

ORIGINAL ARTICLE

**COMPARISON OF PHOTOCATALYTIC EFFICIENCIES OF TiO₂ AND ZnO
IN PRESENCE AND ABSENCE OF O₂**

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Article History: Received 10th June, 2014, Accepted 23rd June, 2014, Published 30th June, 2014

ABSTRACT

The effect of oxygen on the decomposition of PMS and PDS using TiO₂ and ZnO has been investigated. The effect of isopropanol on the decomposition of PMS and PDS in the presence and absence of oxygen has also been investigated. The experimental results indicate that in presence of oxygen the disappearance of either PMS or PDS is always less than in the absence of oxygen (in presence of nitrogen).

Keywords: Photocatalysis, TiO₂ and ZnO, PMS, PDS

1. INTRODUCTION

Photocatalysis is the combination of photolysis and catalysis. Photolysis is light induced chemical reaction whereas catalysis involves acceleration of rate of a chemical reaction by a substance called as catalyst. Photocatalysis is the acceleration of rate of a chemical reaction by catalyst in presence of light. Without catalyst there is no reaction. Without light there is also no reaction. The reaction takes place only in presence of light and catalyst.

Semiconductors are usually used as photocatalysts. Each semiconductor has its own characteristic band gap energy (E_{bg}). Band gap is the energy gap between the completely filled valence band and the empty conduction band.

The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductor is the generation of electron-hole pairs in the semiconductor particles.

If the energy of photon is equal to or greater than the band gap of a semiconductor, then absorption of light takes place. During absorption an electron is transferred from the valence band to the conduction band creating a hole in the valence band and electron in the conduction band.

These charge carriers undergo chemical reaction with the adsorbed substrate molecules. The photoproduced electron reacts with the acceptor molecule to form a reduced anion radical A⁻.

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The hole can react with the donor molecule to form an oxidised cation radical.



In addition to the charge transfer reaction, electron-hole recombination also occurs. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle or on the surface with release of heat.

The photocatalytic degradation of organic compounds on semiconductor surfaces has attracted much attention [Pelizzetti et al., 1987; Mathews, 1986]. In the presence of oxygen, many n-type semiconductor powders have been used as photocatalysts and these promote the oxidation of organic substrates when illuminated with light of energy greater than or equal to the band gap energy of the semiconductor. The electrons and holes, which are formed, are capable of initiating chemical reactions to convert pollutants to innocuous or less harmful form [Carey et al., 1976; Kawaguchi et al., 1983].

Metal semiconductor modification:

Addition of noble metals enhances the photocatalytic activity of a semiconductor. This is due to the trapping of electrons after excitation which decreases e⁻-h⁺ recombination and thereby increasing the efficiency.

For example, the Pt/TiO₂ systems [Sato and White, 1980] is the metal-semiconductor system most commonly studied. Here, the photoproduced electron migrates to the metal where it becomes trapped and e⁻-h⁺ recombination is suppressed. The hole is then free to diffuse to the semiconductor surface where oxidation of adsorbed substrate occurs.

Composite or coupled semiconductor system:

To increase the efficiency of a photocatalyst by increasing the charge separation and extending the absorption towards visible region, coupled semiconductor system is used.

For example, the photoexcitation process for CdS-TiO₂ coupled semiconductor system [Sclafani et al., 1981]. The energy of the excitation light is too small to directly excite the TiO₂ portion of the photocatalyst.

1.3. Surface sensitization:

Surface sensitization of a wide band gap semiconductor photocatalyst such as TiO₂ by chemisorbed or physisorbed dyes can increase the efficiency of the photocatalyst. The photosensitization process can also expand the wavelength range of excitation for the photocatalyst through excitation of the sensitizer in the visible region followed by charge transfer to the semiconductor [Gerischer and Willig, 1976]. Electron from the reduced relay into the conduction band of TiO₂. The surface acts as a quencher accepting an electron from the excited dye molecule. The electron inturn can be transferred to reduce an adsorbed substrate or water molecule.

Application of photocatalysis:

Photocatalysis is applied in the followed fields

1. Fuel production : Production of H₂, CH₄ [Sakata and Kawai, 1981; Mills and Porter, 1982; Cruendet et al., 1986 Thewissen et al., 1985].

2. Waste water treatment : Decomposition of organic and inorganic pollutants present in water [Okamoto et al., 1985; Okamoto et al., 1985; Mathews, 1987; Mathews, 1988; Ekabi et al., 1989; Mathew et al., 1980].

3. Synthesis of useful organics : Synthesis of Ammonia, amino acids [Schrauzer and Guth, 1977; Hemminger et al., 1978; Dunn et al., 1981; Kraeutler and Bard, 1978].

4. Catalysis of some chemical reaction : Hydrogenation [Fraser and Macallum, 1986; Ulman et al., 1982].

2. EXPERIMENTAL

In the photocatalytic experiments the light source was a 250W Tungsten-halogen lamp. A continuous spectrum was available throughout the visible portion of the spectrum. The light was focussed by a lens, passed through a water jacket (to remove IR radiation) and then allowed to enter into the cell containing the reactants. A 100 ml beaker made up of the pyrex glass has been used as the reaction vessel. In all the experiments, 50 mg of the photocatalyst powders (except the experiments involving variation of catalyst amounts) were suspended in 70 ml of the substrate solution, stirred magnetically at a constant rate and then photolysed.

