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Photocatalytic conversion of benzene to phenol using modified TiO_2 and polyoxometalates

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Abstract

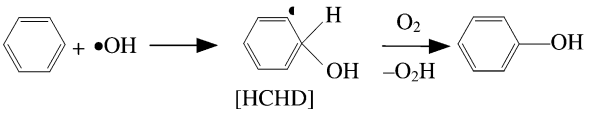
The application of photocatalytic reactions to organic synthesis has attracted interests in view of the development of environmentally benign synthetic processes. This study investigated the effects of various parameters (electron acceptor, surface modification, and the combination of photocatalysts) on the direct synthesis of phenol from benzene using photocatalytic oxidation processes. The OH radicals generated on UV-illuminated TiO_2 photocatalyst directly hydroxylate benzene to produce phenol, hydroquinone, and catechol. The addition of Fe^{3+}, H_2O_2, or $Fe^{3+} + H_2O_2$ highly enhanced the phenol production yield and selectivity in TiO_2 suspension. Surface modifications of TiO_2 had significant influence on the phenol synthetic reaction. Depositing Pt nanoparticles on TiO_2 (Pt/TiO_2) markedly enhanced the yield and selectivity. Surface fluorination of TiO_2 (F-TiO_2) increased the phenol yield two-fold because of the enhanced production of mobile (free) OH radicals on F-TiO_2. Polyoxometalate (POM) in phenol synthesis played the dual role both as a homogeneous photocatalyst and as a reversible electron acceptor in TiO_2 suspension. POM alone was as efficient as TiO_2 alone in the phenol production. In particular, the addition of POM to the TiO_2 suspension increased the phenol yield from 2.6% to 11% (the highest yield obtained in this study). Reaction mechanisms for each photocatalytic system were discussed in relation to the phenol synthesis.

Keywords: Photocatalysis; Phenol synthesis; TiO_2; Polyoxometalate; Environmentally benign reaction

1. Introduction

Phenol is considered one of the most important industrial chemicals due to its wide usage such as a disinfectant, a precursor of phenolic resins, a reagent in chemical analysis, and a preservative for pharmaceutic aid [1]. In order to meet this high demand, phenol is being produced over 5×10^6 t/yr globally [2,3]. The current manufacturing process of phenol starts from benzene and consists of three steps (so-called *cumene process*): benzene alkylation to cumene (isopropylbenzene), cumene oxidation to cumene hydroperoxide, and decomposition of the latter to phenol and acetone. However, this multistage process has a low overall yield (less than 5%), requires high energy [2,3], and accompanies the generation of undesirable by-products such as acetophenone, 2-phenylpropan-2-ol, and α-methylstyrene. The development of alternative synthetic processes of phenol that are more efficient and environmentally benign is highly desirable.

A direct synthesis of phenol from benzene has been tried using various methods: thermal catalysis [2–4], oxidation reaction using H_2O_2 [5,6], Fenton process [7–13], and semiconductor photocatalysis [14]. In Fenton process in which OH radicals are generated from the reaction of $Fe^{2+} + H_2O_2$, benzene can be directly converted into phenol through the reaction with OH radicals (reaction (1)). The hydroxyl radical adds directly to benzene to produce a hydroxycyclohexadienyl (HCHD) radical, which subsequently undergoes an H-atom abstraction by oxidants (e.g., O_2, Fe^{3+}, and Cu^{2+}) to yield phenol [9,11,12,15,16]. The OH radical addition to benzene is a diffusion-limited process ($k_{OH} = 8 \times 10^9$ M^{-1} s^{-1}) [17]:



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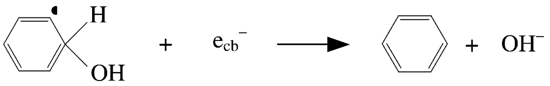
It is widely accepted that OH radicals can also be generated on illuminated TiO_2 surfaces. The photogenerated valence band (VB) holes oxidize surface hydroxyl groups into OH radicals. Therefore, TiO_2 photocatalysis has been applied to the hydroxylation of aromatic compounds for synthetic purposes [14,18,19] but the conversion efficiency in photocatalysis was lower than that of Fenton processes. Reported yield (Y_P) and selectivity (S_P) of phenol production from benzene were about 5% and 80–90% in Fenton process [7–13], and ca. 0.5% and 80% in TiO_2 photocatalysis [14], respectively. The efficiency of the photocatalytic phenol synthesis can be enhanced by optimizing various experimental parameters. First of all, the surface modifications of TiO_2 should change the reaction yield and selectivity. Photocatalytic reaction kinetics and mechanisms of surface-modified TiO_2 can be often very different from those of pure TiO_2 [20–24]. The kind of electron acceptors available is also important in determining Y_P and S_P because reductive electron transfers as well as reactions of OH radicals are involved in the overall reaction mechanism [25]. Conduction band (CB) electron transfer to electron acceptors (e.g., O_2) should increase Y_P because of the retarded charge pair recombination but the CB electron transfer to a HCHD radical regenerates benzene with decreasing Y_P (reaction (2)) [11]:



(2)

In addition, the OH radicals are so reactive and non-selective that most reactions of organic compounds with these result in oxidative degradation and mineralization. Therefore, minimizing the unwanted pathways such as the oxidative degradation and reductive back reaction (reaction (2)) is important for achieving selective hydroxylation.

