In Situ Infrared Spectroscopic Studies of Adsorption of Lactic Acid and Related Compounds on the TiO_2 and CdS Semiconductor Photocatalyst Surfaces from Aqueous Solutions

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In situ attenuated total reflectance infrared (ATR-IR) spectroscopy has been used to determine the structure of adsorbed lactic acid (LA) compounds on the surfaces of titanium dioxide (TiO_2) and cadmium sulfide (CdS) photocatalysts. LA was found to chelate onto the TiO_2 in a bidentate fashion, while in the CdS case, LA was adsorbed electrostatically as the lactate ion. These differing surface interactions are likely to determine the selectivity in the photo-products of LA.

The specificity in the synthesis of the desired product is of particular interest to organic chemistry. Differences in the photo-products of LA with CdS and TiO_2 semiconductors have been investigated by Harada and co-workers.[1] They have shown that Pt-loaded TiO_2 gave acetaldehyde as the product, while CdS formed pyruvic acid. From electrolytic and chemical oxidation studies of LA, they have proposed that the selectivity depending on the semiconductors are attributed to the differing oxidation mechanisms and/or the structure of the adsorbed molecules on the semiconductor surfaces, rather than the position of the valence bands of the respective photocatalysts.[1] However no vibrational spectroscopic observations have been carried out so far to support this speculation. This paper briefly describes the application of an *in situ* ATR-IR technique in determination of adsorbate structure at the photocatalyst surfaces. The infrared spectra have revealed the different adsorption behaviour of LA on the TiO_2 and CdS surfaces.

TiO_2 sol was prepared by hydrolysis of $TiCl_4$.[2] Colloidal CdS was prepared by slow mixing of aqueous $Cd(NO_3)_2$ and Na_2S solutions.[3,4] These sols have been shown previously to have efficient photocatalytic ability.[5] All solutions were prepared using Milli-Q water and purged with oxygen-free nitrogen prior to mixing. Colloidal TiO_2 and CdS films were deposited on a ZnSe 45° single reflection ATR prism (Harrick Scientific Corporation) by room-temperature evaporation in air of 100 mm^3 of the respective colloidal solutions. All films were treated with an alkaline wash prior to use to remove any surface contaminants.[6,7] All infrared spectra were recorded in the dark on a Digilab FTS60 spectrometer fitted with a DTGS detector and a Harrick Prism Liquid Cell accessory. The details of similar measurements have been given previously.[8]

The infrared spectrum of species adsorbed on a TiO_2 sol-gel film from a $1x10^{-3}$ mol dm^{-3} aqueous LA solution is shown in Figure 1(a). The spectrum shows absorption bands at 1614 and 1381 cm^{-1}, assigned to the antisymmetric and symmetric stretch modes of the carboxylate groups.[9] The additional bands at ~1120 and ~1050 cm^{-1} are assigned to vibrations of the methyl group (CH_3-C). The contributions of solution species are negligible at this concentration, since no appreciable peaks were observed with the bare ZnSe prism.

The infrared spectrum of aqueous LA (Figure 1(c)), in contact with the bare ZnSe prism, has absorptions at 1726 and 1234 cm^{-1}, corresponding to the stretch modes of the carboxylic acid group. The spectrum of the aqueous lactate ion (Figure 1(d)) is dominated by the antisymmetric CO_2^- stretch band at 1574 cm^{-1}. The symmetric CO_2^- stretch mode occurs as a weak absorption at 1413 cm^{-1}.[10] The adsorption of glycolic acid (GA) was also investigated on the TiO_2 sol-gel film (Figure 2(a)). GA differs structurally in chain length with respect to LA. For GA adsorbed on TiO_2, bands were situated at 1611 and 1370 cm^{-1} and similarly assigned, as for LA on TiO_2, to the stretch modes of the carboxylate groups. Propanoic acid was found not to adsorb to TiO_2, indicating the α-hydroxy group is essential in the surface coordination.

