

Photocatalysis with ZrO_2 : oxidation of aniline

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Abstract

ZrO_2 photocatalyzes the oxidation of aniline to azobenzene. The oxidation with natural sunlight and UV irradiation (365 nm) in ethanol was investigated as a function of [aniline], catalyst loading, airflow rate, solvent composition, etc. The photocatalyst exhibits sustainable catalytic activity. The product formation is larger with illumination at 254 nm than at 365 nm. Electron donors like triphenylphosphine, diphenylamine and hydroquinone enhance the photocatalysis. Singlet oxygen quencher, azide ion does not inhibit the catalysis. The photocatalysis occurs in protic as well as aprotic solvents. The mechanism of photocatalysis is discussed and the product formation examined using a kinetic model. TiO_2 , V_2O_5 , ZnO, Fe_2O_3 , CdO, CdS and Al_2O_3 also photocatalyze the oxidation of aniline to azobenzene; with UV light of wavelength 254 nm ZrO_2 is more efficient than other photocatalysts studied, the photocatalytic activities are of the order $ZrO_2 > ZnO > V_2O_5 > Fe_2O_3 > CdS > Al_2O_3 > CdO > TiO_2$. However, ZrO_2 loses its edge over others on illumination at longer wavelength (365 nm) and with sunlight.

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1. Introduction

Applications of UV-irradiated semiconductors to organic synthesis are numerous and TiO_2 as well as ZnO (bandgap energy, $E_g = 3.2$ eV, $\lambda < 385$ nm) are the extensively used photocatalysts [1–4]. ZrO_2 , a widely used heterogeneous catalyst, is an *n*-type semiconductor with bandgap energy of 5.0 eV [5] (reported values range between 3.25 and 5.1 eV [6] depending on the preparation technique of the sample but the most frequent and accepted value is 5.0 eV) and conductance and valence band potentials of -1.0 and $+4.0$ V versus NHE, respectively, allowing its use as a photocatalyst in the production of hydrogen through water decomposition. Although ZrO_2 presents an adsorption maximum around 250 nm, some samples show a non-negligible absorption in the near UV range (290–390 nm) [6] and photocatalytic reactions could be performed under irradiation in this range; Litter and co-workers [6] listed many ZrO_2 -photocatalyzed

reactions including production of hydrogen from water. Photochemical reactions attract much attention as possible routes for harnessing solar energy but reports using natural sunlight are a few and preliminary [7–9]. Here we report for the first time the results of solar photocatalysis; the problem of variation of intensity of sunlight even under clear sky is overcome by conducting set of experiments simultaneously and comparing the results. Air-equilibrated solution of aniline yields azobenzene on irradiation at 365 nm with benzophenone sensitizing the oxidation [10,11]. UV-irradiated ZnO brings in the oxidation of aniline to azobenzene [12,13] and aniline undergoes photocatalytic degradation on TiO_2 immobilized on porous nickel [14].

2. Experimental

2.1. Materials

ZrO_2 (Chemco, India), V_2O_5 (Johnson Matthey), TiO_2 (Merck), ZnO (Merck), Fe_2O_3 (SD Fine, India), CdO

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(Chemco, India), CdS (Chemco, India) and Al₂O₃ (Merck) were used as supplied. The BET surface areas were determined as ZrO₂ 15.12, V₂O₅ 16.14, TiO₂ 14.68, ZnO 12.16, Fe₂O₃ 17.84, CdO 14.45, CdS 15.47, Al₂O₃ 10.63 m² g⁻¹. The particle sizes were measured using Easy particle sizer M1.2, Malvern Instruments (focal length 100 mm, beam length 2.0 mm, wet (methanol) presentation); ZrO₂: 27.6, 23.8, 20.5, 17.7, 11.4, 8.5, 4.1, 3.5 μm at 27.0, 19.0, 12.5, 1.4, 1.8, 31.5, 2.2, 3.8%; V₂O₅: 57.7, 49.8, 42.9, 32.0, 27.6, 23.8, 11.4, 9.8, 8.5 μm at 1.2, 6.2, 2.9, 1.3, 41.8, 15.5, 1.7, 24.1, 5.2%; TiO₂: 27.6, 23.8, 20.5, 17.7, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0, 2.6 μm at 9.1, 18.0, 15.0, 1.4, 12.1, 17.7, 10.5, 1.2, 4.6, 6.5, 2.0%; ZnO: 27.6, 23.8, 20.5, 17.7, 11.4, 9.8, 8.5, 4.1, 3.5 μm at 12.0, 18.9, 12.3, 1.1, 2.1, 30.7, 6.6, 5.2, 10.3%; Fe₂O₃: 27.6, 23.8, 20.5, 17.7, 11.4, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0, 2.6 μm at 4.8, 7.3, 17.6, 2.2, 1.7, 22.2, 15.0, 10.6, 1.7, 5.8, 7.1, 2.1%; CdO: 11.4, 9.8, 8.5, 4.1, 3.5, 3.0, 2.6 μm at 3.0, 44.2, 8.6, 3.3, 10.4, 23.5, 6.4%; CdS: 9.8, 8.5, 7.3, 6.3, 4.1, 3.5, 3.0, 2.6 μm at 13.9, 20.9, 28.6, 1.4, 1.5, 10.8, 17.8, 3.6%; Al₂O₃: 57.7, 49.8, 42.9, 11.4, 9.8, 8.5, 7.3, 3.5, 3.0, 2.6 μm at 3.8, 17.8, 8.7, 1.8, 28.2, 15.3, 10.0, 1.0, 9.7, 3.0%. TiO₂ used is of anatase form (99%+); the XRD pattern of the sample totally matches with the standard pattern of anatase (JCPDS) and the rutile lines are insignificant (Siemens D-5000 XRD, Cu Kα X-ray, λ = 1.54 Å, scan: 5–60°, scan speed: 0.2°/s). Aniline, AR was distilled before use. Commercially available ethanol was distilled over calcium oxide; other organic solvents were of LR grade and distilled prior to use.

