The Photocatalysed Reduction of Aqueous Sodium Carbonate to Carbon using Platinised Titania

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Four doped titania powders, a Tioxide anatase and Degussa P25 samples were photoplatinised using visible, u.v.–visible, or 254 nm radiation; a suspension of a platinised sample in Na_2CO_3 solution, irradiated with visible or u.v.–visible radiation, produced carbon and a much smaller yield of HCHO.

Since the publication of Fujishima and Honda's paper in 1972,[1] research aiming at solar energy conversion and storage has increased rapidly and has concentrated on the splitting of water.[2] However, the single crystal semiconductors initially used have been advantageously replaced by powders and, more recently, by colloids.

The alternative process of the photoreduction of CO_2 to give a variety of products[3,4] has recently been applied to suspensions of a semiconductor in aqueous carbonate.[5,6] The advantages of the photoreduction of CO_2 have been discussed with emphasis on the production of MeOH, which can be used as a fuel additive.[4]

Although carbon is a convenient possible[7] reduction product for use as a fuel, apparently it has not been detected. We have recently observed the formation of carbon produced on irradiating a suspension of platinised titania in aqueous Na_2CO_3 irradiated with u.v.–visible light. This reaction is the reverse of the burning of coal and coke which contributes to the undesirable accumulation of CO_2 in the atmosphere. A visible dispersion of carbon on the catalyst was observed in 1 M Na_2CO_3 (150 cm^3) containing platinised 0.5 a/o Cr–TiO_2 (0.50 g) (a/o = atom %) after 3 h irradiation in a cylindrical vessel surrounding the quartz thimble of a medium pressure mercury lamp (125 W, Applied Photophysics). Nitrogen gas was passed continuously through the vessel. The doped titania, prepared by the hydrolysis of $TiCl_4$ as described elsewhere,[8] was loaded with Pt by irradiating 1.0 g in H_2PtCl_6 solution (10 cm^3, 5.6 × 10^{-4} M) neutralised by the dropwise addition of concentrated

NaOH followed by glacial acetic acid to adjust the pH to 4.[9] The suspension, kept at 55 ± 1 °C under nitrogen, was irradiated for 12 h, through a Pyrex window,† with a xenon lamp (250 W, Thorn). After filtration and washing, the powder was dried at 120 °C before use as a photocatalyst. Alternatively the powder may be described as a photosensitizer.

For later runs, a lower level of platinisation was achieved by suspending titania (1.0 g) in H_2PtCl_6 solution (25 mg Pt) and glacial acetic acid (75 cm^3). The pH was adjusted to 5.5[10] before making the volume of liquid up to 150 cm^3. The suspension was irradiated with the medium pressure lamp prior to filtration, and washed and dried as described above. The platinised titania was then suspended in 1 M Na_2CO_3 solution and irradiated with the mercury lamp for 11 h using the same conditions as before. The powder, which acquired a darker colour owing to the formation of carbon, was heated in a porcelain boat inside a silica tube using an electric furnace at 1000 °C for 4—6 h in an air stream freed from CO_2 by two bubblers containing 0.5 M NaOH and a saturated $Ba(OH)_2$ monitoring bubbler. The CO_2 formed by burning the photoproduced carbon was initially confirmed by precipitation in saturated $Ba(OH)_2$ in NaOH solution placed at the exit of the air stream. In later runs, CO_2 was collected in excess standard 0.5 M NaOH solution and the carbonate formed was determined by titration against 0.1 M standard HCl using thymol blue–cresol red mixed indicator.[11] The mass of carbon oxidised, calculated from the titres, was in fair agreement with the loss in weight of the titania after heating. The final colour of titania was apparently lighter than its colour before burning off the carbon. After filtering the photolysed suspension, the filtrate was used to determine HCHO spectrophotometrically using the Hantzsch reaction.[12,13] The concentration of HCHO was obtained by interpolation from a calibration plot.

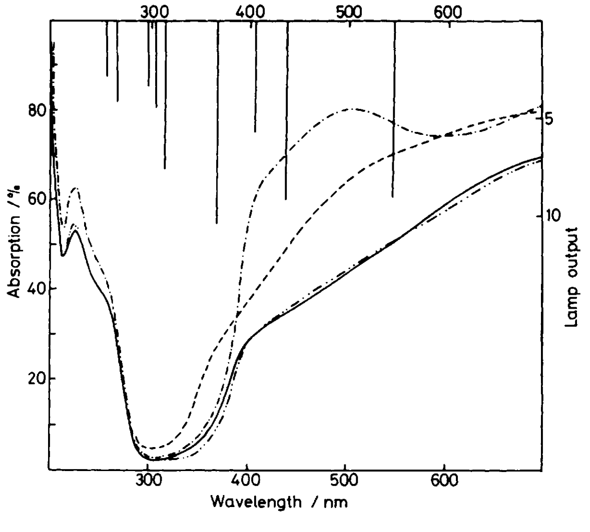

Figure 1. The output mercury lines of the medium pressure lamp, in arbitrary units, compared with the reflectance spectra of the doped titania samples: 0.5 a/o Cr (·—·—·), 0.5 a/o Mn (——), 0.5 a/o Mn (– – –),‡ 0.25 a/o Mn, 0.25 a/o Cr (··—··—).

In a parallel experiment, platinised titania (0.10 g), prepared as described above and suspended in 1 M Na_2CO_3 (30 cm^3) was irradiated with a xenon lamp through a Pyrex window under the same conditions as specified above. The photoproduced carbon and HCHO were determined as described earlier.