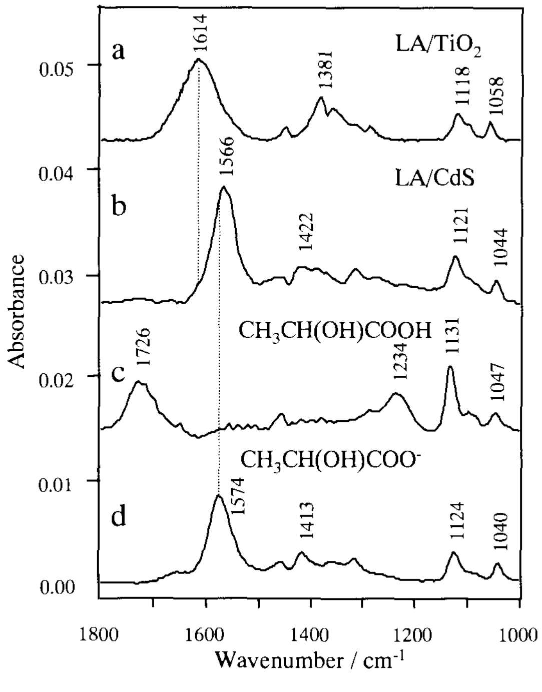


Figure 1. Internal reflection infrared spectra of (a) $1x10^{-3}$ mol dm^{-3} aqueous LA solution in contact with TiO_2 sol-gel film, (b) $1x10^{-3}$ mol dm^{-3} aqueous LA solution in contact with CdS sol-gel film, (c) $1x10^{-3}$ mol dm^{-3} aqueous LA solution and (d) $1x10^{-3}$ mol dm^{-3} LA in 0.2 mol dm^{-3} aqueous NaOH solution. Reference spectra were of (a) and (b) TiO_2 and CdS films in contact with 0.1 mol dm^{-3} aqueous NaOH solution and (c) and (d) a bare ZnSe prism in contact with water.

The appreciable increase in the magnitude of splitting of the CO_2^- stretch modes on adsorption of LA and GA to TiO_2 (161 and 172 cm^{-1} to 233 and 241 cm^{-1} respectively) is usually indicative of the formation of coordinated monodentate carboxylates.[11] The bands at 1040~1090 cm^{-1} in the spectra of aqueous GA (Figure 2(c)) and LA can be assigned to the C-O stretch of the α-hydroxy group. This band appears at 1075 and 1040 cm^{-1} for the respective aqueous carboxylate ions. On adsorption on TiO_2, a shift to higher wavenumbers, of ~20 cm^{-1}, with respect to the free carboxylate ions was observed. The observed shift of the alcohol ν(C-O) mode is associated with lactate or glycolate coordination onto TiO_2. A similar shift has been previously reported in the aryl-O stretch mode on adsorption of 8-quinolinol to TiO_2, ZrO_2 and Al_2O_3 sol-gel films, forming a bidentate chelate surface structure.[12] The present results indicate the involvement of the –OH substituent group in the surface coordination of glycolate and lactate on the TiO_2 to form a bidentate surface structure.

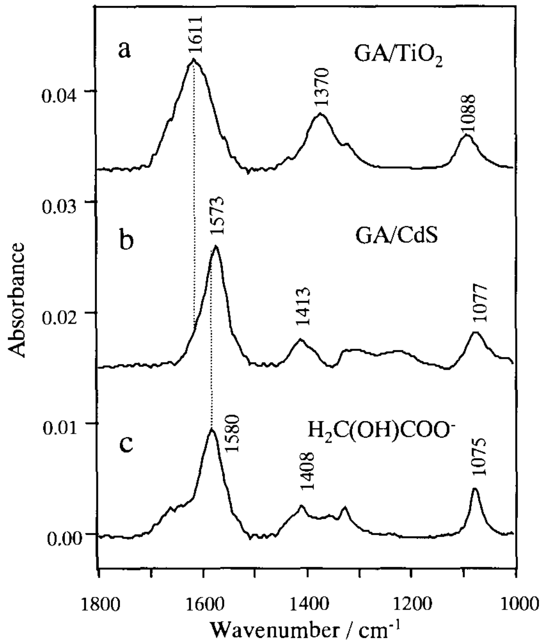
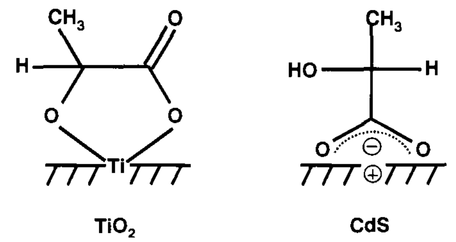


Figure 2. Internal reflection infrared spectra of (a) 1x10^{-3} mol dm^{-3} aqueous GA solution in contact with TiO_2 sol-gel film, (b) 1x10^{-3} mol dm^{-3} aqueous GA solution in contact with CdS sol-gel film and (c) 1x10^{-3} mol dm^{-3} GA in 0.2 mol dm^{-3} aqueous NaOH solution. Reference spectra were of (a) and (b) TiO_2 and CdS films in contact with 0.2 mol dm^{-3} aqueous NaOH solution and (c) a bare ZnSe prism in contact with water.

