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Inhibition of photooxidation of iron(II) by some semiconductors

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Abstract

The photooxidation of iron(II) in aqueous ethanol is less in presence of TiO_2, ZrO_2, V_2O_5, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2, CdS, ZnS and Al_2O_3 than in their absence. The photogeneration of iron(III) was studied at different $[Fe^{2+}]$, amounts of semiconductors suspended, airflow rates, light intensities, solvent compositions and wavelengths of illumination. The catalysts show sustainable photocatalytic activity. The metal oxides and sulfides reduce iron(III), formed by the homogeneous photooxidation of iron(II). TiO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 effectively suppress the photooxidation of iron(II); ZrO_2, ZnS and CdS also suppress but not completely. At high catalyst-loading V_2O_5 catalyses the photooxidation of iron(II). The mechanisms of the photocatalytic processes are discussed.

Keywords: Iron(II) photooxidation; Iron(III) photoreduction; Semiconductors

1. Introduction

Production of energy-bearing chemicals through thermodynamically uphill reactions is the objective of solar energy conversion and storage, and one such reaction is the oxidation of iron(II) to iron(III) ($\Delta G^\circ = +74.4\ \mathrm{kJ\ mol^{-1}}$). Iron(II) in aqueous solution undergoes UV photooxidation ($\lambda = 265$ nm) generating hydrogen and in near neutral solution (pH 6–4.8) hydrated electron has been detected as intermediate [1]; also, the primary quantum yield is independent of temperature [2]. Studies in acidic solution show that the oxidation rate of iron(II) falls off with irradiation time due to the reduction of iron(III) [3]. $FeCl_3$ in methanol is photoreduced ($\lambda = 404$ nm) but irradiation of $FeCl_3$ with $FeCl_2$ results in the oxidation of iron(II) [4]. Iron(III) complexes (e.g. iron(III) porphyrins) undergo photoreduction [5,6]. UV irradiation leads to ligand to metal charge transfer transition setting in an intramolecular redox process; iron(III) is reduced and the ligand is oxidized. Iron(III) photocatalyzes mineralization of a variety of organic compounds [7–9]. Although homogeneous photooxidation of iron(II) is extensively reported, literature lacks studies using semiconductor metal oxides and sulfides as catalysts and hence this work; the results of photooxidation of iron(II) in presence of cheap commercially available TiO_2, ZrO_2, V_2O_5, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2, CdS, ZnS and Al_2O_3 under identical conditions reveal inhibition of photooxidation by these metal oxides and sulfides.

2. Experimental

2.1. Materials

TiO_2 (Merck), ZrO_2 (Chemco, India) V_2O_5 (Johnson Matthey), CeO_2 (Schering-Kahlbaum A.G.), ZnO (Merck), Fe_2O_3 (SD Fine, India), CdO (Chemco, India), PbO (Fischer, India), SnO_2 (BDH), CdS (Chemco, India), ZnS (SD Fine, India), Al_2O_3 (Merck), ferrous ammonium sulfate (AR, SD Fine, India), ferric ammonium sulfate (AR, Himedia, India), KSCN (BDH) and HCl (AR, Fisher, India) were used as received. Commercially available ethanol was distilled over calcium oxide. Deionized distilled water was employed throughout the study. TiO_2 used is of anatase form (>99%);