2.2. Solar photocatalysis

The solar photocatalyzed oxidations were carried out from 10.30 am to 12.30 pm during summer (March–July) under clear sky. The intensity of solar radiation was measured using Global pyranometer, MCPT, supplied by Industrial Meters, Bombay; it could not be done using lux meter Lx-101A, Lutron, Taiwan, as the intensity was beyond the maximum limit of 50 000 lux. Fresh solutions of aniline of required concentrations were taken in wide cylindrical glass vessels of uniform diameter and appropriate height; the catalyst powder covered the entire bottom of the vessel. Air was bubbled using a micro pump without disturbing the catalyst bed. The volume of the reaction solution was 25 mL; the loss of solvent due to evaporation was compensated periodically. One milliliter of the reaction solution was withdrawn at regular intervals, diluted 5-times and the absorbance measured at 375 nm using Hitachi U-2001 or Jasco UVIDECE-340 UV–vis spectrophotometer.

2.3. UV photocatalysis

Photocatalytic studies with UV light were made in a Heber multilamp photoreactor (HML MP88) fitted with eight 8 W mercury UV lamps of wavelength 365 nm (Sankyo Denki, Japan) and highly polished anodized aluminum reflector; the sample was placed at the centre. Four cooling fans mounted

at the bottom of the reactor dissipate the generated heat. The reaction vessel was borosilicate glass tube of 15 mm inner diameter. Photooxidation was also carried out in a Heber micro photoreactor (HMI SL W6) fitted with a 6 W 254 nm low-pressure mercury lamp and a 6 W 365 nm mercury lamp. Quartz and borosilicate glass tubes were used for 254 and 365 nm lamps, respectively. The light intensity (I_0) was determined by ferrioxalate actinometry.

The volume of the reaction solution was always maintained as 25 mL in the multilamp photoreactor and 10 mL in the micro reactor. Air was bubbled through the reaction solution that effectively stirs the solution and keeps the suspended catalyst under constant motion. The absorbance was measured at 375 nm after centrifuging the catalyst and diluting the solution 5-times to keep the absorbance within the Beer–Lambert law limit.

2.4. Product analysis

Solar photooxidation of aniline in ethanol on ZrO₂ yields azobenzene as the only product. The GC-mass [m/z with relative intensities in parentheses 182 (14), 152 (5), 105 (17), 77 (100), 51 (39)], IR and UV–vis spectra of the extracted solid product are identical with those of *trans*-azobenzene (Fluka).

2.5. Product estimation

In both solar and UV photocatalysis, the UV–vis spectra of the reaction solution recorded during the progress of the reaction are similar (Fig. 1; λ_{max} = 375 nm) but not identical with that of the extracted product (λ_{max} = 434 nm). This is because of formation of both *cis* and *trans*-azobenzenes during the course of the reaction and the unstable *cis* form (*Z*) transforms to the *trans* form (*E*) slowly on standing. The UV–vis spectrum of the irradiated reaction solution but allowed to stand for a couple of days in dark is identical with that of the authentic *trans*-azobenzene confirming the slow transformation of the unstable *cis* form to *trans* form. For a

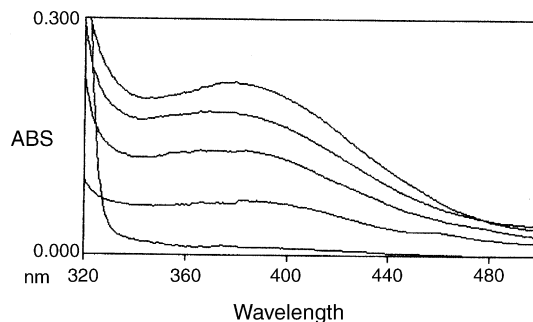


Fig. 1. Solar photooxidation of aniline in ethanol on ZrO₂. The UV–vis spectra of the reaction solution diluted 5-times and recorded at 0, 30, 60, 90 and 120 min (↑); [aniline] = 0.113 M, ZrO₂ bed = 12.5 cm², weight of ZrO₂ = 1.0 g, airflow rate = 4.75 mL s⁻¹, volume of reaction solution = 25 mL.

