Visible Light Assisted Heterogeneous Catalysis. Decomposition of Peroxomonosulfate over Doped and Undoped WO_3 Dispersions in Aqueous Medium

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Aqueous suspension of RuO_2-loaded WO_3 powder on illumination with light of $\lambda \geqslant 410$ nm was found to decompose peroxomonosulfate (PMS, HSO_5^-) efficiently. The rate and other kinetic parameters indicated that the decomposition process followed Langmuir kinetics; at low concentrations of HSO_5^- (0.54—2.06×10^{-3} mol dm^{-3}) the reaction obeyed a first-order kinetics and at higher concentrations, ($[HSO_5^-]>3.00\times10^{-3}$ mol dm^{-3}) the rate became independent of $[HSO_5^-]$. The effects of pH and the molar percentage of the dopant on the rates were also investigated. Small amount of doping by RuO_2 (2.5 molar percentage) was found to increase the photocatalytic decomposition of HSO_5^- whereas the higher amount of doping decreased the rate. Added 2-propanol to the system was found to increase the rate of decomposition of peroxomonosulfate. The proposed mechanism of the decomposition of PMS involves the reactions of the photogenerated valence band holes and the conduction band electrons of WO_3, by radiation of wavelength $\geqslant 410$ nm, in presence and absence of 2-propanol. The rate constants and quantum yields have also been evaluated. The photocatalytic decomposition of peroxomonosulfate is one of the few examples of a unimolecular reaction catalyzed by both the photogenerated holes (h^+_{vb}) and electrons (e^-_{cb}).

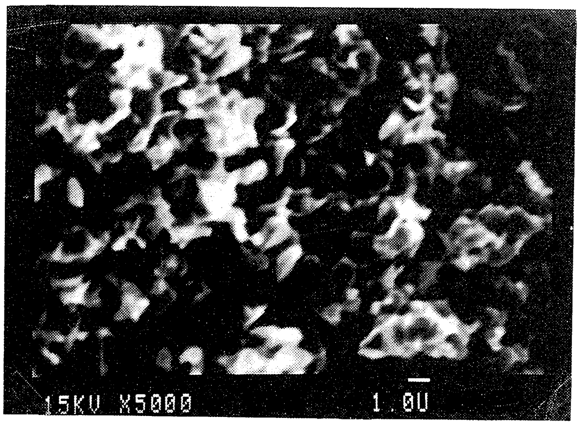
The photocatalytic and photosynthetic reactions involving homogeneous and heterogeneous catalyses have recently attracted much attention because of their possible applications in solar energy conversion processes.[1] Particular interest has been focussed on the generation of hydrogen from water using semiconductors[2] and radiations of wavelength matching the sunlight. Recent works involve the simplified conventional photoelectrochemical cell with the use of semiconductor dispersions to carry out photocatalytic[3] and photosynthetic[4] reactions. These dispersed particles consist of single semiconductor alone or metallized semiconductor.[5,6] It has also been shown that a combination of redox systems with metal catalysts is indispensable for the efficient transfer of photon-induced conduction band electrons and valence band holes for redox reactions as well as protection of semiconductors against photocorrosion.[7,8] Since the photons absorbed in a thin layer close to the semiconductor–electrolyte interface alone are responsible for the chemical process, a large surface area of the active catalyst is desirable. This is best provided by catalysts in the form of powders and colloids. Although the area of illuminated surfaces is almost independent of the total surface area, as the size of the particle is decreased the density of the catalyst in the form of powder or colloid in the area of illumination gets increased and hence the catalytic efficiency will also be increased. Krasnovskii and Brin[9] have investigated the photocatalytic oxygen evolution reaction using WO_3 as a photocatalyst and Fe^{3+} as the electron acceptors. Darwent and Mills[10] have investigated the effect of RuO_2-loaded on WO_3 on oxygen evolution from water using Fe^{3+} as an electron acceptor. Recently Gratzel and coworkers[11] have reported the reactions of WO_3-coated electrodes and Nozik et al. have explored the electron-transfer reactions with WO_3 colloids.[12]