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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, $\lambda = 1.54$ Å, scan: 5–60°, scan speed: 0.2° s^{-1}). The BET surface areas of the photocatalysts employed are ($m^2\,g^{-1}$): TiO_2 14.68, ZrO_2 15.12, V_2O_5 16.14, CeO_2 96.06, ZnO 12.16, Fe_2O_3 17.84, CdO 14.45, PbO 0.28, SnO_2 114.68, CdS 15.47, ZnS 7.67 and Al_2O_3 10.63. The particle sizes were determined using laser scattering particle size distribution analyzer, Horiba LA-910 and Easy particle sizer M1.2, Malvern Instruments (focal length 100 mm, beam length 2.0 mm, wet (methanol) presentation; TiO_2: 27.6, 23.8, 20.5, 17.7, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0 and 2.6 μm at 9.1, 18.0, 15.0, 1.4, 12.1, 17.7, 10.5, 1.2, 4.6, 6.5 and 2.0%; ZrO_2: 27.6, 23.8, 20.5, 17.7, 11.4, 8.5, 4.1 and 3.5 μm at 27.0, 19.0, 12.5, 1.4, 1.8, 31.5, 2.2 and 3.8%; V_2O_5: 57.7, 49.8, 42.9, 32.0, 27.6, 23.8, 11.4, 9.8 and 8.5 μm at 1.2, 6.2, 2.9, 1.3, 41.8, 15.5, 1.7, 24.1 and 5.2%; CeO_2: 34.25, 29.91, 26.11, 22.80, 19.90, 17.38, 15.17, 13.25, 11.56, 10.10, 8.816, 7.697, 6.720 and 5.867 μm at 1.43, 4.01, 7.74, 11.34, 13.18, 13.27, 12.03, 10.59, 8.33, 6.04, 4.14, 2.74, 1.79 and 1.16%; ZnO: 27.6, 23.8, 20.5, 17.7, 11.4, 9.8, 8.5, 4.1 and 3.5 μm at 12.0, 18.9, 12.3, 1.1, 2.1, 30.7, 6.6, 5.2 and 10.3%; Fe_2O_3: 27.6, 23.8, 20.5, 17.7, 11.4, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0 and 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 and 2.1%; CdO: 11.4, 9.8, 8.5, 4.1, 3.5, 3.0 and 2.6 μm at 3.0, 44.2, 8.6, 3.3, 10.4, 23.5 and 6.4%; PbO: 13.25, 11.56, 10.10, 8.816, 7.697, 6.720, 5.867, 5.122 and 4.472 μm at 3.18, 9.96, 19.30, 24.39, 20.81, 10.80, 5.76, 2.87 and 1.27%; SnO_2: 17.38, 15.17, 13.25, 11.56, 10.10, 8.816, 7.697, 6.720, 5.867, 5.122, 4.472, 3.905, 3.409, 2.976, 2.599, 2.269, 1.981, 1.729, 1.510, 1.318 and 1.151 μm at 2.11, 3.84, 6.59, 9.13, 10.66, 10.75, 10.15, 7.87, 6.50, 5.21, 4.11, 3.31, 2.71, 2.30, 2.01, 1.80, 1.65, 1.53, 1.42, 1.30 and 1.14%; CdS: 9.8, 8.5, 7.3, 6.3, 4.1, 3.5, 3.0 and 2.6 μm at 13.9, 20.9, 28.6, 1.4, 1.5, 10.8, 17.8 and 3.6%; ZnS: 2.599, 2.269, 1.981, 1.729, 1.510, 1.318, 1.151, 1.005, 0.877, 0.766, 0.669, 0.197, 0.172, 0.150, 0.131 and 0.115 μm at 1.27, 2.88, 5.65, 9.25, 12.78, 14.05, 12.08, 8.43, 5.11, 2.88, 1.61, 1.62, 2.61, 3.42, 3.91 and 6.13%; Al_2O_3: 57.7, 49.8, 42.9, 11.4, 9.8, 8.5, 7.3, 3.5, 3.0 and 2.6 μm at 3.8, 17.8, 8.7, 1.8, 28.2, 15.3, 10.0, 1.0, 9.7 and 3.0%.

2.2. Photoreactors

Photochemical studies were carried out in a multilamp photoreactor (HML MP88, Heber Scientific, India) 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 heat generated. The reaction vessel was borosilicate glass tube of 15 mm inner diameter. Photooxidations were also made in a micro photoreactor (HMI SL W6), supplied by Heber Scientific, fitted with a 6 W 254 nm low-pressure mercury lamp and a 6 W 365 nm mercury lamp. Borosilicate glass and quartz sample tubes were used for 365 and 254 nm lamps, respectively. Absorption spectral measurements were made using Hitachi U-2001 UV–vis spectrophotometer.

