HETEROGENEOUS PHOTOCATALYTIC OXIDATION OF AROMATIC COMPOUNDS ON

SEMICONDUCTOR MATERIALS: THE PHOTO-FENTON TYPE REACTION[1]

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Heterogeneous photocatalytic oxidation of aromatic compounds by H_2O_2 formed from dissolved O_2 in the presence of illuminated TiO_2 powders was investigated with reference to the Fenton reaction. All the products expected from the Fenton reaction were obtained. The effect of other semiconductor materials and Fe^{2+} on the reaction was also investigated.

The formation of H_2O_2 from dissolved O_2 and organic reducing agents in the presence of the illuminated ZnO powders was first mentioned in 1927[2] and has received considerable attention since then.[3-12] The reaction in the absence of any intentionally added reducing agent is also described.[2,3,7-9] Several investigators have demonstrated that dissolved oxygen gas is necessary for the reaction.[7,10,11] In some of the later investigations, it was shown analytically that the organic reducing agents are oxidized during the H_2O_2 formation.[10-12] However, there has been no report aimed at the heterogeneous photocatalytic oxidation of aromatic compounds as a synthetic method by utilizing these phenomena, although the principles of modern photoelectrochemistry at semiconductor electrode are about to clarify the mechanism.[13-15]

On the other hand, a reaction with Fenton's reagent (H_2O_2 + Fe^{2+})[16] has been studied very extensively to date.[17] In this reaction, H_2O_2 decomposes into hydroxy radical and hydroxide anion as follows:[18]

$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO\cdot + Fe^{3+} \qquad (1)$$
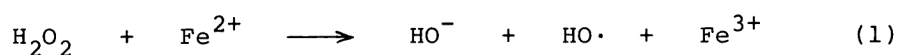
$HO\cdot$ formed is very reactive and is used for hydroxylation of aromatic ring and side chain-oxidation of alkylbenzenes.[19-21] The combination of the principles of photoelectrochemistry at semiconductor electrodes and of the Fenton reaction enabled us to succeed in the heterogeneous photocatalytic oxidation of the various aromatic compounds, i.e., "the photo-Fenton type reaction".

In this letter, we will describe the Fenton type reaction utilizing H_2O_2 formed on TiO_2[22] powders by the photosynthetic reduction of oxygen which is obtained either from ambient atmosphere or from the photoanodic decomposition of water on the same TiO_2 photocatalyst. The effect of semiconductor materials other than TiO_2 and Fe^{2+} ion for the $HO\cdot$ formation on the reaction will be also described.

As photocatalysts, TiO_2 (Aerosil P-25 from Aerosil Nippon, 99.99% anatase, and 99.99% rutile from Rare Metallic), ZnO, $SrTiO_3$, and SiC were used. The latter three kinds of catalysts were 99.99% grade from Furuuchi Chemicals. Each photocatalyst (1 g), in a mixture of doubly distilled water(50 or 100 cm^3) and an organic substrate

Table 1. Effect of Catalyst Material and Fe^{2+} on Distribution of Products and Yields
for Heterogeneous Photocatalytic Oxidation of Toluene under Air