In this article we report the photocatalytic decomposition reactions of an inorganic peroxide namely peroxomonosulfate, $HOOSO_3^-$ (PMS) in aqueous suspension of WO_3 powder with radiation of wavelength $\geqslant$410 nm. During the decomposition of PMS by the e^-_{cb} and h^+_{vb} of WO_3, oxidation of water to oxygen was also observed. Hence PMS may be considered as a sacrificial agent for the production of oxygen from water. PMS itself is an oxidizing agent ($E^\circ=1.82$ V) similar to peroxodisulfate and undergoes radiolytic and photolytic reactions.[13,14] It does not undergo photochemical decomposition unless the wavelength used is $\leqslant$260 nm. However, in presence of WO_3 powder, with and without RuO_2 loading, efficient decomposition of PMS is observed on illumination with light of $\lambda \geqslant$410 nm. The effects of (i) pH, (ii) catalyst amount, (iii) percentage doping of RuO_2, and (iv) 2-propanol on the heterogeneous photocatalytic decomposition of PMS are discussed. The significance of this investigation is that the substrate chosen (PMS) itself is an oxidant, but capable of simultaneously scavenging the e^-_{cb} and h^+_{vb} formed by band-gap irradiation of WO_3. The reaction is also a typical example for visible light induced catalytic decomposition of PMS which otherwise happens by UV irradiation.

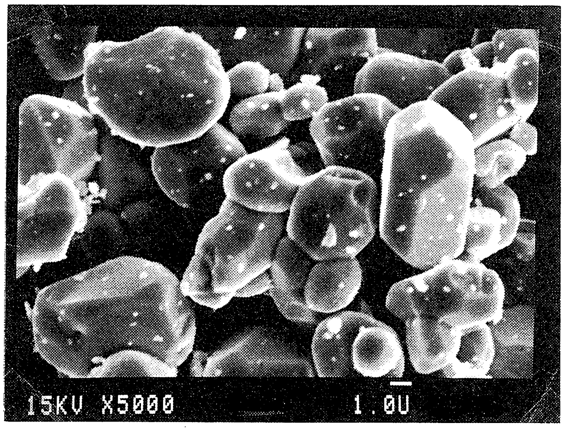
Experimental

WO_3 used was from Fluka (>99.99%). RuO_2 loading was done using the technique described by Gratzel and coworkers[15] by dissolving calculated amount of $RuCl_3\cdot H_2O$ in water and mixing thoroughly with WO_3. The slurry was dried and heated in a muffle furnace in argon atmosphere at 800—900 °C for 4 h. Diffuse reflection measurements were taken using Beckman Quartz Spectrophotometer (Model-DU: Serial 92906) at room temperature in the wavelength region 350—700 nm. Scanning Electron Microscope pictures (Fig. 1) were taken with JEOL JSM-35 CF Model. The particle sizes varied from 1—10 µm. An interesting observation in SEM pictures is that the doping increases the crystallinity of WO_3 semiconductor powders.

The surface areas of the catalysts were determined by BET method and found to be 1.0 to 1.5 m^2g^{-1}. PMS was from E.I. du Pont de Nemours & Co., USA, in the form of triple salt ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and was used as such. Other chemicals used were of the purest research grade available. Photocatalytic reactions were carried out in a rectangular all quartz reactor. Prior to irradiation, WO_3 dispersions were freed from dissolved oxygen by purging with purified Argon. A high pressure Mercury lamp (250 watt, Applied Photophysics, London) in combination with suitable cut-off filters emitting the light of $\lambda \geqslant 410$ nm was used as the light source. The intensity of the incident radiation, I_0, determined by trisoxalatoferrate(III) actinometry[16] was 6.91×10^{-8} Eins s^{-1}. The emission spectrum of the mercury lamp shows that the emitted light above 410 nm has the maximum intensity (ca. 99%) only at λ=436 nm. The IR radiations were removed using a water jacket. The change in the concentration of PMS with time was estimated iodometrically as reported in literature.[13] Unless otherwise mentioned, all the reactions were carried out with 25 mg of the 2.5% RuO_2/WO_3 photocatalyst in 35 ml of the reaction mixture.



(A)



(B)

Fig. 1. SEM photographs of (A) unloaded WO_3 (sintered at 800—900 °C) and (B) 2.5% RuO_2/WO_3 (sintered at 800—900 °C).

Quantum yields (Φ) of the photocatalytic reactions were determined using the relation,

$$\Phi = \frac{\text{Rate of decomposition of PMS}}{[(I_0 \times \text{Absorbance of the catalyst at } \lambda = 436\,\text{nm})/100]} \tag{a}$$

which has been derived from the basic definition,

$$\Phi = \frac{\text{Number of moles decomposed per unit time}}{\text{Number of Einsteins absorbed per unit time}}$$

In this study the number of moles decomposed per unit time is nothing but the rate of decomposition of PMS. From the diffuse reflection spectra it has been found that the catalyst powder absorbs only a fraction of the total incident radiation at λ=436 nm. Hence number of Einstein absorbed per unit time from the total incident radiation (I_0) has been calculated using the expression written in the denominator of the relation (a). Also the absorbances of undoped and 2.5% RuO_2 doped WO_3 are found to be 70% and 87% of the incident radiations respectively. Oxygen evolution was identified using TL's Digital Oxygen Analyser Model DP 2M.