2.3. Method

Aqueous solutions of iron(II) and iron(III) of desired concentrations were prepared fresh and used. The reactions were carried out in aqueous ethanol and the volume of the reaction solution was always maintained as 20 mL in the multilamp photoreactor and 10 mL in the micro reactor. The time of illumination was 30 min in the former and 15 min in the latter. Air was passed through the reaction solution using a micro pump that effectively stirs the solution and keeps the suspended catalyst under constant motion. The iron(III) was estimated spectrophotometrically by centrifuging the catalyst and diluting the solution to double its volume after acidifying with concentrated hydrochloric acid and complexing with thiocyanate. Similarly, the concentration of iron(III) in the reaction solution before irradiation was also determined; calibration curve was constructed using standard iron(III) solution. The photon flux of the light source (I_0) was determined by ferrioxalate actinometry.

3. Results and discussion

The photooxidation of iron(II) in 60% (v/v) aqueous ethanol in the presence of air and photocatalyst (TiO_2, ZrO_2, V_2O_5, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2, CdS, ZnS and Al_2O_3) was studied using a multilamp photoreactor with mercury UV lamps of wavelength 365 nm. The TiO_2 suspended in water does not settle down completely even after centrifuging for hours together, fails to yield clear and transparent solution but at and above 60% aqueous ethanol the centrifuged solution is clear. The formation of iron(III), in the absence and presence of photocatalysts, was confirmed by thiocyanate and salicylic acid tests and iron(III) was estimated spectrophotometrically ($\lambda = 480$ nm) by complexing with thiocyanate in acid medium. The homogeneous photooxidation of iron(II) is not unknown [1–3]; irradiation at 254 nm yields iron(III) with liberation of hydrogen. But the present results show that the photooxidation of iron(II) occurs with UV light of longer wavelength (365 nm) which is used in semiconductor photocatalysis.

3.1. Photooxidation without semiconductors

The homogeneous photooxidation of iron(II) at different $[Fe^{2+}]$, in the presence as well as in the absence of air, reveals that it is less susceptible to $[Fe^{2+}]$; the quantum yields of iron(III) formation in the presence and absence of air at 2.5, 5.0, 10.0 and 25.0 mM iron(II) are 0.006, 0.007, 0.007, 0.009 and 0.005, 0.007, 0.007 and 0.009, respectively ($[H^+]$ = 2.0 mM, airflow rate = 7.8 mL s^{-1}, $\lambda = 365$ nm, $I_0 = 1.92 \times 10^{-5}$ einstein $L^{-1}\,s^{-1}$, 60% (v/v) aqueous ethanol). This is in agreement with the earlier report that the photooxidation rate using light of wavelength 254 nm is not susceptible to [Fe^{2+}] up to 0.1 M. Also, there is no significant difference in the photooxidation rates in the presence and absence of air. The solvent was not deoxygenated and hence dissolved oxygen could even be responsible for the observed parallel experimental results in the presence and absence of air; the photooxidation was studied not beyond 4% conversion of iron(II) to iron(III). Earlier investigations reveal photooxidation of iron(II) even in the absence of air [1,3]. Thermal oxidation of iron(II), under identical conditions but in dark, both in the presence and absence of air is small at all the [Fe^{2+}] studied. The homogeneous photooxidation of iron(II) is independent of airflow rate; the quantum yield of iron(III) formation remains as 0.007 at airflow rates of 0, 4.8, 7.8 and 21 mL s^{-1} ([Fe^{2+}] = 5.0 mM, [H^+] = 2.0 mM, λ = 365 nm, I_0 = 1.92 × 10^{-5} einstein L^{-1} s^{-1}, 60% (v/v) aqueous ethanol). The quantum yield of iron(III) formation, both in the presence and absence of air, decreases with increase of the intensity of illumination; at 0.95 × 10^{-5}, 1.92 × 10^{-5} and 3.86 × 10^{-5} einstein L^{-1} s^{-1}, the quantum yields are 0.010, 0.006 and 0.005, respectively, both with and without passing air ([Fe^{2+}] = 5.0 mM, [H^+] = 5.0 mM, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, 60% (v/v) aqueous ethanol). The photooxidation was carried out with two, four and eight (8 W) UV mercury lamps, the angles sustained by the adjacent lamps at the sample are 180°, 90° and 45°, respectively. The dark reaction is negligible. Increase of the ethanol content of the medium favors the photooxidation of iron(II). The quantum yield increases from 0.007 to 0.018 on increasing the percentage of ethanol in the reaction solution from 60 to 80 ([Fe^{2+}] = 5.0 mM, [H^+] = 2.0 mM, airflow rate = 7.8 mL s^{-1}, I_0 = 1.92 × 10^{-5} einstein L^{-1} s^{-1}). Investigation of photooxidation of iron(II) using a 6 W 365 nm mercury lamp (I_0 = 1.74 × 10^{-5} einstein L^{-1} s^{-1}) and a 6 W 254 nm low-pressure mercury lamp (I_0 = 0.50 × 10^{-5} einstein L^{-1} s^{-1}) separately in the micro reactor under identical conditions reveals that high energy radiation is more effective in bringing out photooxidation. For 15 min illumination, the quantum yields of iron(III) formation in 60% (v/v) aqueous ethanol are 0.015 and 0.068 at 365 and 254 nm, respectively ([Fe^{2+}] = 5.0 mM, [H^+] = 2.0 mM, airflow rate = 7.8 mL s^{-1}).