Photocatalytic experiments were carried out with the undoped TiO₂ and ZnO powders individually, in solution containing PMS or PDS (1.0 x 10⁻³ mol dm⁻³) with and without 2-propanol in presence and absence of atmospheric oxygen. The pH of the medium, catalyst amount and [2-propanol] were kept constant in all the experiments. These experiments were carried out in order to compare the

catalytic efficiencies for the decomposition of PMS and PDS and to find out the role of oxygen on the rate of the reaction.

PMS solutions of known concentrations (0.5-2.5 x 10⁻³ mol dm⁻³) were taken in the pyrex cell and deaerated. The photocatalyst powder was added and then photolysed. Aliquots of the irradiated solutions were withdrawn at known intervals of time and transferred quantitatively in to a conical flask containing excess of 5% KI solution and titrated against standardised thiosulphate solution using starch indicator. The amount of PMS decomposed with respect to time were calculated.

Potassium peroxydisulphate (PDS) from Fluka (>99.9%) was used as such. In photocatalytic experiments, the amount of PDS decomposed with time was estimated by iodometry after keeping the aliquots of the irradiated solutions mixed with KI solutions for about 40 minutes in stoppered iodine flasks.

3. RESULTS AND DISCUSSION

The results are presented in tables 1-4, it is seen that the rates of disappearance of either PMS or PDS in presence of atmospheric oxygen is always less than those in nitrogen atmosphere. This is also true for the experiments conducted under similar conditions containing 2-propanol. The disappearance of PMS in presence of ZnO is approximately three times higher than that in presence of TiO₂ and in presence of O₂ and N₂ (Tab. 1 and 3). For the similar reaction in presence of 2-propanol, ZnO is approximately 1.5 times more active than TiO₂.

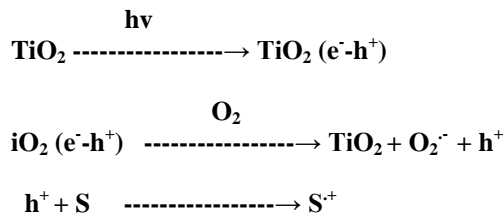
Table 1 : TiO₂ - PMS SYSTEM Comparison of Photocatalytic efficiency of TiO₂ in presence of O₂ and N₂ atmosphere; Catalyst amount = 50 mg/70ml; pH = 4.0; [2-Propanol] = 1.0 x 10⁻⁴ mol dm⁻³; T=25°C

[PMS] ₀ X 10 ³ , mol dm ⁻³	1.0	1.0	1.0	1.0
System	in O ₂ atm. (without 2-PrOH)	in N ₂ atm. (without 2-PrOH)	in O ₂ atm. (with 2-PrOH)	in N ₂ atm. (with 2-prOH)
Time (min.)	← 4 + Log[PMS] _t →			
10	0.968	0.959	0.952	0.898
20	0.950	0.918	0.870	0.792
30	0.888	0.880	0.810	0.672
40	0.806	0.839	0.704	0.522
Rate x 10 ⁸ , mol dm ⁻³ S ⁻¹	10.29	15.28	30.86	47.90

Table 2 : TiO₂ - PDS SYSTEM Comparison of Photocatalytic efficiency of TiO₂ in presence of O₂ and N₂ atmosphere; Catalyst amount = 50 mg/70ml; pH = 4.0; [2-Propanol] = 1.0 x 10⁻⁴ mol dm⁻³; T=25°C

[PMS] ₀ X 10 ³ , mol dm ⁻³	1.0	1.0	1.0	1.0
System	in O ₂ atm. (without 2-PrOH)	in N ₂ atm. (without 2-PrOH)	in O ₂ atm. (with 2-PrOH)	in N ₂ atm. (with 2-prOH)
Time (min.)	← 4 + Log[PDS] _t →			
10	0.990	0.973	0.974	0.968
20	0.982	0.953	0.954	0.928
30	0.974	0.934	0.930	0.890
40	0.952	0.915	0.912	0.858
Rate x 10 ⁸ , mol dm ⁻³ S ⁻¹	4.68	7.64	8.06	14.13

All these results stress an important point, i.e., the role of atmospheric oxygen in the above reactions investigated. In presence of oxygen (also in presence of 2-propanol) the disappearance of either PMS or PDS is always less than in the absence of oxygen (in presence of N₂ atmosphere). Usually in photocatalytic oxidation [Serpone et al., 1995] of any substrate, the role of dissolved oxygen is to trap e⁻CB and h⁺VB to oxidise substrate and also to prevent e⁻CB - h⁺VB recombination.



and further reactions. In the present investigation, the reactive species are e⁻CB and h⁺VB with PMS and e⁻CB with PDS. In presence of dissolved oxygen, most of the e⁻CB would be trapped by O₂ to form less reactive O₂⁻ and the available e⁻CB would be less for reaction with PMS and PDS. Hence, in presence of atmospheric oxygen the disappearance of either PMS or PDS is always less than those in presence of N₂ atmosphere.