solution of *cis* and *trans*-azobenzenes

$$[E] = \frac{\text{abs}_{281}\varepsilon_Z(433) - \text{abs}_{433}\varepsilon_Z(281)}{\varepsilon_E(281)\varepsilon_Z(433) - \varepsilon_Z(281)\varepsilon_E(433)}$$

and

$$[Z] = \frac{\text{abs}_{281}\varepsilon_E(433) - \text{abs}_{433}\varepsilon_E(281)}{\varepsilon_Z(281)\varepsilon_E(433) - \varepsilon_Z(433)\varepsilon_E(281)}$$

where ε is the corresponding molar extinction coefficient. Calculation of the ratio $[E]/[Z]$ using the above equations, the experimentally determined $\varepsilon_{E(433)}$ and $\varepsilon_{E(281)}$, the reported $\varepsilon_{Z(433)}$ and $\varepsilon_{Z(281)}$ and the measured absorbance of the reaction solution at 433 and 281 nm at different periods of the reaction shows that the ratio remains practically the same (1.31) during the course of the photooxidation followed. The total concentration of azobenzene, $([E] + [Z]) = \text{abs}_{375} \{1 + ([E]/[Z])\} / \{\varepsilon_{Z(375)} + \varepsilon_{E(375)}([E]/[Z])\}$; $\varepsilon_{E(375)}$ was determined experimentally and $\varepsilon_{Z(375)}$ calculated from the measured abs_{375} ; $\text{abs}_{375} = \{\varepsilon_{Z(375)} + \varepsilon_{E(375)}([E]/[Z])\}[Z]$.

3. Results and discussion

3.1. Obtaining solar oxidation results

The measurement of solar radiation shows fluctuation of sunlight intensity ($530 \pm 40 \text{ W m}^{-2}$) during the course of the photooxidation even under clear sky. Now, for the first time, identical sunlight intensity was maintained for a set of photooxidation experiments of different reaction conditions by carrying out the experiments simultaneously, thus making possible the comparison of the solar results. The solar photooxidation results are reproducible. For example, Fig. 2 presents the linear increase of the absorbance of the reaction solution with the reaction time, one set of experiments conducted in ethanol and benzene side by side on one day and the other set similarly on another day. The ratio of the slopes of the absorbance-time profiles of the reactions in ethanol and benzene remains the same (1.3) although the experiments were conducted on different days, obviously under different sunlight intensities. This reproducibility is not surprising as the fluctuation of sunlight intensity is identical in test and control (standard) experiments and the ratio turns out to be independent of fluctuation of light intensity. Further, the results of a pair of experiments performed simultaneously confirm the reproducibility of the rates of solar photocatalysis. Fig. 3 presents the solar photoformation of azobenzene in ethanol under identical conditions and carried out simultaneously. The ratio of the rates obtained from the linear plots is unity (1.03).

3.2. Factors influencing solar photocatalysis

The influence of various factors on the solar photocatalysis in ethanol was examined by carrying out the given set

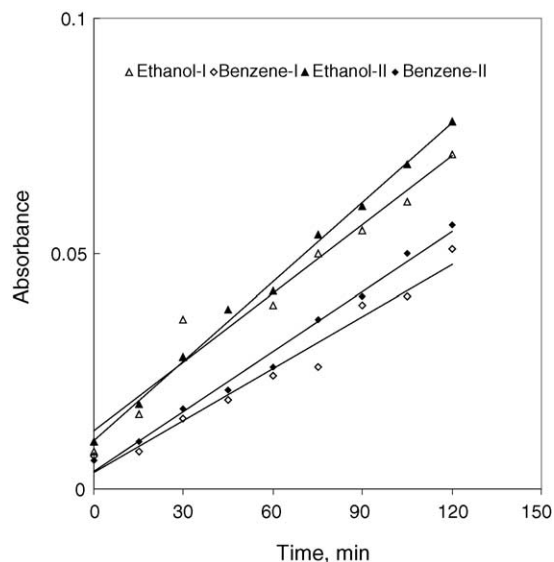


Fig. 2. Solar photooxidation of aniline in ethanol and benzene on ZrO_2 . Absorbance-time plots (experiments in each set conducted simultaneously and sets I and II on different days; the reaction solution diluted 5-times prior to absorbance measurements); $[\text{aniline}] = 0.113 \text{ M}$, ZrO_2 bed = 12.5 cm^2 , weight of $\text{ZrO}_2 = 1.0 \text{ g}$, airflow rate = 4.75 mL s^{-1} , volume of reaction solution = 25 mL .

of experiments simultaneously; the data in each figure correspond to a set of photocatalytic experiments conducted simultaneously. The least-squares slope of the linear plot of [azobenzene] versus time (e.g. Fig. 3) provides the rate of formation of azobenzene. Experiments at different concentrations of aniline shows that the reaction rate increases with [aniline] (Fig. 4) and the variation conforms to the

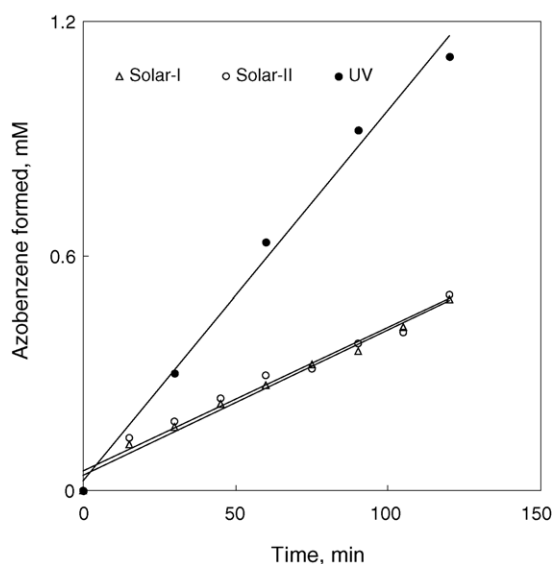


Fig. 3. Photoformation of azobenzene in ethanol on ZrO_2 ; $[\text{aniline}] = 0.113 \text{ M}$, weight of $\text{ZrO}_2 = 1.0 \text{ g}$, volume of reaction solution = 25 mL , airflow rate = 4.75 mL s^{-1} ; solar: ZrO_2 bed = 12.5 cm^2 ; UV: $\lambda = 365 \text{ nm}$, $I_0 = 2.46 \times 10^{-5} \text{ einstein L}^{-1} \text{ s}^{-1}$.