This study investigated the hydroxylation reactions of benzene in several photocatalytic systems using TiO_2 as a heterogeneous photocatalyst and polyoxometalate (POM) as a homogeneous photocatalyst. Effects of various electron acceptors such as O_2, Fe^{3+}, H_2O_2, Ag^+, N_2O, and POM were tested to find out optimal conditions for the phenol synthesis. Surface-modified TiO_2 (platinization, fluorination, and silica loading) was also used to investigate how the surface properties affect the hydroxylation reaction.

2. Experimental

2.1. Materials and reagents

TiO_2 (Degussa P25, anatase:rutile = 8:2), $HNa_2PW_{12}O_{40}$ (Sigma), $H_4SiW_{12}O_{40}$ (Fluka), and $H_3PMo_{12}O_{40}$ (Fluka) were used as heterogeneous and homogeneous photocatalysts. Benzene (Aldrich), phenol (Junsei), hydroquinone (Aldrich), catechol (Aldrich), CH_3CN (Aldrich), $FeCl_3{\cdot}6H_2O$ (Kanto), $AgNO_3$ (Aldrich), and H_2O_2 (30%, Aldrich) were used as received. For the preparation of surface-modified TiO_2 photocatalysts (i.e., metal-deposited TiO_2, surface fluorinated TiO_2, and silica-loaded TiO_2), the following reagents were used: HF (J.T. Baker), NaF (Aldrich), $H_2Pt^{IV}Cl_6{\cdot}xH_2O$ (Aldrich), $Pd^{II}Cl_2$ (Aldrich), CH_3OH (Mallinckrodt), and $(CH_3CH_2O)_4Si$ [TEOS: tetraethylorthosilicate] (Aldrich). Gases (O_2 and N_2O) used were of >99% purity: O_2 was obtained from BOC Gases and N_2O from Dongbang Inc. Water used was ultrapure ($\geq$18 MΩ cm) and prepared by a Barnstead purification system.

2.2. Surface Modifications of TiO_2

Metallization of TiO_2 surface (Pt/TiO_2 and Pd/TiO_2) was carried out using a photodeposition method [20]. An aqueous suspension of TiO_2 (0.5 g/L) with 0.1 mM chloroplatinic acid (H_2PtCl_6) or palladium chloride ($PdCl_2$) and 1 M methanol (electron donor) was irradiated with a 200 W mercury lamp, and then the metal-loaded TiO_2 particles were filtered, washed and dried. A typical Pt and Pd loading on TiO_2 was estimated to be ca. 3 and 2 wt.%, respectively, by comparing the initially added aqueous Pt (or Pd) concentration and the remaining aqueous Pt (or Pd) concentration after photodeposition that were determined by inductively coupled plasma-atomic emission spectroscopy. The TEM image of Pt/TiO_2 exhibited Pt particles with a size range of 1–4 nm dispersed on TiO_2 particles (20–30 nm diameter). Surface fluorinated TiO_2 (F-TiO_2) was obtained by adding 10 mM NaF to the TiO_2 suspension (1 g/L) at pH 3.4–3.7 [21,22]. Rutile TiO_2 was prepared from selectively etching out the anatase phase of P25 TiO_2 by HF solution (10 wt.%) to obtain rutile particles with comparable particle size to P25 [23]. The fluoride contaminants adsorbed on the rutile surface were removed by washing with alkaline (1N NaOH) solution. Silica-loaded TiO_2 (SiO_2/TiO_2) was prepared by mixing 0.5 g of TiO_2 with 0.1 mL TEOS, drying at room temperature and subsequent heating at 700 °C for 1 h.

