Photocatalytic Activity of CdS

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***Abstract*— Photocatalysis is utilized to synthesis energy rich products and can also mineralize toxic compounds to less toxic or almost harmless species. The photocatalytic degradation of aldehyde over cadmium sulphide was investigated. The effect of various parameters was observed and tentative mechanism has been proposed for the photocatalytic degradation of aldehyde using cadmium sulphide semiconductor as catalyst.**

Keywords— Photocatalysis, aldehyde, cadmium sulphide, semiconductor

I. Introduction

Photocatalysis is termed for the photochemical reactions carried out in the presence of a semiconducting substance. Though binary chalcogenides of various metals are commonly used semiconducting substances, but the use of ternary chalcogenides cannot be ruled out. Semiconductors, which are most extensively investigated, are oxides of zinc and titanium. However the use of cadmium sulphide as photocatalyst has driven positive results. Photocatalysis is used to synthesize energy rich products as well as to mineralize toxic compounds to less toxic or almost harmless species which help us to protect the environment.

The field of photocatalysis has been excellently reviewed by Tanaka [1], Gratzel [2], Pelizzetli et al [3] and Ameta et al.CdS supported on a solid surface for photocatalysis has been used by Mayo et al [5]. The effect of surface structures on photocatalytic CO_2 reduction using quantized CdS noncrystallites has been observed by Fujiwara et al[6]. The preparation and photocatalytic activities of a semiconductor composite of CdS embedded in TiO_2 gel as a stable oxide semiconducting matrixhas been reported by Fijii et al [7]. Kumar et al [8] reported the photocatalytic oxidative C-C bond cleavage of the pyrrole ring in 3-methyl indole reduced by colloidal CdS particles. Herterich and Kisch [9] used CdS-ZnS as a photocatalyst for photodehydrodimerization of 2,5-dihydrofuran. Shiragoni et al [10] reported the effect of light intensity on CdS catalysed photolysis of organic substrate. Photocatalytic oxidation of sulphite ion over semiconducting cadmium sulphide has been observed by Parakh et al [11].

Although the photocatalytic oxidation of various organic compounds has been studied a lot, negligible information is available on the fate of aldehydes after photocatalytic degradation over semiconductor cadmium sulphide. In the present investigation the effect of various parameters such as pH, amount of photocatalyst, concentration of aldehyde and light intensity was observed and a tentative mechanism has been proposed for the photocatalytic degradation of aldehydes in the presence of semiconducting CdS powder. The aldehydes used for the purpose of study were acetaldehyde and bezaldehyde.

II. Experimental

A known amount of aldehyde was dissolved in a known volume of doubly distilled water to get a solution of known concentration, which is divided into four parts and placed in four beakers.

- The first part was kept in dark.
- The second part was kept in light.
- The third part with a known amount of CdS was kept in dark and
- The fourth part with a known amount of CdS was exposed to light

It was observed that in first and third part of aldehyde solution, the amount of unreacted aldehyde remained virtually unaffected, however in the fourth part the optical density of the aldehyde solution decreases with increasing time of exposure negligible change was also observed in the third part of the aldehyde solution.

Taking into account the above mentioned fact, various parameters like the effect of aldehyde concentration, effect of amount of photocatalyst CdS and effect of light intensity was studied to deduce the fate of aldehyde via photocatalytic pathway.

III. A Typical Run

Photocatalytic degradation of acetaldehyde and benzaldehyde was observed by taking their known solution and 0.20g of CdS was added to it. This solution was exposed to light intensity = $70 mWcm^{-2}$ from a 200 Watt tungsten lamp. At regular time interval an aliquot of 2.0 mL was taken out from the reaction mixture, to which 0.5 mL Schiff's reagent was added.The optical density of this solution was measured with the help of spectrophotometer at regular time intervals (λ_{max} = 355 nm).

Table .1: *A Typical Run.* [a]

Light Intensity = 70.0 mW cm^{-2}, CdS = 0.20 g
Temperature = 308 K

TIME(min.)	1+log O.D. (bezaldehyde)	1+log O.D. (Acetaldehyde)
0	0.5026	0.9162
30	0.4774	0.9093
60	0.4526	0.9024
90	0.4291	0.8953
120	0.4036	0.8874
	K = 3.19×10^{-5}	**K= 8.52×10^{-6}**

[a] *Observation of 1+log O.D. against time*

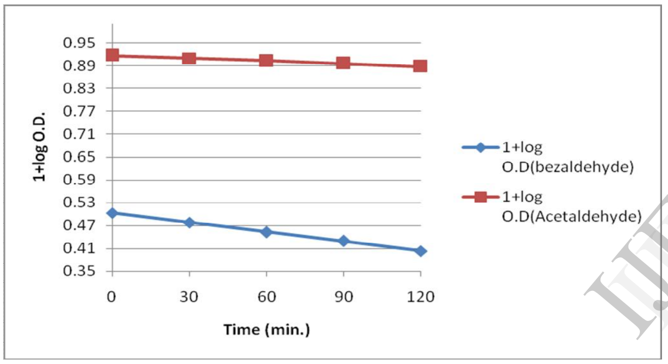

Fig.1. A Typical Run

It was observed that the amount of aldehydes decreased with increasing time of exposure. A plot of 1 + log O.D. against time was linear and the rate constant was measured by the expression k = 2.303 x slope. The results are reported in the Table.1. and represented by graph in Fig .1.

IV. TENTATIVE MECHANISM

A tentative mechanism of photocatalytic degradation of aldehydes in the presence of semiconducting CdS powder has been proposed.

$$CdS \xrightarrow{h\nu} e^-_{CB} + h^+_{VB}$$

$$h^+_{VB} \longrightarrow h^+_s \text{ (s denotes CdS surface)}$$

$$H_2O + h^+_s \longrightarrow \dot{O}H + H^+$$

$$RCHO + 2\dot{O}H \longrightarrow RCOOH + H_2O$$

$$RCOOH \leftrightarrow RCOO^- + H+$$

$$RCOO^- + h^+_s \longrightarrow RCO\dot{O}$$

$$RCO\dot{O} \longrightarrow \dot{R} + CO_2$$

$$H^+ + e^-_{CB} \longrightarrow \dot{H}$$

$$\dot{R} + \dot{H} \longrightarrow R\text{-}H$$

$$\dot{R} + \dot{R} \longrightarrow R\text{-}R$$

$$\dot{H} + \dot{H} \longrightarrow H_2$$

$$\dot{O}H + \dot{O}H \longrightarrow H_2O_2$$

V. RESULT AND DISCUSSION

When CdS particles are exposed to light, a hole is created in the valence band (h^+_{VB}) and an electron from the valence band is excited to conduction band (e^-_{CB}). This hole creates an electron deficiency (h^+_s) at semiconductor surface [12], which dissociates water into hydroxyl radical and a proton [13]. This hydroxyl radical reacts with the aldehyde forming carboxylic acid and water. The acid dissociates to give carboxylate ion and a hole can convert it into carboxylate radical which may further decarboxylate to generate alkyl radical. There is a possibility of hydrogen radical generation by combination of a proton with an electron in the conduction band and this hydrogen radical can combine with alkyl radical to form hydrocarbon; however, the possibility of dimerisation of alkyl, hydrogen and hydroxyl radicals to give dialkyl, hydrogen and hydrogen peroxide, respectively, cannot be ruled out.

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