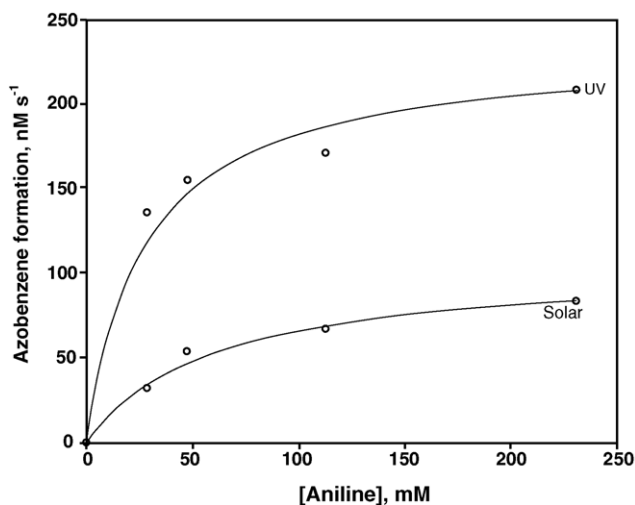


Fig. 4. Azobenzene formation in ethanol on ZrO_2 at different [aniline]; weight of ZrO_2 = 1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 mL s^{-1} (solar), 7.8 mL s^{-1} (UV); solar: ZrO_2 bed = 12.5 cm^2 ; UV: $\lambda = 365 \text{ nm}$, $I_0 = 2.46 \times 10^{-5} \text{ einstein L}^{-1} \text{ s}^{-1}$.

Langmuir–Hinshelwood model. The double reciprocal plot of rate versus [aniline] yields a straight line with a positive y-intercept. The variation of the amount of ZrO_2 spread at the bottom of the reaction vessel (catalytic bed) does not lead to any appreciable change in the photocatalysis rate (Fig. 5); the bottom of the cylindrical reaction vessel was fully covered by the catalyst in all the cases and the increase of the amount of ZrO_2 does not lead to increase of the area of the catalyst bed but only results in increased thickness of the ZrO_2 bed. In the absence of the photocatalyst the reaction is an uncatalyzed one and hence a small rate. The photoformation of azobenzene increases almost linearly with the apparent area of the catalyst bed (Fig. 6). Study of the photooxidation as a function of airflow rate reveals enhancement of photocatalysis by oxygen (Fig. 7). The variation of reaction rate with the airflow rate indicates Langmuir–Hinshelwood kinetics and the linear double reciprocal plot of reaction rate versus air-

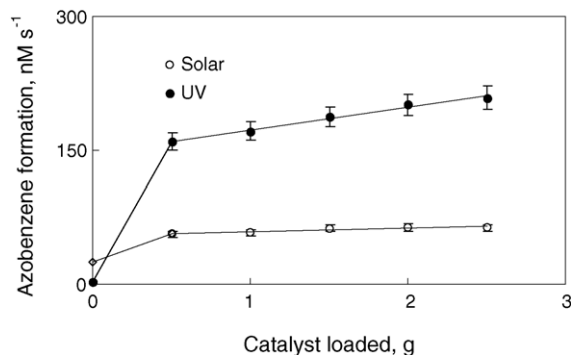


Fig. 5. Azobenzene formation in ethanol at different amounts of ZrO_2 loading; [aniline] = 0.113 M, volume of reaction solution = 25 mL, airflow rate = 4.75 mL s^{-1} (solar), 7.8 mL s^{-1} (UV); solar: ZrO_2 bed = 12.5 cm^2 ; UV: $\lambda = 365 \text{ nm}$, $I_0 = 2.46 \times 10^{-5} \text{ einstein L}^{-1} \text{ s}^{-1}$.

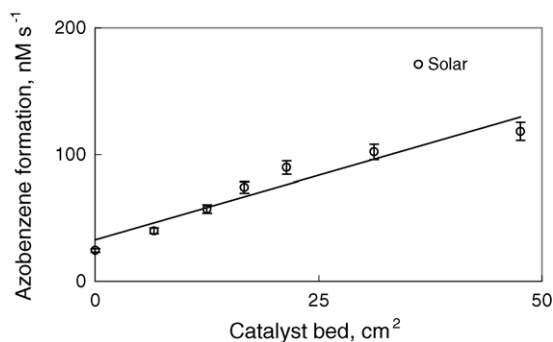


Fig. 6. Azobenzene formation (solar) in ethanol at varying areas of ZrO_2 bed; [aniline] = 0.113 M, weight of ZrO_2 = 1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 mL s^{-1} .