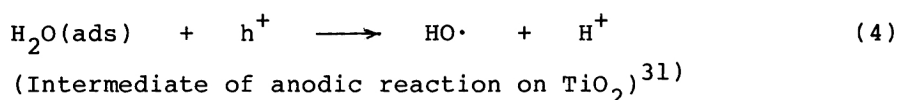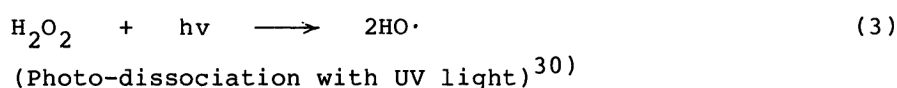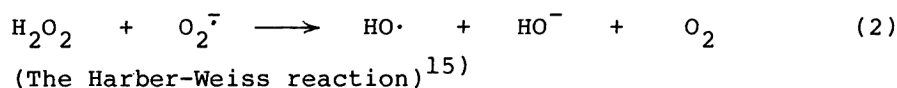| Run no.	Type of[a] catalyst	Conditions[b]	Product/μmol[c]							Total[d] /μmol	Quantum yield/%
			BzOH	PhCHO	o-Cr	m-Cr	p-Cr	BiBz	Dimer		
1	r,u		—	2.0	2.1	2.6	1.3	—	—	8.0	0.04
2	P-25,u	e)	—	10.7	5.6	5.0	2.0	—	—	23.3	0.06
3	a,u		—	11.8	32.7	14.0	9.9	—	—	68.4	0.32
4	a,u		—	9.4	14.7	8.4	7.5	—	—	40.0	0.19
5	a,u		—	11.7	17.7	9.0	8.1	—	—	46.5	0.22
6	a,u		—	8.9	12.9	8.3	6.3	—	—	36.4	0.17
7	a,u	e)	—	27.3	30.5	19.2	11.2	—	5.0	88.2	0.22
8	a,u	under N_2	—	—	—	—	—	—	—	—	—
9	P-25,u	under N_2	—	—	—	—	—	—	—	—	—
10	a,d		—	13.2	9.5	7.6	4.8	—	—	35.1	0.16
11	a,d,Pt		trace	14.8	64.8	33.4	23.2	4.4	3.6	145.0	0.67
12	a,RuO_2		—	16.2	15.9	13.1	6.0	—	3.5	51.2	0.24
13	ZnO,u		—	5.6	2.8	—	9.4	—	6.8	17.8	0.08
14	$SrTiO_3$, u	e) Fe^{2+}= 5 mM[f]	—	trace	—	—	—	—	—	trace	—
15	SiC,u	e) Fe^{2+}= 5 mM	—	34.2	10.3	6.6	3.0	—	—	54.1	0.13
16	a,u	Fe^{2+}= 1 mM	—	25.7	25.4	17.7	7.4	0.2	3.7	76.6	0.35
17	a,u	Fe^{2+}= 5 mM	—	27.2	41.5	25.7	10.5	—	5.0	104.9	0.49
18	a,u	Fe^{2+}= 50 mM	—	1.3	1.5	1.2		—	—	4.0	0.02

a) a = anatase, r = rutile, P-25 = Aerosil P-25, Pt = platinized photoelectrochemically
by the method in the literature,[23] d = doped by heating at 600°C for 3 h in
vacuo,[24] u = undoped, RuO_2 = sintered at 700°C for 3 h with 1 wt% of RuO_2. b)
Irradiated with a 500 W high pressure Hg lamp for 2 h through a Toshiba UV filter
UV-D35; initial solution composition, toluene/catalyst/H_2O(5 cm^3: 1 g : 100 cm^3)
unless otherwise noted. c) BzOH = benzyl alcohol, PhCHO = benzaldehyde, Cr = cresol,
BiBz = bibenzyl. d) Calculated by excluding dimer. e) without UV filter. f) M ≡ mol
dm^{-3}

(5 cm^3), was irradiated by a 500 W Xe-lamp or a 500 W high pressure mercury lamp in a
100 cm^3 Pyrex glass round-bottomed flask with a condenser cooled with running water.
To keep the solution saturated with oxygen in the air and to maintain homogeneous
mixing of the suspension, the solution was stirred by a magnetic stirrer. If
necessary, nitrogen was bubbled for deaeration. After photolysis, the solution was
made acidic by HCl addition, then extracted with ether, and finally concentrated
under a reduced pressure. A Shimadzu GC-4CM gas chromatograph was used for the
analysis of the products. The amount of a gaseous product, CO_2, was determined by the
method in the literature.[15]

Benzene, toluene, and acetophenone were tested as the organic substrates. All
the products expected from knowledge of the Fenton reaction were obtained: phenol

and biphenyl from benzene, benzaldehyde, cresols, and bibenzyl from toluene, and hydroxyacetophenone and phenol from acetophenone were obtained as the main products. These results are discussed in more detail elsewhere.[25] Some of the products have been found as the reaction intermediates for the oxidative photocatalytic decomposition of hydrocarbons to CO_2.[15,26] No or very little oxidation of aromatics was observed in the control experiments where the test solutions were either irradiated in the absence of oxygen (e.g. nos. 8,9 in Table 1) or left to stand without the irradiation in the presence of oxygen.