Results and Discussion

About 90% of PMS was decomposed in about three hours of illumination of an aqueous slurry containing PMS ($0.54—2.06 \times 10^{-3}$ mol dm^{-3}) and RuO_2/WO_3 (25 mg). No dissolution of WO_3 was observed even after six hours of continuous irradiation. Blank experiments were also conducted under the similar conditions without the photocatalyst and there was no decomposition of PMS observed even after four hours of prolonged irradiation.

Effect of Initial Concentrations of PMS. At low concentrations of PMS, the initial rate (r_0) of decomposition of PMS, $-d[PMS]/dt$ was found to increase with increase in the initial concentrations but at higher concentrations, the rate became independent of $[PMS]_0$. The plots of r_0 vs. $[PMS]_0$ exhibited a curvature, characteristic of saturable surface and the rates are described by a simple Langmuir form,

$$r_0 = \frac{kK[PMS]_0}{1 + K[PMS]_0} \tag{1}$$

where k is the proportionality constant and K is the equilibrium constant. The first order rate constant k_1 can be calculated from k using the relation, $k_1 = k/[PMS]_0$. These observations are conveniently demonstrated by the linearity of the plot of $1/r_0$ vs. $1/[PMS]_0$ (Fig. 2) as given by the relation,

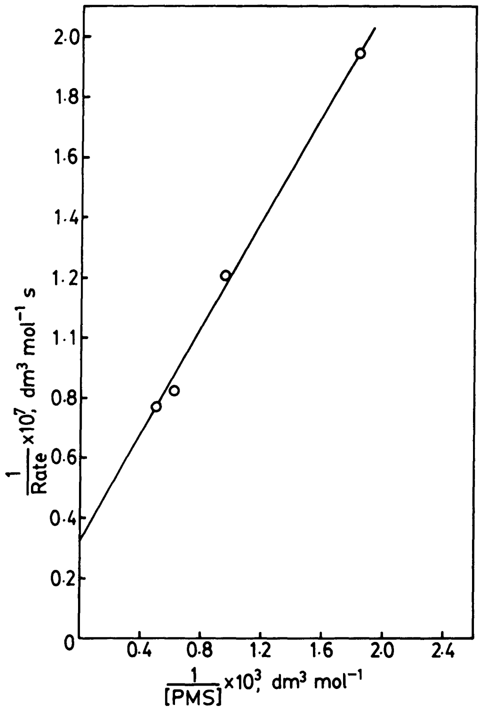


Fig. 2. Evaluation of *k* and *K*.

$$\frac{1}{\text{rate}_0} = \frac{1}{kK[\text{PMS}]_0} + \frac{1}{K} \quad . \tag{2}$$

From the slope and intercept of the above plot, the values of k and K were evaluated as 3.19×10^{-7} mol dm^{-3} s^{-1} and 3.52×10^{2} dm^3 mol^{-1} respectively. At lower concentrations of PMS, Eq. 1 is reduced to

$$\text{rate}_0 = kK[\text{PMS}]_0 \tag{3}$$

and the overall reaction obeyed a first-order kinetics (assuming the surface to be truly Langmurian).

Effect of pH. The photocatalytic decomposition of PMS over RuO$_2$-doped WO$_3$ powders at different pH (1.0—5.0), at constant [PMS]$_0$ (1.00×10^{-3} mol dm^{-3}) as well as catalyst amount (25 mg) exhibited a maximum rate at pH=3.0 (Fig. 3) with a sharp decrease above and below this pH. Since the pK_a values of PMS (pK_1<0 and pK_2=9.4)$^{17)}$ are not within the pH of the reaction slurry, the rate profile with pH may be due to the energetics of the conduction band and valence band edges with respect to the redox potential of PMS ($E°$=1.82 V).$^{18)}$ Photocatalysis implies an excess charge carrier transfer between the catalyst and reactant across the interface. The efficiency of the catalytic process is determined by the contribution of this transfer to the total excess charge carrier decay. This charge transfer between WO$_3$ and PMS is probably much favored at pH=3 as evidenced by the kinetic data.

Effect of Catalyst Amount. The photocatalytic effect of RuO$_2$/WO$_3$ powders is proved by its successful cleavage of PMS. The reactivity of the catalyst is maintained even after its successive participation in the photodecomposition reaction of PMS. The nonphotocorrosive nature of this catalyst is seen by the absence of tungsten ions in the reaction solution even after six hours of prolonged irradiation. Increase in the amount of catalyst is found to increase the rate of decomposition of PMS at constant [PMS]$_0$ (1.00×10^{-3} mol dm^{-3}). The calculated rates for different catalyst amounts at constant [PMS]$_0$ are given in Table 1.