flow rate confirms the same. The reaction was also studied without bubbling air but the solution was not deaerated. The dissolved oxygen itself brings in the oxidation but the photocatalysis is slow. The reaction does not occur in dark. The photocatalyst does not lose its catalytic activity on repeated use. Reuse of the photocatalyst yields identical results. Addition of water to the reaction medium slows down the reaction (Fig. 8). Electron donors like triphenylphosphine (TPP), hydroquinone (HQ), diphenylamine (DPA) and triethylamine (TEA), enhance the photoformation of azobenzene. Addition of TEA (0.287 M) to the reaction solution results in an increase of azobenzene formation rate by ca. 49% (the reaction conditions as in Fig. 9). The variation of the enhanced photoformation rate with [TPP], [HQ] and [DPA] (Fig. 9) reveals Langmuir–Hinshelwood kinetics and the linear double reciprocal plots of the enhanced rate (the difference in the rates of formation of azobenzene in the presence and absence of sacrificial electron donors) versus [TPP], [HQ] and [DPA] confirm

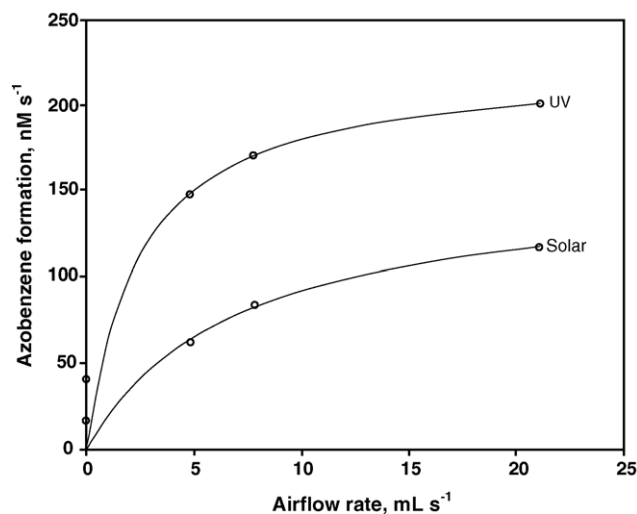


Fig. 7. Azobenzene formation in ethanol on ZrO_2 at different airflow rates; [aniline] = 0.113 M, weight of ZrO_2 = 1.0 g, volume of reaction solution = 25 mL; solar: ZrO_2 bed = 12.5 cm^2 ; UV: $\lambda = 365 \text{ nm}$, $I_0 = 2.46 \times 10^{-5} \text{ einstein L}^{-1} \text{ s}^{-1}$.

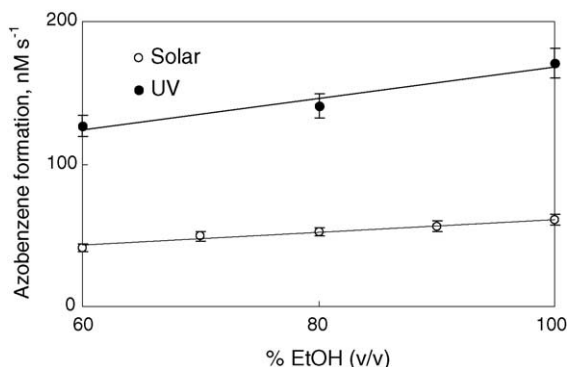


Fig. 8. Azobenzene formation on ZrO_2 in aq. EtOH; [aniline]=0.113 M, weight of ZrO_2 =1.0 g, volume of reaction solution=25 mL, airflow rate=4.75 mL s⁻¹ (solar), 7.8 mL s⁻¹ (UV); solar: ZrO_2 bed=12.5 cm²; UV: λ =365 nm, I_0 =2.46 \times 10⁻⁵ einstein L⁻¹ s⁻¹.

the same. Use of sacrificial electron donors leads to hole trapping resulting in enhanced photocatalysis [1]. Both anionic and cationic surfactants enhance the photocatalysis; addition of anionic surfactants aerosol OT (sodium *bis*-2-ethylhexyl sulfosuccinate, 0.0225 M) and sodium lauryl sulfate (SLS, 0.0347 M) and cationic surfactant cetyltrimethylammonium bromide (CTAB, 0.0274 M) to the reaction solution (conditions as in Fig. 9) increases the photoformation rate by 23, 74 and 43%, respectively. Vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) neither suppress the photocatalysis nor undergo polymerization indicating the absence of free radicals in the reaction solution during the course of photocatalysis.

3.3. Factors influencing UV photocatalysis

The photocatalyzed oxidation of aniline in ethanol in the presence of air on ZrO_2 was investigated using a multi-

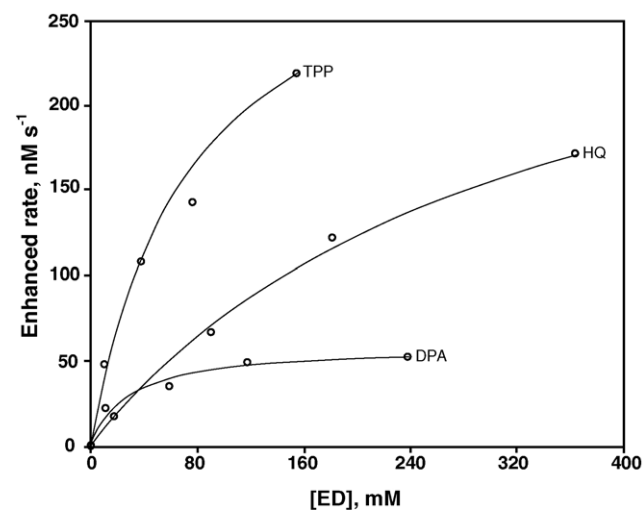


Fig. 9. Azobenzene formation (solar) in ethanol on ZrO_2 in presence of electron donors (ED); [aniline]=0.113 M, weight of ZrO_2 =1.0 g, volume of reaction solution=25 mL, airflow rate=4.75 mL s⁻¹; ZrO_2 bed=12.5 cm².