Figure 1(b) shows the infrared spectrum of species adsorbed on a CdS sol-gel film from a 1x10^{-3} mol dm^{-3} aqueous LA solution. Comparison of this spectrum with that in Figure 1(d) indicates that the species adsorbed on CdS is almost unmodified from that of the aqueous lactate ion. Similarly, the infrared spectrum of GA (Figure 2(b)) adsorbed on CdS is very similar to the spectrum of the free carboxylate ion. Little change is also noted in the position of the substituent C-O stretch modes between the adsorbed and free carboxylate species. The slight change in the spectra on adsorption may indicate either the formation of a bridging bidentate or an electrostatically-adsorbed surface carboxylate species.[7] The surface lactate species were found to be weakly adsorbed to CdS, being easily removed on washing with water. This indicates that an electrostatically-bound surface species is most likely formed on adsorption of lactic acid to CdS sol-gel films.

The adsorptions of pyruvic acid (PA) onto TiO_2 and CdS films were also investigated. On TiO_2, similar spectral features to the LA system were obtained, with the CO_2^- stretch modes occurring at 1640 and 1380 cm^{-1} (cf. 1602 and 1395 cm^{-1} for aqueous pyruvate ion). The ketone ν(C=O) vibration of the aqueous pyruvate ion is absent, suggesting a similar chelating bidentate coordination to that described for LA.



Scheme 1. Structures of lactic acid adsorbed on TiO_2 and CdS photocatalyst surfaces.

From the infrared spectral data of TiO_2 in contact with aqueous LA solution, lactate was found to adsorb as a chelating bidentate ligand to a surface Ti(IV) ion, with the involvement of the α-hydroxyl and the carboxylate functional groups. This type of adsorption was confirmed from studies of GA and PA adsorption to TiO_2. For CdS, on the other hand, LA was determined to be adsorbing as the lactate ion via electrostatic interactions (Scheme 1).

A possible interpretation of the different photocatalytic products formed is that the adsorption structure of the lactate species controls the oxidation mechanism. Bidentate chelation of the lactate onto the TiO_2 surface may allow direct transfer of the electron (or hole) to promote decarboxylation by weakening the (CH_3CH)-(C=O) bond to form acetaldehyde. Conversely the electrostatic interaction of the lactate to the positively charged protonated surface hydroxyls CdS surface[3,13] may yield the formation of OH• radicals to mediate α-hydrogen abstraction to form PA. The negligible adsorption of PA on the CdS surface supports the selective formation of PA without the subsequent oxidation. A detailed investigation of LA photolysis at TiO_2 and CdS surfaces monitored *in situ* using ATR-IR spectroscopy, will be reported elsewhere.[14]

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References and Notes

1 H. Harada, T. Ueda, and T. Sakata, *J. Phys. Chem.*, **93**, 1542 (1989).
2 J. Moser and M. Grätzel, *J. Am. Chem. Soc.*, **105**, 6547 (1983).
3 T. Awatani, MSc thesis, Otago University (1998).
4 J. J. Ramsden and M. Grätzel, *J. Chem. Soc., Faraday Trans I*, **80**, 919 (1984).
5 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, **95**, 49 (1995).
6 T. Awatani and A. J. McQuillan, *J. Phys. Chem. B*, **102**, 4110 (1998).
7 K. D. Dobson, P. A. Connor, and A. J. McQuillan, *Langmuir*, **13**, 2614 (1997).
8 K. D. Dobson and A. J. McQuillan, *Langmuir*, **13**, 3392 (1997).
9 K. Nakamoto, P. J. McCarthy, and B. Miniatas, *Spectrochim. Acta*, **21**, 379 (1965).
10 G. Cassanas, M. Morssli, E. Fabregue, and L. Bardet, *J. Raman Spectrosc.*, **22**, 409 (1991).
11 R. C. Mehrota and R. Bohra, "Metal Carboxylates," Acacdemic Press, New York (1983).
12 P. A. Connor, K. D. Dobson, and A. J. McQuillan, *Langmuir*, **11**, 4193 (1995).
13 T. Awatani and A. J. McQuillan, to be published.
14 T. Awatani, K. D. Dobson, A. J. McQuillan, B. Ohtani, and K. Uosaki, in preparation.