

Photocatalytic Oxidation of Acetic Acid over CdS

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Abstract: The photocatalytic degradation of acetic acid over cadmium sulphide semiconductor was investigated. The effect of various parameters, such as pH, concentration of acetic acid, amount of catalyst, effect of light intensity were observed. A tentative mechanism has been proposed for the photocatalytic degradation of acetic acid using CdS semiconductor as catalyst.

Keywords: acetic acid, cadmium sulphide, photocatalytic degradation, semiconductor

I. Introduction

Photocatalysis is a research area with a number of fronts. On one hand, it is utilized to synthesize energy rich products, which can serve as synthetic fuels and mineralizing toxic compounds to less toxic or almost harmless species, thus protecting the environment on the other hand. Ordinarily an oxidant is required to oxidize the organic substrates which will leave additional contaminants in the solution after oxidation. In this context, photocatalytic oxidation over semiconducting powders will get an edge over other conventional or classical oxidation reactions as it will not contaminate the solution further.

Wang and Herron [1] studied chemical effects on the optical properties of semiconductor particles. Pichat[2] discussed surface properties, activities and selectivity of bifunctional powder photocatalysts. Ampoet *al.* [3] observed photocatalytic reactions on native and platinum loaded titanium dioxide. Richard *et al.*[4] reported that oxidizing species involved in the photocatalytic transformations on zinc oxide is either hole or hydroxyl radicals. de Mayo *et al.*[5] used CdS supported on a solid surface for catalysis. A kinetic study of photoinduced electron transfer reactions sensitized by colloidal CdS has been reported by Green and Mills [6].

Yoneyama *et al.*[7] discussed various factors affecting the product distribution in photocatalytic decomposition of acetic acid on platinumized TiO₂ in aqueous medium whereas the effects of additives on the reaction was given by Nagashima *et al.*[8] Bideau *et al.*[9] observed the photooxidation of acetic acid by oxygen in presence of TiO₂ and dissolved copper ions. Ralmisano *et al.*[10] reported the photodecomposition of acetic acid adsorbed over semiconductor and insulator oxide. Kaise *et al.* [11] reported the photocatalytic reactions of acetic acid on platinum loaded TiO₂ and ESR evidence of radical intermediate in the photo-Kolbe reaction.

Awatani *et al.*[12] studied the in situ infrared spectroscopy of adsorption of lactic acid and related compounds on TiO₂ and CdS semiconductor photocatalyst surfaces from aqueous solutions. A kinetic study with a mechanistically based reaction model for photocatalytic degradation of dichloroacetic acid has been reported by Ballari *et al.*[13]

Although a lot of work has been carried out in the field of photocatalytic oxidation of various organic compounds, negligible or no information is available on the fate of acetic acid photocatalytic degradation over semiconductor cadmium sulphide powder and therefore, investigations were done to know the details of such degradation.

The effect of various parameters on rate of photocatalytic degradation of acetic acid was observed:

II. Experimental

100.0 mL of glacial acetic acid was dissolved in 100.0 mL of doubly distilled water to prepare 8.77 M solution, which is then divided into four parts (50mL each) and placed in four beakers.

- (i) First beaker containing only acetic acid solution was kept in dark.
- (ii) The second beaker containing only acetic acid solution was exposed to light.
- (iii) The third beaker having acetic acid solution and 0.12g of CdS was kept in dark.
- (iv) The fourth beaker, containing acetic acid solution and 0.12g of CdS was exposed to light.

After keeping these beakers for three hours, the amount of unreacted acetic acid was measured in each solution. It was observed that there was no or negligible change in the amount of unreacted acetic acid in the first three beakers, whereas in the fourth beaker, the amount of unreacted acetic acid decreases with the increasing period of exposure. This reaction follows a photocatalytic route as it requires light as well as semiconductor CdS, both.