Typical results for toluene are given in Table 1. Among the untreated TiO_2 catalysts, anatase shows the highest efficiency (nos. 1-3). The efficiency of Aerosil P-25 of ultra fine particle size (~30 nm) is in between those of anatase and rutile in spite of its high surface area to mass ratio. X-ray diffraction shows that P-25 consisted of rutile and anatase. These results indicate that the efficiency is determined mainly by the type of catalyst and is independent of the particle size. The reproducibility of the experiments was fairly good (nos. 3-7). If oxygen is removed completely, the only possible cathodic reaction on the illuminated TiO_2 powders will be the reduction of hydrogen ions to form hydrogen.[26] However such a process is known to be very inefficient in an unbiased semiconductor photoelectrosynthetic cell with TiO_2 and Pt.[14,27,28] The doped anatase rather gave a lower yield (no. 10), which can be attributed to a higher recombination rate compared with the undoped anatase.[29] In the present work, the highest efficiency was attained by reducing the overpotential of cathodic reaction of O_2 to H_2O_2 on the platinized doped anatase (no. 11), while the attempt to lower the overpotential of the anodic reaction by sintering undoped anatase with 1 % in weight of RuO_2 did not result in any appreciable increase in efficiency (no. 12). On ZnO, where the anodic reaction is not the oxidation of water, the formation of an intermediate product HO· by the anodic reaction cannot occur. However, the heterogeneous photocatalytic oxidation of toluene proceeded on ZnO as well as on TiO_2, although the distribution of the product is different from those observed on TiO_2 (no. 13). This result supports the present idea that the oxidation of aromatics on TiO_2 can be attributed to HO· radical formed from the cathodic reaction product, H_2O_2, as in the Fenton reaction. Of course, the possibility of participation of the anodic reaction intermediate, HO· , in the oxidation reaction cannot be excluded from this result. In the absence of catalyst such as Fe^{2+} for HO· formation (Eq. (1)), the following reactions will be responsible for HO· formation as the probable paths.

$$H_2O_2 \ + \ O_2^{\bar{\cdot}} \ \longrightarrow \ HO\cdot \ + \ HO^- \ + \ O_2 \qquad (2)$$
(The Harber-Weiss reaction)[15]

$$H_2O_2 \ + \ h\nu \ \longrightarrow \ 2HO\cdot \qquad (3)$$
(Photo-dissociation with UV light)[30]

$$H_2O(ads) \ + \ h^+ \ \longrightarrow \ HO\cdot \ + \ H^+ \qquad (4)$$
(Intermediate of anodic reaction on TiO_2)[31]

In terms of flat-band potential, V_{fb}, and the redox potential of O_2/H_2O_2, one would expect $SrTiO_3$ to be better than TiO_2 for the production of H_2O_2, but the result appears to be totally unexpected (no. 14). The reason for this has not been clear

yet. The flat-band potential of SiC is the most negative among those of catalysts tested.[32] Consequently, illuminated SiC is expected to be most effective to reduce oxygen. In run no. 15, Fe^{2+} ions were added to the solution with a view to promoting the anodic reaction and the formation of HO· (Eq. (1)) simultaneously. However the yield was not so high as expected (cf. no. 17).

The effect of Fe^{2+} concentration on the photocatalytic oxidation was examined with undoped anatase (nos. 16-18). As expected, at lower concentrations of Fe^{2+}, the yield increased with increase in Fe^{2+} concentration but in the presence of 50 mM Fe^{2+}, the yield dropped. This decrease is attributable to the "short circuiting" by the reversible redox reaction as follows:

$$Fe^{2+} + h^+ \longrightarrow Fe^{3+} \qquad (5)$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad (6)$$
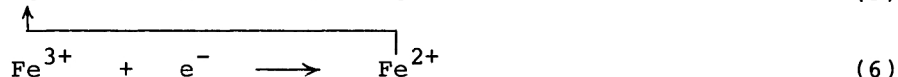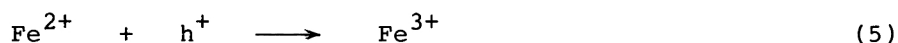
Although the amount of CO_2 evolved was not determined for every run of the experiment, it seems quite difficult to avoid the partial photocatalytic oxidative decomposition of aromatics into CO_2,[15,25,26] under the present conditions. For example, 96 μmol of CO_2 was formed on run no. 6.

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