amp photoreactor with mercury UV lamps of wavelength 365 nm. Linear increase of azobenzene-concentration with illumination time provides the photochemical formation rate (e.g. Fig. 3) and the rates are reproducible to \pm 6%. Rate measurements at different [aniline] show increase of the oxidation rate with [aniline] (Fig. 4) and the increase indicates Langmuir–Hinshelwood kinetics. The increase of the amount of ZrO_2 suspended in the reaction medium results in only an insignificant increase in azobenzene formation (Fig. 5). Study of the photooxidation as a function of air-flow rate reveals enhancement of photocatalysis by oxygen and the variation of the reaction rate with flow rate conforms to the Langmuir–Hinshelwood kinetics (Fig. 7). The reaction was also studied without bubbling air but the solution was not deoxygenated. The dissolved oxygen itself brings in the oxidation but the photocatalysis is slow. The photooxidation was examined as a function of light intensity. The oxidation was carried out with two, four and eight lamps, the angles sustained by the adjacent lamps at the sample are 180°, 90° and 45°, respectively. Fig. 10 is the variation of rate with the light intensity. The reaction does not occur in dark. Study of the photocatalysis with a 6 W 365 nm mercury lamp (I_0 =1.81 \times 10⁻⁵ einstein L⁻¹ s⁻¹) and a 6 W 254 nm low-pressure mercury lamp (I_0 =5.22 \times 10⁻⁶ einstein L⁻¹ s⁻¹) separately in the micro reactor under identical conditions reveals that high energy radiation is more effective in bringing out the photocatalysis. Azobenzene formed in 10 min on illumination at 365 and 254 nm are 182 and 722 μ M, respectively ([aniline]=0.113 M, ZrO_2 suspended=0.2 g, airflow rate=7.8 mL s⁻¹, volume of reaction solution=10 mL). The metal oxide does not lose its photocatalytic activity on illumination. Reuse of the catalyst reveals sustainable photocatalytic efficiency. Addition of water to the reaction solution suppresses the photocatalysis (Fig. 8). Electron donors like triphenylphosphine, hydroquinone and diphenylamine enhance azobenzene formation and the variation of the photocatalysis rate with [TPP], [HQ] and [DPA] is similar to that of the solar photooxidation. However, triethylamine (0.287 M)

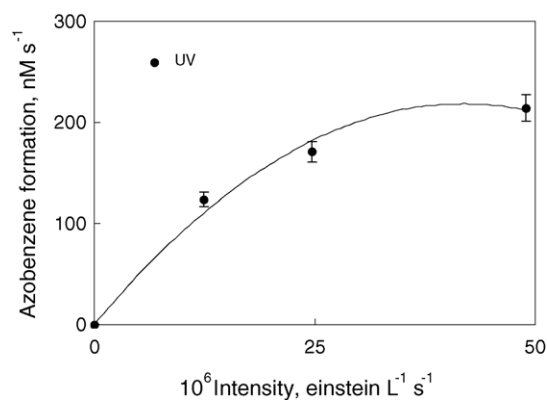
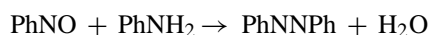
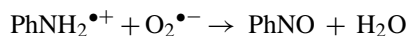
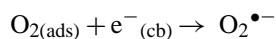
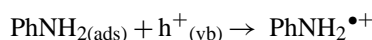
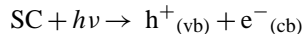


Fig. 10. Azobenzene formation in ethanol on ZrO_2 at different light intensities; [aniline]=0.113 M, ZrO_2 suspended=1.0 g, airflow rate=7.8 mL s⁻¹, λ =365 nm, volume of reaction solution=25 mL.

does not facilitate azobenzene formation. While aerosol OT (0.0225 M) fails to significantly influence the UV photocatalysis SLS (0.0347 M) and CTAB (0.0274 M) enhance the reaction by 95 and 20%, respectively. Also, vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) do not inhibit the photocatalysis. Nor do they polymerize. Azide ion (0.154 M), a singlet oxygen quencher, fails to suppress the formation of azobenzene indicating the absence of involvement of singlet oxygen in the photocatalysis.

3.4. Mechanism

Illumination of the semiconductor with light of required energy leads to bandgap excitation of the semiconductor resulting in creation of electron–hole pairs; holes in the valence band and electrons in the conductance band. Since the recombination of photogenerated electron–hole pairs in semiconductors are so rapid (occurring in a picosecond time scale), for an effective photocatalysis the reactants are to be adsorbed on the photocatalyst [3]. The hole reacts with adsorbed aniline molecule to form aniline radical-cation ($\text{PhNH}_2^{\bullet+}$). In the presence of oxygen, transfer to the adsorbed oxygen molecule resulting in highly active superoxide radical-anion, $\text{O}_2^{\bullet-}$, effectively removes the electron [1]. The reaction of aniline radical-cation with superoxide radical-anion results in nitrosobenzene. Condensation of nitrosobenzene with aniline, present in large excess, yields azobenzene.



Ethanol may undergo oxidation in the presence of illuminated semiconductor and generation of radicals is possible [15,16]. If the photooxidation of aniline were due to the radicals generated from solvent ethanol, contrary to the experimental observations, azobenzene formation should not depend on [aniline]; the photogenerated radicals are short lived and react almost instantaneously demanding non-dependence of the reaction rate on [aniline]. Also, the oxidation occurs in a number of organic solvents (*vide infra*).