From the tables 1 and 2, it is understood that the rate of disappearance of PMS is at least twice greater (in the absence of 2-propanol) than that of PDS in oxygen or nitrogen atmosphere. In presence of 2-propanol the rate of disappearance of PMS is more than 3.6 times higher than that of PDS in presence of atmospheric oxygen or nitrogen.

Table 3 : ZnO - PMS SYSTEM Comparison of Photocatalytic efficiency of ZnO in presence of O₂ and N₂ atmosphere; Catalyst amount = 50 mg/70ml; pH = 4.0; [2-Propanol] = 1.0 x 10⁻⁴ mol dm⁻³; T=25^oC

[PMS] ₀ X 10 ³ , mol dm ⁻³	1.0	1.0	1.0	1.0
System	in O ₂ atm. (without 2-PrOH)	in N ₂ atm. (without 2-PrOH)	in O ₂ atm. (with 2-PrOH)	in N ₂ atm. (with 2-prOH)
Time (min.)	← 4 + Log[PMS] _t →			
10	0.948	0.869	0.882	0.814
20	0.830	0.724	0.764	0.613
30	0.728	0.580	0.612	0.410
40	0.650	0.477	0.457	0.225
Rate x 10 ⁸ , mol dm ⁻³ S ⁻¹	38.61	50.67	54.77	72.16

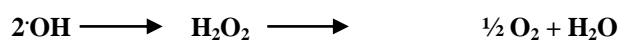
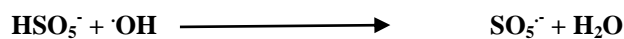
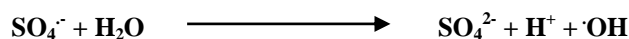
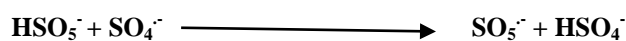
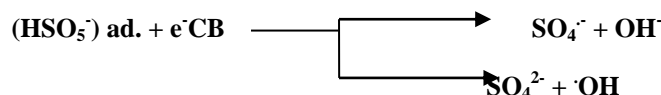
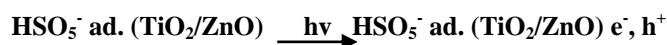
Table 4 : ZnO - PDS SYSTEM Comparison of Photocatalytic efficiency of ZnO in presence of O₂ and N₂ atmosphere; Catalyst amount = 50 mg/70ml; pH = 4.0; [2-Propanol] = 1.0 x 10⁻⁴ mol dm⁻³; T=25^oC

[PMS] ₀ X 10 ³ , mol dm ⁻³	1.0	1.0	1.0	1.0
System	in O ₂ atm. (without 2-PrOH)	in N ₂ atm. (without 2-PrOH)	in O ₂ atm. (with 2-PrOH)	in N ₂ atm. (with 2-prOH)
Time (min.)	← 4 + Log[PDS] _t →			
10	0.980	0.944	0.972	0.951
20	0.966	0.903	0.848	0.911
30	0.946	0.881	0.920	0.850
40	0.930	0.855	0.892	0.799
Rate x 10 ⁸ , mol dm ⁻³ S ⁻¹	6.53	11.10	10.29	19.84

4. MECHANISM:

Decomposition of PMS:

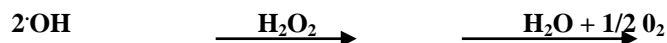
The proposed mechanism consists of the reaction of conduction band electron with PMS generating SO₄⁻ or ·OH and the valence band hole oxidising PMS generating SO₅⁻. The radical and radical anions favour the evolution of oxygen appreciably greater than that due to water oxidation by valence band holes alone



The reaction of e⁻ ad with PMS takes two different courses as proved by electron-pulse radiolysis experiments [Maruthamuthu and Neta, 1977]. The steps involving the formation of SO₅⁻, SO₄⁻ and ·OH are similar to those proposed in radiolytic and photochemical reactions [Kanakaraj and Maruthamuthu, 1998] involving PMS. Oxygen evolution in this study was identified qualitatively using an oxygen sensitive electrode.

Decomposition of PDS:

The following reaction pathways may be proposed for the photocatalytic decomposition of PDS.



The valence band holes and SO₄⁻ oxidise water to evolve oxygen. The water oxidation may be effected directly by h⁺VB and indirectly by e⁻CB via SO₄⁻ generated. PDS serves as a sacrificial agent for the evolution of oxygen from water.

5. CONCLUSIONS

All these results stress an important role of atmospheric oxygen in the decomposition of PMS and PDS by TiO₂ and ZnO photocatalysts. From the above experimental results we conclude that the rate of disappearance of PMS is at least twice greater than that of PDS in oxygen or nitrogen atmosphere. In presence of atmospheric oxygen the disappearance of either PMS or PDS is always less than these in presence of nitrogen atmosphere.

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