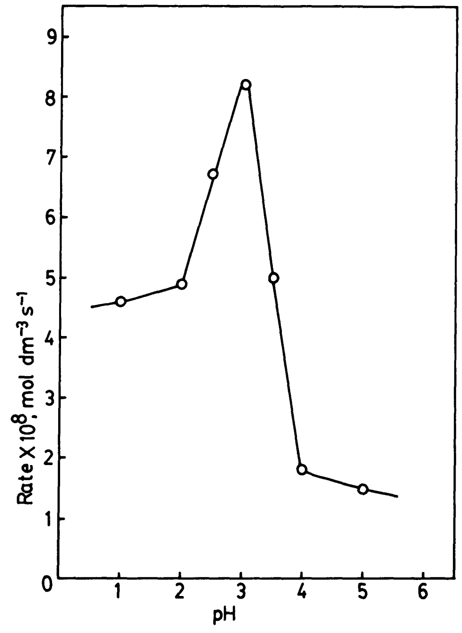


Fig. 3. Effect of pH.

Table 1. Effect of Catalyst Amount

Catalyst amount/mg	Rate×10^7/mol dm^{-3} s^{-1}
15	0.44
25	0.82
35	1.20
45	1.29

Effect of RuO$_2$ Loading. Doping at different molar percentages (1.0%—12.5%) of RuO$_2$ shows that upto 2.5% loading of RuO$_2$ on WO$_3$ increases PMS decomposition beyond which there is a decrease. Although RuO$_2$ is a well-known catalyst for oxygen evolution$^{19)}$ it has been widely employed as a good catalyst for hydrogen evolution.$^{20)}$ Sakata and coworkers$^{19)}$ have examined the catalytic properties of RuO$_2$ on n-type semiconductors under illumination for both oxygen and hydrogen evolution from water. In the present investigation, the rates of decomposition of PMS for 1.0 and 2.5% RuO$_2$/WO$_3$ photocatalysts are more than that for undoped WO$_3$ and the rates decrease beyond this percentage (Table 2). This might be due to the nature of deposition of RuO$_2$ on WO$_3$ surface. RuO$_2$ is deposited very finely (Fig. 1B)

Table 2. Effect of RuO_2-Loading

Molar percentage of RuO_2 loading	Rate$\times 10^8$/mol dm^{-3} s^{-1}
Undoped WO_3	3.00
1.0	5.95
2.5	8.23
5.0	3.26
7.5	2.50
10.0	1.82
12.5	1.56

on the WO_3 surface. With increasing amount of RuO_2, the density of deposition is increased. For this kind of deposition, RuO_2 particles on WO_3 surface would be expected to function as recombination centers since the distance between the particles becomes shorter than the distance at which the image force to both electron and hole is effective. The other reason would be that the photoejected electrons are also consumed for the reduction of RuO_2 prior to PMS reduction.

Reaction Pathway. It has been shown by Krasnovskii[9] that the aqueous dispersions of WO_3 illuminated by visible light produce oxygen as a result of the reaction of the valence band holes (h_{vb}^+) with water,

$$4h_{vb}^+ + 2H_2O \longrightarrow O_2 + 4H^+ . \qquad (4)$$

It is also proved by Gratzel and co-workers[11a] that valence band hole of WO_3 is capable of oxidizing SO_4^{2-} to $SO_4^{\dot{-}}$. Hence it is probable that PMS is also attacked by h_{vb}^+ eventhough PMS is a powerful oxidizing agent ($E°=1.82$ V).[18] Moreover, it is well established that electrons (e_{aq}^-) react with PMS almost at a diffusion controlled rate.[14a] Hence, it is not surprising that both h_{vb}^+ and e_{cb}^- react with PMS. This type of reactivity of PMS, as an electrophile as well as nucleophile, has already been observed by us[21] in visible light induced photochemical reactions of PMS with excited state $[Ru(bpy)_3]^{2+}$. While the conduction band electrons generate $SO_4^{\dot{-}}$ and/or $\dot{O}H$, the valence band holes are capable of removing the hydrogen atom from $HOOSO_3^-$ forming $SO_5^{\dot{-}}$. These radicals and radical ions should favor the evolution of oxygen appreciably than the water oxidation by h_{vb}^+ alone. Considering these reactions, we propose the following mechanism (Fig. 4):

