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NOTE

Use of Imines and Their Complexes as Photosensitizers in Photoreduction of CO_2

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The surface of the Pt/TiO_2 semiconductor was modified by adsorption of photoactive imines derived from 2-amino-6-ethoxybenzothiazole with 2-furancarboxaldehyde (SB^1), and 2-thiophenecarboxaldehyde (SB^2) and their Co(II), Ni(II) and Cu(II) complexes. Illumination of the system, containing CO_2, surface modified semiconductor and L-ascorbic acid as a supersensitizer, produces appreciable amounts of HCHO and HCOOH.

The recent report on dye-sensitization technique in TiO_2 semiconductor particulate system[1–3] had indicated that the charge injection to the conduction band of TiO_2 from the electronically excited adsorbed dye photoactive center in imines of thiazole[4] and as a part of our continued interest in photoreduction of N_2 [5] and CO_2[6], was planned to carry out the present investigation.

Schiff bases and their complexes were prepared by following the published procedure[7], from 2-amino-6-ethoxybenzothiazole (6-Oet-2ABT) with 2-furancarboxaldehyde (SB^1) or 2-thiophenecarboxaldehyde (SB^2).

Photolysis Studies

Semiconductor grade TiO_2 was loaded with Pt (4%) by following the reported procedure[8]. The surface of the Pt/TiO_2 was modified with SB^1, SB^2 and their complexes. For this purpose 25 mg of Pt/TiO_2 powder was added to a 25 mL of methanolic solution of photosensitizers (1×10^{-3} M) and stirred for 3 h under illumination with a Xe-lamp (250 W, Applied Photophysics). The surface modified semi-conductor was separated by centrifugation and dried at room temperature. The amounts of absorbed photosensitizers on the semiconductor surface were calculated by measuring the decrease in absorbance of the supernatant liquid. Without illumination, the amount of absorbed photosensitizers on the surface of semiconductor was very low. 25 mL reaction mixture contained 25 mg of surface modified Pt/TiO_2 semiconductor powder, 1 mmole of L-ascorbic acid, dissolved CO_2 and H_2O. Pure CO_2 was allowed to bubble through the reaction mixture at 500 mL/min sufficient to keep the reaction mixture saturated with CO_2. The reaction mixture was illuminated with a 250 W Xenon lamp (applied photophysics). Aliquots were withdrawn from reaction mixture at 1 h interval of time and freed from semiconductor particles by centrifugation and subjected to product analysis for formic acid and formaldehyde. The products formic acid and formaldehyde were analysed spectrophotometrically by using Nash reagent[9]. The formation of formic acid was also confirmed by HPLC analysis. Several control experiments (in dark, in absence of sensitizer and in absence of super-sensitizer) were also done for verification of photoproducts.

Electrical conductivity of the photosensitizers was observed at the room temperature, as well as the temperature downfall upto liquid nitrogen. As the temperature falls, conductivity decreases and vice-versa. The reason for this is the energy required to detach the electron from donor level to the acceptor level. Due to semiconductor nature and imine linkage of the Schiff bases, both behave as catalyst and sensitizer also.

During illumination, the surface adsorbed photosensitizer gets excited and transfer electrons to the conduction band of TiO_2 semiconductor which is channeled through the predeposited platinum to the surface adsorbed CO_2 and thus giving the reduction products HCOOH and HCHO involving 2 and 4 electron transfer respectively, represented by eqs. (1) and (2)[10] (Fig. 1).

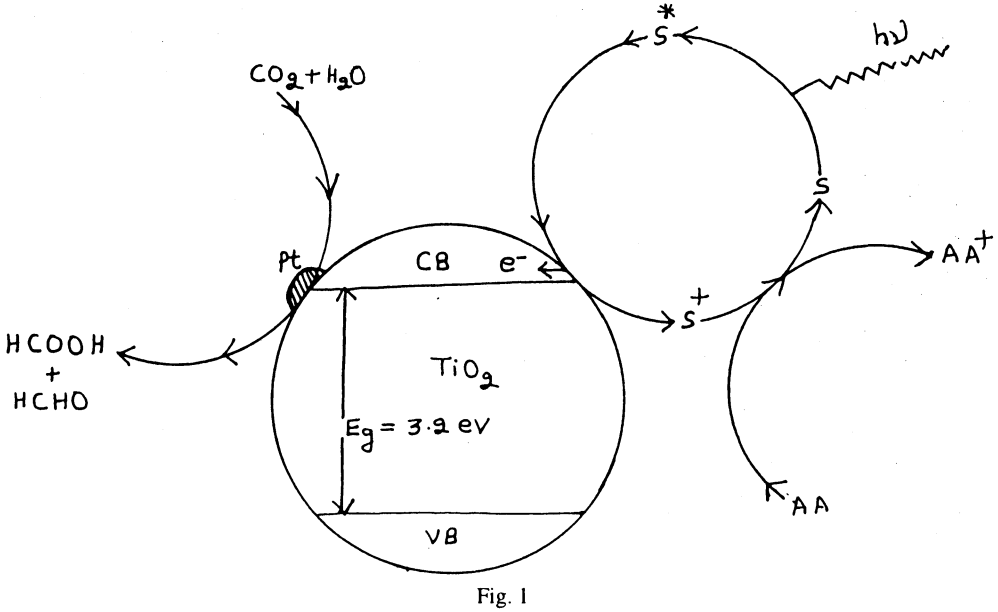

Fig. 1

$$CO_2 + 2H^+ + 2e^- \text{ (CB)} \rightarrow HCOOH \tag{1}$$

$$CO_2 + 4H^+ + 4e^- \text{ (CB)} \rightarrow HCHO + H_2O \tag{2}$$

The imine species gets reduced by supersensitizer L-ascorbic acid (electron donor) to repeat the photocatalytic cycle. In conclusion, Schiff bases and their complexes are photosensitizers which have a chromophoric group and can adsorb significantly on the surface of the Pt/TiO_2 semiconductor through imine linkage or heteroatoms of the rings. Rate of photo products increased in the following order.

	Cu	>	Ni	≈	Co	>	SB^1	>	SB^2
HCOOH→	(1.4)		(1.2)		(1.2)		(0.7)		(0.4) m mol
HCHO→	(1.1)		(1.0)		(1.0)		(0.5)		(0.3) m mol

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