] R.W. Matthews, *Res. Water*, *25* (1991) 1169.

[8] N.B. Jackson, C.M. Wang, Z. Luo, J. Schwitzgebel, J.G. Ekerdt, J.R. Brock and A. Heller, *J. Electrochem. Soc.*, *138* (1991) 3660.

[9] J.N. Pitts and J.G. Calver, *Photochemistry*, Wiley, New York, NY, 1966, p.783.

[10] J.P. Young and J.C. White, *Anal. Chem.*, *31* (1959) 393.

[11] C. Mailhe-Randolph, A.J. McEvoy and M. Gratzel, *J. Mater. Sci.*, *26* (1991) 3305.

[12] J.A. Mercier-Smith and D.G. Whitten, *J. Am. Chem. Soc.*, *101* (1979) 6620.

[13] J.E. Bulkowski, R.A. Bull and S.A. Sauerbrunn, in A.J. Nozik (ed.), *Photoeffects at Semiconductor–Electrolyte Interfaces*, ACS Symposium Series 146, American Chemical Society, Washington, DC 1981, p.279.

[14] G.R. Wiese and T.W. Healy, *J. Colloid Interface. Sci.*, *51* (1975) 427.

[15] A. Henglien, *Ber. Bunsenges. Phys. Chem.*, *86* (1982) 241.

[16] J. Cunningham and S. Srijaranai, *J. Photochem Photobiol. A: Chem.*, *43* (1988) 329.

[17] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, NY, 1979.

[18] A.H. Boonstra and C.J. Mutsaers, *J. Phys. Chem.*, *79* (1975) 1940.

[19] H.O. Finklea and R. Vithanage, in J.S. Miller (ed.), *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, ACS Symposium Series 192, Washington, DC, 1982, p.185.

[20] S. Sato, *Langmuir*, *4* (1988) 1156.

[21] A.M. Krstulovic, H. Colin, A. Tchapla and G. Guiochon, *Chromatographia*, *59* (1987) 2309.

[22] J.G. Dorsey and K.A. Dill, *Chem. Rev.*, *89* (1989) 331.

[23] K. Verschueren (ed.), *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Rheinhold, New York, 2nd Edn., 1983, p. 37.

[24] H. Yoneyama, S. Haga and S. Yamanaka, *J. Phys. Chem.*, *93* (1989) 4833.