3.5. Kinetic analysis

The kinetic law that governs heterogeneous photocatalyzed reaction in a continuously stirred tank reactor (CSTR) [17] is

$$\text{rate} = \frac{kK_1K_2SI_0C[\text{PhNH}_2]\gamma}{(1 + K_1[\text{PhNH}_2])(1 + K_2\gamma)}$$

where K_1 and K_2 are the adsorption coefficients of aniline and oxygen on ZrO_2 , k is the specific rate of oxidation of aniline, γ the airflow rate, S the specific surface area of ZrO_2 , C the amount of ZrO_2 suspended per liter and I_0 the light intensity in $\text{einstein L}^{-1} \text{s}^{-1}$. Linear double reciprocal plots of rate of azobenzene formation versus (i) $[\text{PhNH}_2]$ and (ii) airflow rate are in agreement with the kinetic law and afford the adsorption coefficients as $K_1 = 62 \text{ L mol}^{-1}$, $K_2 = 0.41 \text{ mL}^{-1} \text{ s}$, $k = 32 \mu\text{mol L m}^{-2} \text{ einstein}^{-1}$. The data fit to the curves (Figs. 4 and 7), governed by the above kinetic law and drawn using a computer program, support the rate expression. However, the rate of photocatalysis does not increase with the amount of ZrO_2 suspended. This is because of the high catalyst loading. At high catalyst loading, the surface area of the catalyst exposed to illumination does not commensurate with the weight of the catalyst. The amount of ZrO_2 employed is beyond the critical amount corresponding to the volume of the reaction solution and reaction vessel; the whole amount of ZrO_2 is not exposed to illumination. The photocatalysis lacks linear dependence on illumination intensity; less than first power dependence of surface-photocatalysis rate on light intensity at high intensity is well known [18].

3.6. Photocatalysis in different solvents

Adsorption of aniline and oxygen on ZrO_2 and the concentration of dissolved oxygen in the reaction medium vary with the solvent. Contact between a semiconductor and a liquid generally involves a redistribution of electric charges and the formation of a double layer. The bands of the semiconductor bend and this bending is influenced by the solvent [3]. Hence the variation of the photocatalysis rate with the solvent is also likely due to the band bending at the semiconductor–solution interface. The oxidation of aniline on ZrO_2 with sunlight and UV irradiation was carried out in eighteen solvents and the UV–vis spectra reveal formation of azobenzene in all the solvents studied. The least-squares slopes of the linear absorbance-time traces of UV photocatalysis are 31.8, 25.9, 32.7, 44.8, 36.4, 43.2, 80.5, 38.7, 25.4, 17.3, 39.7, 19.4, 18.5, 35.2, 15.8, 10.2, 44.7 and 51.9 (in 10^{-6} s^{-1}) in ethanol, *n*-butanol, *t*-butanol, propane-1,2-diol, 2-butoxyethanol, ethyl methyl ketone, acetic acid, dimethylformamide, acetonitrile, ethyl acetate, 1,4-dioxane, benzene, toluene, chlorobenzene, nitrobenzene, *n*-hexane, chloroform and carbon tetrachloride, respectively ($[\text{PhNH}_2] = 0.113 \text{ M}$, ZrO_2 suspended = 1.0 g, airflow rate = 7.8 mL s^{-1} , $\lambda = 365 \text{ nm}$, $I_0 = 2.46 \times 10^{-5} \text{ einstein L}^{-1} \text{ s}^{-1}$, volume of reaction solution 25 mL). The corresponding relative slopes of solar photocatalysis are: 1.00, 1.95, 1.59, 2.88, 4.53, 2.64, 2.22, 2.10, 1.71, 1.01, 1.47, 0.75, 1.16, 2.69, 0.50, 0.67, 2.95 and 0.36 ($[\text{PhNH}_2] = 0.113 \text{ M}$, weight of $\text{ZrO}_2 = 1.0 \text{ g}$, catalyst bed = 12.5 cm^2 , airflow rate = 4.75 mL s^{-1} , volume of reaction solution = 25 mL). Calculation of the photocatalytic oxidation rates in different solvents requires the molar extinction coefficients of *cis* and *trans*-azobenzenes at appro-

appropriate wavelengths and the ratio at which *cis* and *trans*-azobenzenes are formed in each solvent and hence could not be made. The relative slopes of solar photocatalysis do not conform to those with UV-light, as they are not the true rates.