$$WO_3 \xrightarrow[\lambda \geqslant 410\,nm]{h\nu} h_{vb}^+ + e_{cb}^- \qquad (5)$$

$$[HSO_5^-] + WO_3 \longrightarrow [HSO_5^-]_{ad.}\ WO_3 \qquad (6)$$

$$[HSO_5^-]_{ad.} + e_{cb}^- \longrightarrow SO_4^{\dot{-}} + OH^- \qquad (7a)$$

$$[HSO_5^-]_{ad.} + e_{cb}^- \longrightarrow SO_4^{2-} + \dot{O}H \qquad (7b)$$

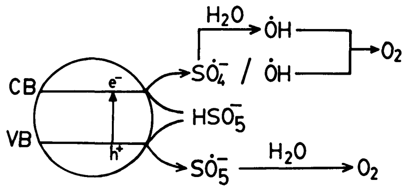


Fig. 4. Schematic representation of PMS decomposition by WO_3 particle.

$$HSO_5^- + SO_4^{\dot{-}} \longrightarrow SO_5^{\dot{-}} + HSO_4^- \qquad (8)$$

$$SO_4^{\dot{-}} + H_2O \longrightarrow SO_4^{2-} + H^+ + \dot{O}H \qquad (9)$$

$$HSO_5^- + \dot{O}H \longrightarrow SO_5^{\dot{-}} + H_2O \qquad (10)$$

$$2\dot{O}H \longrightarrow 1/2O_2 + H_2O \qquad (11)$$

$$[HSO_5^-]_{ad.} + h_{vb}^+ \longrightarrow SO_5^{\dot{-}} + H^+ \qquad (12)$$

$$2SO_5^{\dot{-}} \xrightarrow{H_2O} 2HSO_4^- + O_2 \qquad (13)$$

The reaction of the electron with PMS occurs in two ways, Reactions 7a and 7b. The formation of $SO_5^{\dot{-}}$, $SO_4^{\dot{-}}$, and $\dot{O}H$ as radical products from PMS were identified by optical pulse radiolysis[14a] and in-situ-photolysis ESR investigation using spin-trapping agents[22] such as fumaric and maleic acids.

The overall reaction for the decomposition of PMS by illuminated WO_3 could be written as

$$HSO_5^- \xrightarrow[\lambda \geqslant 410\,nm]{WO_3,\ h\nu} 1/2\,O_2 + SO_4^{2-} + H^+ .$$

The quantum yields (Φ) determined, as explained previously, for the undoped and 2.5% RuO_2 doped WO_3 were 0.62 and 1.36 respectively. Since both the photogenerated e_{cb}^- and h_{vb}^+ are capable of decomposing PMS, the expected quantum yield is 2. The low value observed in our experiments might be due to (i) all the photons hitting the surface of the reaction vessel are not absorbed by the semiconductor slurry (ii) electron–hole recombination and (iii) recombination of $SO_4^{\dot{-}}$ and $\dot{O}H$ to form PMS.

Effect of 2-Propanol. Addition of 2-propanol is found to increase the rate of decomposition of PMS. The reaction was investigated by photolysing aqueous slurry containing various concentrations of 2-propanol (0.25—1.00 mol dm^{-3}) with a constant $[PMS]_0$ (1.00×10^{-3} mol dm^{-3}) and catalyst amount (25 mg). The rate of decomposition of PMS increased with increase in [2-PrOH]. The enhanced decomposition of PMS in the presence of 2-propanol is due to the additional Reactions 14 and 15 along with Reactions 8—13.

$$(CH_3)_2CHOH + h^+_{vb},\ SO_4^{\dot{-}},\ \dot{O}H \longrightarrow (CH_3)_2\dot{C}OH \quad (14)$$

$$(CH_3)_2\dot{C}OH + HSO_5^- \longrightarrow (CH_3)_2C{=}O + SO_4^{\dot{-}} + H_2O \quad (15)$$

In the presence of 2-propanol (0.50 mol dm^{-3}) the Φ values are 2.21 and 2.71 for undoped and 2.5% RuO$_2$ doped WO$_3$ respectively. The comparatively high Φ values observed here could be due to the reaction of $SO_4^{\dot{-}}$ and $\dot{O}H$ with 2-propanol instead of recombination and also due to the reduction of PMS by the alcohol radical formed (Eqs. 14 and 15).

It may be concluded that peroxomonosulfate which is photochemically active at $\lambda \leqslant 260$ nm is found to be decomposed in the presence of WO$_3$, doped and undoped with RuO$_2$, by visible radiation. The presence of 2-propanol further enhanced the decomposition of PMS.

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