The results of runs using different titania samples are collected in Table 1. Carbon was produced in all cases even when the undoped anatase CLDD 1599/2 (Tioxide) or the commercial P25 (Degussa) (surface areas 182 and 50 m^2 g^{-1} respectively) titania were used. The yields of carbon were 9.3 and 15 μmol m^{-2} respectively. However, a strict comparison of the results using the two samples is not feasible since P25 is surface-treated and contains small amounts of Al_2O_3 and SiO_2, unlike CLDD 1599/2. Carbon was also formed when platinisation was carried out by irradiation with visible light (preliminary run) or with the 254 nm radiation from a Hanovia low pressure mercury lamp, although longer platinisation times were necessary in both cases. It is interesting to recall the reported deposition of Pt on irradiating $[PtCl_6]^{2-}$ in aqueous alcohol at all wavelengths at which the complex absorbs.[14]

What is particularly significant for solar energy applications is the production of carbon when a suspension was irradiated with visible light from the xenon lamp. Although the yield per gram of catalyst was higher than that in the corresponding run where u.v.–visible light was used, a strict comparison between the two cases is not permissible since the power of the two lamps used and their spectral output are different, and since the geometry of the irradiation vessels and the depth of the irradiated layer were different in the two cases.

During the photoreduction of Na_2CO_3, the exit gas, bubbled through acidified $PdCl_2$ solution, did not reduce it to Pd, indicating that no measurable amounts of reducing gases such as CO or H_2 could be detected. We are attempting to determine other possible reduction products. The relevant redox data for the reduction of CO_2 to different products are available.[4,7]

The holes photogenerated during irradiation of aqueous suspensions of titania are known to react with the hydroxylated surface of the powder with the resultant photoadsorption of oxygen.[15] However, this aspect has not been investigated. The lack of any correlation between the yields of carbon and of HCHO in the series of runs is worth noting. No relationship

Table 1. The yields of carbon and HCHO generated by the photoreduction of Na_2CO_3 solution.

Titania	Platinisation time/h	Irradiation time/h	Yield of carbon/ mmol	Yield of HCHO/ μmol
0.5 a/o Cr	3	11	2.0	2.4
Second batch	3	11	0.7_8	1.7
Second batch[a]	3	11	0.8_0	0.4_7
0.5 a/o Mn	3	11	0.6_7	2.2
0.5 a/o Mn[b]	3	11	0.6_9	1.8
0.25 a/o Mn, 0.25 a/o Cr	3	11	0.7_3	1.6
P25	4	11	0.7_5	1.2
CLDD	3	11	1.7	1.7
CLDD[c]	11	11	1.1	1.7

[a] Carbonate reduction with visible light. [b] Sample prepared by oxidising the product of hydrolysis of $TiCl_3$, unlike the other doped samples, which were prepared by hydrolysis of $TiCl_4$. [c] Platinisation using 254 nm radiation.

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† The light was focused on the flat window of a small cylindrical cell.

‡ Prepared from $TiCl_3$ unlike the other samples.

between the yields of the products of reduction and the light absorption by the doped photocatalysts could be established. The difficulty can be appreciated by examining Figure 1 where the reflectance spectra of the samples (in the range 200—700 nm)[8] are compared with the relative intensity of the mercury lines of the lamp used. Figure 1 shows that the Cr-doped titania absorbs more strongly than the others at 366 nm but the reverse was observed at the wavelengths of the other mercury lines.

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References

1 A. Fujishima and K. Honda, *Nature*, 1972, **228**, 37.

2 A. Harriman in 'Photochemistry,' (Specialist Periodical Report), ed. D. Bryce-Smith, Royal Society of Chemistry, 1986, vol. 17, p. 601.

3 T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, 1979, **277**, 637.

4 B. Aurian-Blajeni, M. Halmann, and J. Manassen, *Solar Energy*, 1980, **25**, 165.

5 K. Chandrasekaran and J. K. Thomas, *Chem. Phys. Lett.*, 1983, **99**, 7.

6 D. Monheit, S. Grayer, N. Godinger, V. Katzin, and M. Halmann, Abstracts 5th International Conference on Photochemical Conversion and Storage of Solar Energy, Osaka, Japan, Aug. 1984, pp. 75—76.

7 J-M. Lehn and R. Ziessel, *Proc. Natl. Acad. Sci. USA*, 1982, **79**, 701.

8 W. K. Wong and M. A. Malati, *Solar Energy*, 1986, **36**, 168.

9 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 4317.

10 W. W. Dunn, Y. Aikawa, and A. J. Bard, *J. Am. Chem. Soc.*, 1981, **103**, 3456.

11 A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, p. 250.

12 T. Nash, *Biochem. J.*, 1953, **55**, 416.

13 H. G. Wood and H. Gest in 'Methods of Enzymology,' eds. S. P. Colowick and N. O. Kaplan, Academic Press, New York, vol III, pp. 287—289.

14 R. E. Cameron and A. B. Bocarsly, *Inorg. Chem.*, 1986, **25**, 2910; *J. Am. Chem. Soc.* 1985, **107**, 6116.

15 R. I. Bickley, R. K. M. Jayanty, V. Vishwanathan, and J. A. Navio, in 'Homogeneous and Heterogeneous Photocatalysis,' eds. E. Pelizetti and N. Serpone, Reidel, Dordrecht, pp. 555—565.