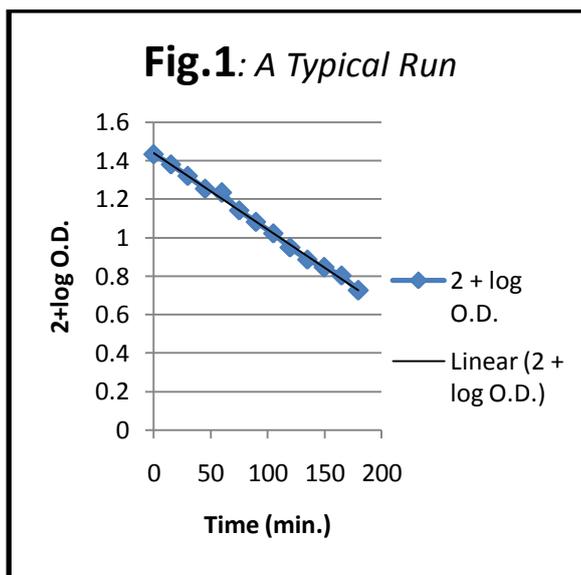
III. A Typical Run

Photocatalytic degradation of acetic acid was observed by taking 8.77 M solution and 0.12 g of CdS was added to it. This solution was exposed to light intensity = 70mWcm⁻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 0.1 mL ammonium hydroxide and 0.2 mL of dilute FeCl₃ solution was added to develop a red color. The optical density of this red solution was measured with the help of spectrophotometer ($\lambda_{max} = 525 \text{ nm}$).

Table .1: A Typical Run.^{a)}

[Acetic Acid] = 8.77 M, pH = 3.0
 Light Intensity = 70.0 mWcm⁻², CdS = 0.12 g
 Temperature = 308 K

Time (min)	2 + log O.D.
0	1.4345
15	1.3820
30	1.3201
45	1.2552
60	1.2329
75	1.1430
90	1.0827
105	1.0211
120	0.9489
135	0.8859
150	0.8450
165	0.8041
180	0.7254



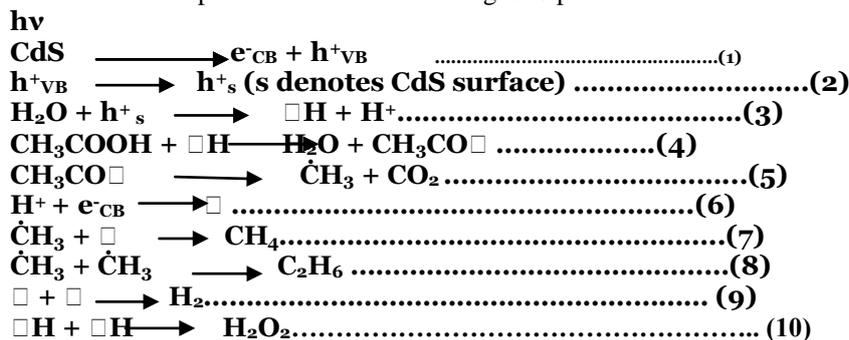
$$K = 1.49 \times 10^{-4} \text{ sec}^{-1}$$

^{a)} Observation of 2+log O.D. against time

It was observed that the amount of acetic acid decreases with increasing time of exposure. A plot of 2 + log O.D. against time was linear and the rate constant was measured by the expression $k = 2.303 \times \text{slope}$. The results are reported in the Table.1. and represented by graph in Fig .1.

IV. Mechanism

On the basis of the observations, a tentative mechanism has been proposed for the photocatalytic degradation of acetic acid in the presence of semiconducting CdS powder.



On exposure of CdS particles, an electron from the valence band is excited to conduction band (e^-_{CB}) leaving behind a hole in the valence band (h^+_{VB}). This hole creates electron deficiency (h^+_s) at semiconductor surface [14], which can dissociate water into hydroxyl radical and a proton [15]. This hydroxyl radical abstracts a hydrogen from acetic acid forming acetate radical which may further decarboxylate to generate methyl 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 methyl radical to form methane gas; however, the possibility of dimerization of methyl, hydrogen and hydroxyl radicals to give ethane, hydrogen and hydrogen peroxide, respectively, cannot be ruled out.

The formation of carbon dioxide was detected by its usual test with lime water. A new Kolbe reaction pathway for heterogeneous photocatalytic synthesis of methane from CH₃COOH has been reported by Kraeutler and Bard [16, 17].

The reaction was also carried out in the presence of hydroxyl radical scavenger like 2-propanol and it was observed that the rate of photocatalytic degradation of acetic acid was drastically reduced: hence, confirming the participation of hydroxyl radical as an active oxidizing species.

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