3.2. Photooxidation with semiconductors

Photooxidation of iron(II) in aqueous ethanol in the presence of metal oxide or sulfide (TiO_2, ZrO_2, V_2O_5, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2, CdS, ZnS and Al_2O_3) and air reveals that the photoformation of iron(III) is less with the photocatalysts than in their absence (Fig. 1). That is, the semiconductors hinder the photooxidation of iron(II). At high [Fe^{2+}], the formation of iron(III) is significant although less than that in the absence of metal oxides and sulfides. Variation of the amount of metal oxides and sulfides suspended in the reaction solution does not show any significant effect except in the case of V_2O_5 where the photoformation of iron(III) increases with the amount of oxide suspended and generates more iron(III) than in its absence at high catalyst-loading. Fig. 2 shows that TiO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 effectively suppress the photooxidation of iron(II) at all the concentrations of metal oxides studied. ZrO_2, ZnS and CdS also suppress the photoformation of iron(III) but not completely. Similarly, the variation of the

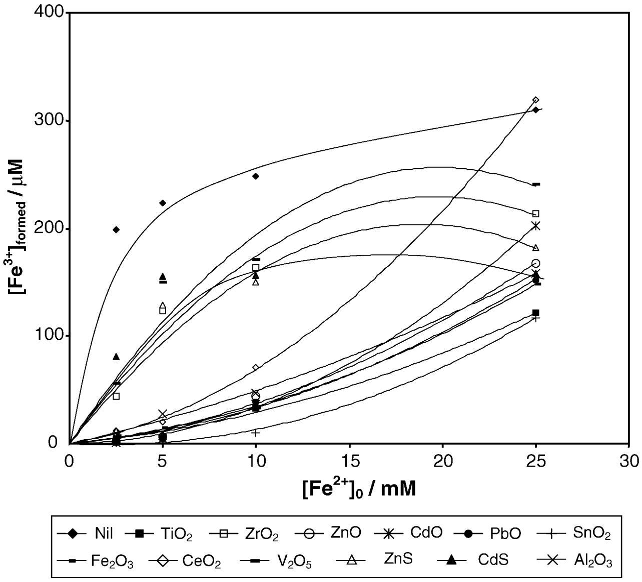

Fig. 1. Photooxidation of iron(II) with and without metal oxides and sulfides at different [Fe^{2+}]$_0$. [H^+] = 2.0 mM, catalyst suspended = 5.0 g L^{-1}, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, I_0 = 1.92 × 10^{-5} einstein L^{-1} s^{-1}, 60% (v/v) aqueous ethanol, illumination time = 30 min.