3.7. Comparison of some photocatalysts

The photooxidation of aniline to azobenzene was studied in ethanol with eight commercially available metal oxides and sulfide, viz., TiO₂, V₂O₅, ZnO, Fe₂O₃, CdO, CdS, Al₂O₃ besides ZrO₂. Under UV illumination of wavelength 254 nm, ZrO₂ is more efficient than other photocatalysts studied. The photocatalytic activities are of the order ZrO₂ > ZnO > V₂O₅ > Fe₂O₃ > CdS > Al₂O₃ > CdO > TiO₂; azobenzene formed in ethanol in 10 min are 722, 656, 631, 553, 487, 436, 363 and 73 μM, respectively ([PhNH₂] = 0.113 M, catalyst suspended = 0.2 g, airflow rate = 7.8 mL s⁻¹, λ = 254 nm, I₀ = 5.22 × 10⁻⁶ einstein L⁻¹ s⁻¹, volume of reaction solution 10 mL). However, ZrO₂ loses its edge over other photocatalysts on illumination at longer wavelength and with sunlight. The catalytic efficiencies with UV light of wavelength 365 nm are as follows: V₂O₅ > ZnO > ZrO₂ > Fe₂O₃ > Al₂O₃ > CdS > CdO > TiO₂. The rates of azobenzene formation in ethanol are 239, 181, 171, 122, 111, 78, 62 and 16 nM s⁻¹, respectively ([PhNH₂] = 0.113 M, catalyst suspended = 1.0 g, airflow rate = 7.8 mL s⁻¹, λ = 365 nm, I₀ = 2.46 × 10⁻⁵ einstein L⁻¹ s⁻¹, volume of reaction solution 25 mL). The relative catalytic efficiency of ZrO₂ is further lowered with sunlight. The solar photocatalytic efficiencies are of the order V₂O₅ > ZnO > Fe₂O₃ > CdO > ZrO₂ > Al₂O₃ > CdS > TiO₂; the solar photoformation of azobenzene under identical conditions in 30 min are 290, 270, 230, 210, 180, 80, 70 and 30 μM, respectively ([PhNH₂] = 0.113 M, catalyst weight = 1.0 g, catalyst bed = 12.5 cm², airflow rate = 4.75 mL s⁻¹, volume of reaction solution = 25 mL).

4. Conclusions

The effects of [aniline], airflow rate, solvent, sacrificial electron donors, etc. on the rates of solar photocatalyzed oxidation of aniline on ZrO₂ are similar to those with UV light. With UV light of wavelength 254 nm, ZrO₂ is more efficient than TiO₂, V₂O₅, ZnO, Fe₂O₃, CdO, CdS and Al₂O₃ in the photooxidation of aniline in ethanol. However, ZrO₂ loses its edge over other photocatalysts on illumination at longer wavelength (365 nm) and with sunlight.

Appendix

$$\text{abs}_{281} = \varepsilon_{Z(281)}[Z] + \varepsilon_{E(281)}[E] \quad (l = 1 \text{ cm}) \quad (1)$$

$$\text{abs}_{433} = \varepsilon_{Z(433)}[Z] + \varepsilon_{E(433)}[E] \quad (2)$$

$$\varepsilon_{Z(281)}\varepsilon_{Z(433)}[Z] + \varepsilon_{E(281)}\varepsilon_{Z(433)}[E] - \text{abs}_{281}\varepsilon_{Z(433)} = 0 \quad (3)$$

$$\varepsilon_{Z(433)}\varepsilon_{Z(281)}[Z] + \varepsilon_{E(433)}\varepsilon_{Z(281)}[E] - \text{abs}_{433}\varepsilon_{Z(281)} = 0 \quad (4)$$

$$(3) - (4)$$

$$\varepsilon_{E(281)}\varepsilon_{Z(433)}[E] - \varepsilon_{Z(281)}\varepsilon_{E(433)}[E] + \text{abs}_{433}\varepsilon_{Z(281)} - \text{abs}_{281}\varepsilon_{Z(433)} = 0 \quad (5)$$

$$[E] = \frac{\text{abs}_{281}\varepsilon_{Z(433)} - \text{abs}_{433}\varepsilon_{Z(281)}}{\varepsilon_{E(281)}\varepsilon_{Z(433)} - \varepsilon_{Z(281)}\varepsilon_{E(433)}} \quad (6)$$

$$\varepsilon_{Z(281)}\varepsilon_{E(433)}[Z] + \varepsilon_{E(281)}\varepsilon_{E(433)}[E] - \text{abs}_{281}\varepsilon_{E(433)} = 0 \quad (7)$$

$$\varepsilon_{Z(433)}\varepsilon_{E(281)}[Z] + \varepsilon_{E(433)}\varepsilon_{E(281)}[E] - \text{abs}_{433}\varepsilon_{E(281)} = 0 \quad (8)$$

$$(7) - (8)$$

$$\varepsilon_{Z(281)}\varepsilon_{E(433)}[Z] - \varepsilon_{Z(433)}\varepsilon_{E(281)}[Z] - \text{abs}_{281}\varepsilon_{E(433)} + \text{abs}_{433}\varepsilon_{E(281)} = 0 \quad (9)$$

$$[Z] = \frac{\text{abs}_{281}\varepsilon_{E(433)} - \text{abs}_{433}\varepsilon_{E(281)}}{\varepsilon_{Z(281)}\varepsilon_{E(433)} - \varepsilon_{Z(433)}\varepsilon_{E(281)}} \quad (10)$$

$$\text{abs}_{375} = \left\{ \varepsilon_{Z(375)} + \varepsilon_{E(375)} \left(\frac{[E]}{[Z]} \right) \right\} [Z] \quad (11)$$

$$[Z] = \frac{\text{abs}_{375}}{\varepsilon_{Z(375)} + \varepsilon_{E(375)}([E]/[Z])} \quad (12)$$

$$[Z] + [E] = [Z] \left\{ 1 + \left(\frac{[E]}{[Z]} \right) \right\} \quad (13)$$

$$= \text{abs}_{375} \frac{1 + ([E]/[Z])}{\varepsilon_{Z(375)} + \varepsilon_{E(375)}([E]/[Z])} \quad (14)$$

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