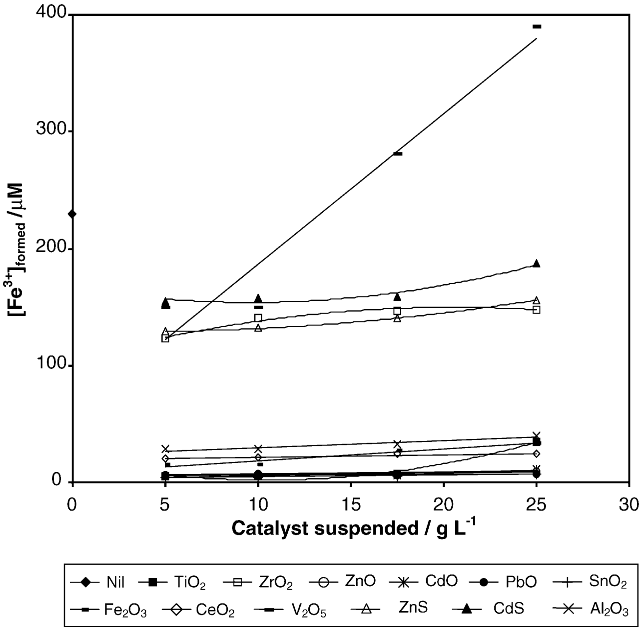

Fig. 2. Photooxidation of iron(II) at different amounts of metal oxides and sulfides suspended. [Fe^{2+}]$_0$ = 5.0 mM, [H^+] = 2.0 mM, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, I_0 = 1.92 × 10^{-5} einstein L^{-1} s^{-1}, 60% (v/v) aqueous ethanol, illumination time = 30 min.

airflow rate has little influence with TiO_2, ZrO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 but V_2O_5, ZnS and CdS show increased formation of iron(III) with increasing airflow rate although it is less than that in their absence (Fig. 3). The reaction was also studied without passing air but the solutions were not deoxygenated. The dissolved oxygen could participate in the photoreaction. The photooxidation in presence of metal oxides and sulfides and air was examined as a function of photon flux; the reaction was carried out with two, four and eight 8 W UV mercury lamps, the adjacent lamps sustain angles of 180°, 90° and 45°, respectively, at the sample. Except V_2O_5, ZrO_2, ZnS and CdO all other metal oxides show insignificant effect on increasing the intensity of illumination (Fig. 4). The oxidation of iron(II) does not occur in dark. Increase of acidity of the medium enhances the photooxidation of iron(II). The iron(III) formed by photooxidation is large at high acidity; the reaction was studied at 2.0, 32, 83 and 182 mM hydrochloric acid. However, the acid catalysis of the photooxidation was not quantified; dissolution of some of the metal oxides in the reaction solution due to increased acidity, even in trace, could not be ruled out. Increase of ethanol content in the reaction medium facilitates the photooxidation of iron(II) (Table 1). Investigation of iron(II) oxidation using a 6 W 254 nm low-pressure mercury lamp and a 6 W 365 nm mercury lamp separately in the micro reactor under identical conditions reveals that high energy radiation is more effective in generating iron(III) (Table 2). The metal oxides and sulfides do not lose their photocatalytic activity on illumination. Reuse of the photocatalysts reveals sustainable catalytic efficiency; with fresh and reused catalysts the photoyield of iron(III) under identical conditions are almost the same.

3.3. General mechanism

The photooxidation of iron(II) in the presence and absence of metal oxides and sulfides show that the photocatalysts hinder the photooxidation. It may be by blocking the passage of light or photoreducing the iron(III) formed. This ambiguity was sorted out by conducting experiments with iron(III) solution. Separate studies with iron(III) in the presence of photocatalysts reveal photoreduction of iron(III) on the surfaces of all the metal oxides and sulfides; under the condition: $[Fe^{3+}]_0$ = 167 μM, $[H^+]$ = 2.0 mM, catalyst suspended = 5.0 g L^{-1}, airflow rate 7.8 mL s^{-1}, λ = 365 nm, I_0 = 1.92 × 10^{-5} einstein L^{-1} s^{-1}, 60% (v/v) aqueous ethanol, the iron(III) reduced in 30 min are 65, 74, 165, 104, 56, 100, 139, 127, 65, 94, 63 and 79 μM with TiO_2, ZrO_2, V_2O_5, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2, CdS, ZnS and Al_2O_3, respectively; the photoreduction of iron(III) on TiO_2 [10] and CdS [11] has been reported. In the absence of the photocatalysts, under identical conditions, iron(III) is not reduced. Hence, the reactions in the presence of metal oxides and sulfides are the homogeneous photooxidation of iron(II) yielding iron(III) and simultaneous photoreduction of iron(III) on the surface of the photocatalyst.

The photolysis of iron(II) solution in the presence of metal oxides and sulfides at different amounts of catalysts suspended reveals that TiO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 reduce almost completely the iron(III)

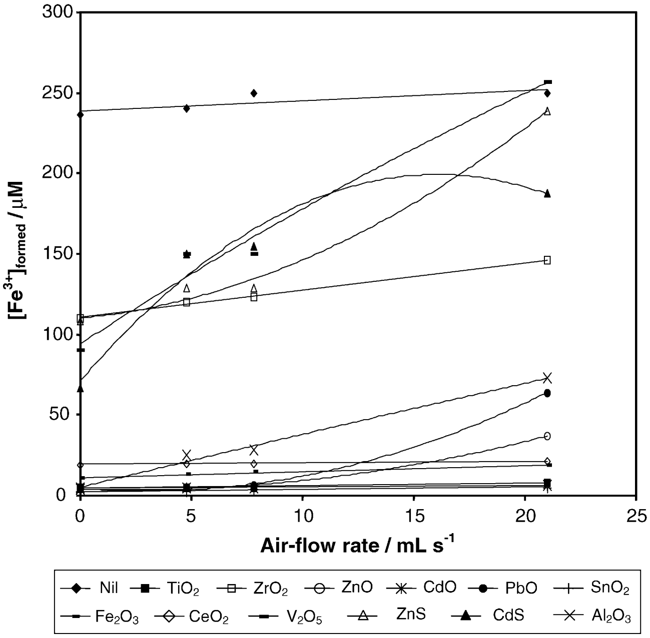

Fig. 3. Photooxidation of iron(II) with and without metal oxides and sulfides at different airflow rates. $[Fe^{2+}]_0$ = 5.0 mM, $[H^+]$ = 2.0 mM, catalyst suspended = 5.0 g L^{-1}, λ = 365 nm, I_0 = 1.92 × 10^{-5} einstein L^{-1} s^{-1}, 60% (v/v) aqueous ethanol, illumination time = 30 min.

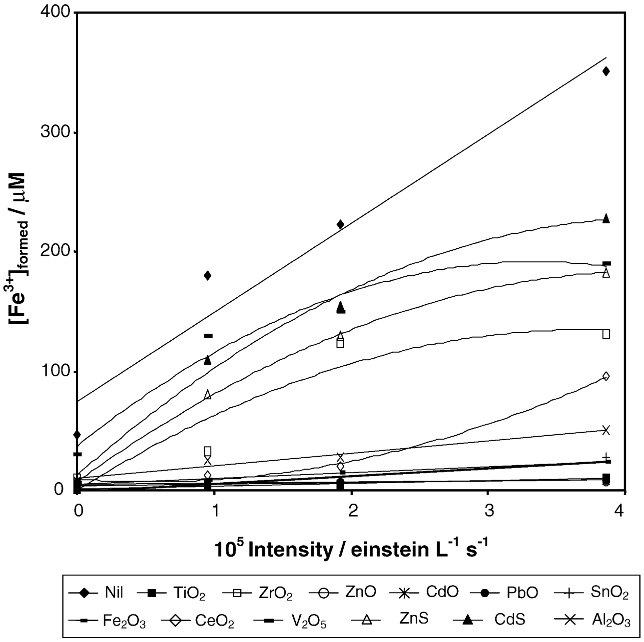

Fig. 4. Photooxidation of iron(II) with and without metal oxides and sulfides at different illumination intensities. $[Fe^{2+}]_0$ = 5.0 mM, $[H^+]$ = 2.0 mM, catalyst suspended = 5.0 g L^{-1}, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, 60% (v/v) aqueous ethanol, illumination time = 30 min.

Table 1
Photooxidation of iron(II) in aqueous ethanol[a]

EtOH–H_2O (% v/v)	$[Fe(III)]_{formed}$ (μM)												
	Nil	TiO_2	ZrO_2	V_2O_5	CeO_2	ZnO	Fe_2O_3	CdO	PbO	SnO_2	CdS	ZnS	Al_2O_3
60–40	243	5	123	150	20	6	15	5	6	4	155	129	28
80–20	615	55	283	325	64	29	31	36	21	14	361	140	91

[a] $[Fe^{2+}]$ = 5.0 mM, $[H^+]$ = 2.0 mM, catalyst suspended: 10.0 g L^{-1}, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, $I_0 = 1.92 \times 10^{-5}$ einstein L^{-1} s^{-1}, volume of reaction solution = 20 mL, reaction time = 30 min.

formed irrespective of the amount of catalysts. But with ZrO_2, ZnS and CdS, the iron(III) reduced remains almost constant at different catalyst-loading. V_2O_5 results in steady increase of $[Fe^{3+}]$ with increasing amount of catalyst. These results indicate that both the photoreduction of iron(III) to iron(II) and photooxidation of iron(II) to iron(III) occur on the surfaces of metal oxides and sulfides. The net photoreaction on TiO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 surfaces is photoreduction of iron(III). But on the surfaces of V_2O_5, ZrO_2, ZnS and CdS the photoreduction and photooxidation are competing processes.

Photolysis of iron(II) solution with the twelve photocatalysts reveals that the formation of iron(III) increases with increasing $[Fe^{2+}]$ although in most of the cases it is less than that in their absence. However, with CeO_2 at high $[Fe^{2+}]$ it is very close to that in absence of photocatalyst. The photooxidation of iron(II) at different airflow rates in presence of photocatalysts shows that photocatalysis by TiO_2, ZrO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 are independent of the airflow rate but with V_2O_5, ZnS and CdS the photoformation of iron(III) increases with the airflow rate and approaches close to that in absence of catalyst at high airflow rate. Photolysis of iron(II) solution in presence of metal oxides and sulfides shows that TiO_2, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 reduce almost completely the iron(III) formed at all the light intensities studied. However, the photoreduction of iron(III) on the surfaces of V_2O_5, ZrO_2, ZnS and CdS decreases with increase of light intensity. These results reveal both photoreduction of iron(III) and photooxidation of iron(II) on the catalytic surfaces.

Of the 12 photocatalysts employed in this study Al_2O_3 is an insulator providing non-reactive surface while others are semiconductors with finite bandgap energies. The bandgap energies of TiO_2 [12], ZrO_2 [13], V_2O_5 [14], CeO_2 [15], ZnO [12], Fe_2O_3 [16], CdO [16], PbO [17], SnO_2 [17], CdS [12] and ZnS [17] are 3.2, 3.25–5.1 (depending on the preparation technique of the sample), 2.8, 3.4, 3.2, 2.2, 2.2, 2.8, 3.5, 2.5 and 3.6 eV, respectively. Illumination of the semiconductors with light of energy greater than the bandgap leads to bandgap excitation of semiconductors 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 photocatalysts [12].

$$Fe^{2+}_{(aq)} + h\nu \rightarrow Fe^{3+}_{(aq)} + e^{-}_{(aq)} \quad [1]$$

$$e^{-}_{(aq)} + H^{+} \rightarrow H^{\bullet}$$

$$2H^{\bullet} \rightarrow H_2$$

$$SC + h\nu \rightarrow h^{+}_{vb} + e^{-}_{cb}$$

$$Fe^{3+} + e^{-}_{cb} \rightarrow Fe^{2+}$$

$$h^{+}_{vb} + H_2O \rightarrow H^{+} + HO^{\bullet}$$

$$H^{\bullet} + HO^{\bullet} \rightarrow H_2O$$

$$Fe^{2+} + h^{+}_{vb} \rightarrow Fe^{3+}$$

$$O_2 + e^{-}_{cb} \rightarrow O_2^{\bullet -}$$

$$H^{+} + O_2^{\bullet -} \rightarrow HO_2^{\bullet}$$

$$Fe^{2+}_{(aq)} + HO_2^{\bullet} + H^{+} \rightarrow Fe^{3+}_{(aq)} + H_2O_2 \quad [3]$$

$$Fe^{2+}_{(aq)} + H_2O_2 \rightarrow Fe^{3+}_{(aq)} + HO^{-} + HO^{\bullet}$$

$$Fe^{2+}_{(aq)} + HO^{\bullet} \rightarrow Fe^{3+}_{(aq)} + HO^{-}$$

Scheme 1.

Table 2
Photooxidation of iron(II) with illumination at different wavelengths[a]

λ (nm)	$[Fe(III)]_{formed}$ (μM)												
	Nil	TiO_2	ZrO_2	V_2O_5	CeO_2	ZnO	Fe_2O_3	CdO	PbO	SnO_2	CdS	ZnS	Al_2O_3
365[b]	227	163	224	200	117	48	207	176	51	47	100	170	214
254[c]	307	282	254	272	189	134	193	239	160	91	117	193	264

[a] $[Fe^{2+}]$ = 5.0 mM, $[H^+]$ = 2.0 mM, catalyst suspended = 5.0 g L^{-1}, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, 60% (v/v) aqueous ethanol, volume of reaction solution = 10 mL, reaction time = 15 min.

[b] $I_0 = 1.74 \times 10^{-5}$ einstein L^{-1} s^{-1}.

[c] $I_0 = 0.50 \times 10^{-5}$ einstein L^{-1} s^{-1}.

Iron(III), in the presence of chloride ion, forms $FeCl^{2+}$ [18]; calculation of the relative concentration of $FeCl^{2+}$ to Fe^{3+} ($[FeCl^{2+}]/[Fe^{3+}]$) reveals that about 6% of iron(III) is complexed as $FeCl^{2+}$ and $FeCl^{2+}$ may compete with Fe^{3+} in the photoreduction. Non-reactive surfaces such as Al_2O_3 provide an ordered two-dimensional environment for effective electron transfer from the donor to the acceptor. The acceptor iron(III) undergoes photoexcitation followed by electron transfer from water molecule, both adsorbed on the photocatalyst surface. The acceptor excitation leads to an electron jump from the donor level to the vacant acceptor level [12] (Scheme 1).

Comparison of the catalytic activities of the metal oxides and sulfides shows that the photocatalytic efficiency is susceptible to $[Fe^{2+}]$, airflow rate, the amount of catalyst loaded and illumination intensity. V_2O_5 is found to be better than others in bringing out the photooxidation of iron(II). Examination of the bandgap energies reveals that they do not solely determine the efficiencies of the photocatalysts. However, the photooxidation rates of vanillin and salicylaldehyde oximes are reported to increase with the increase in the bandgap energy of the semiconductors [19].

4. Conclusions

Iron(II) undergoes homogeneous photooxidation generating iron(III) which is simultaneously photoreduced on the surfaces of TiO_2 (anatase), ZrO_2, V_2O_5, CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2, CdS, ZnS and Al_2O_3. Detailed study reveals that both the photoreduction of iron(III) to iron(II) and the photooxidation of iron(II) to iron(III) occur on the catalytic surfaces. On the surfaces of TiO_2 (anatase), CeO_2, ZnO, Fe_2O_3, CdO, PbO, SnO_2 and Al_2O_3 the net reaction is the photoreduction of iron(III) to iron(II). The photoreduction of iron(III) and the photooxidation of iron(II) are competing on the surfaces of V_2O_5, ZrO_2, ZnS and CdO. At high catalyst-loading V_2O_5 catalyses the photooxidation of iron(II). The photocatalytic efficiencies of the metal oxides and sulfides studied are susceptible to $[Fe^{2+}]$, airflow rate, the amount of catalysts loaded and illumination intensity; the photocatalytic activity is not solely determined by the bandgap energy.

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