2.3. Photochemical synthesis and product analysis

Photocatalytic benzene conversion reactions were carried out in aqueous TiO_2 suspension containing benzene (20 mM) and acetonitrile as a co-solvent (typically 4 vol.%). Plain or surface-modified TiO_2 powder (25 mg) was suspended in 24 mL distilled water, and an aliquot of acetonitrile (1 mL) containing benzene (50 μL) was added to the suspension and mixed well. When necessary, electron donors, acceptors or other reagents were added to the suspension. A 450 W Xe arc lamp (Oriel) was used as a light source. Light passed through a 10 cm IR water filter and a cutoff filter ($\lambda > 300$ nm), and then the filtered light was focused onto the reactor. Sample aliquots were withdrawn by a 1 mL syringe intermittently during illumination and filtered through a 0.45 μm PTFE filter (Millipore) to removal TiO_2 particles. Benzene, phenol, and other aromatic intermediates were analyzed with a reverse-phase high performance liquid chromatograph (HPLC, Agilent 1100 series). The eluent solution was composed of acetonitrile (20%) and phosphoric acid-added water (80%).

3. Results and discussion

3.1. Phenol production and the effect of electron acceptors

Fig. 1(a) shows the time-dependent production of phenol and di-hydroxylated products such as hydroquinone (HQ) and catechol (CT) in UV-illuminated TiO_2 suspension. The production of benzoquinone and resorcinol was negligible. The total concentration refers to the sum of all hydroxylated products. After 4 h illumination, the phenol concentration reached 0.52 mM, which corresponds to 2.6% conversion of benzene. Although this yield is higher than a previously reported value (ca. 0.5%) [14], it is still a low yield. Fig. 1(b) shows the effect of acetonitrile as a co-solvent on the production of phenol. The addition of CH_3CN up to 4 vol.% slightly increased the yield of phenol but further addition gradually reduced the yield. Therefore, the concentration of CH_3CN as a co-solvent was fixed at 4 vol.% throughout this work. Although the presence of the co-solvent prevents benzene in water from volatilizing during reaction, it also plays the role of an OH radical scavenger. Thus, with high concentration of CH_3CN, both CH_3CN and benzene compete for OH radicals with reducing the phenol production yield. In addition, water is essential as a precursor of hydroxyl radicals whose production cannot be sustained in non-aqueous environment. Therefore, the phenol production in pure acetonitrile was lower than 0.05 mM.

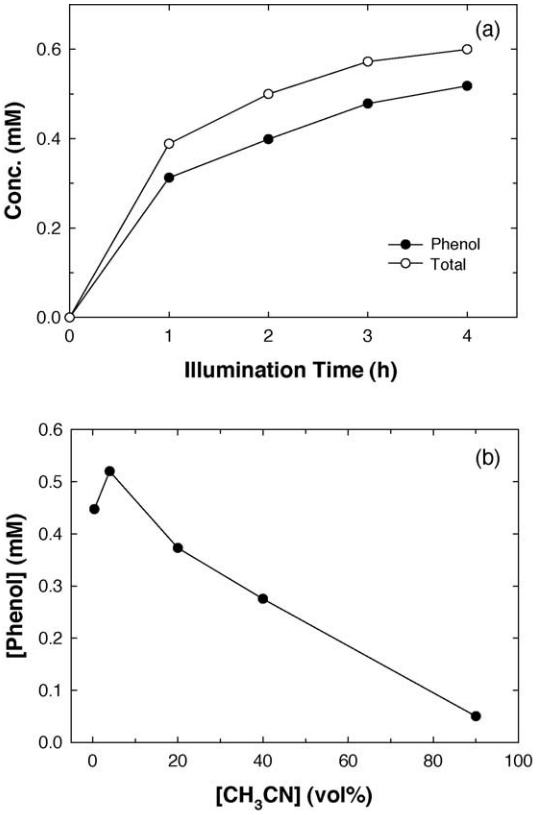


Fig. 1. (a) Time profiles of photocatalytic production of phenol and total hydroxylated benzenes (total = [phenol] + [HQ] + [CT]); (b) effect of acetonitrile addition as a co-solvent on the photocatalytic conversion (after 4 h illumination). $[TiO_2]$ = 1 g/L; [benzene] = ca. 20 mM; open to air; $[CH_3CN]$ = 4 vol.% in (a).

The presence of suitable electron acceptors is essential for photocatalytic conversion reactions since they scavenge CB electrons to inhibit fast charge pair recombination. In aqueous TiO_2 suspension, dissolved O_2 serves as an electron acceptor (reaction (3)). The presence of additional electron acceptors such as Fe^{3+} and Ag^+ may enhance the conversion yield (reaction (4)). Table 1 lists the yields of phenol and other di-hydroxylated products generated in TiO_2 suspensions in the presence of additional electron acceptors. When the O_2 supply was limited in a closed reactor (1b), the hydroxylation reaction was greatly reduced, which indicates the importance of O_2. The addition of Fe^{3+} or Ag^+ increased

Table 1
Hydroxylation of benzene in illuminated TiO_2 suspensions with various electron acceptors

Entry #	Conditions[a]	Products[b] (mM)				Y_P[c] (%)	S_P[d] (%)	RY_P[e]
		HQ	CT	PhOH	Total			
1a	TiO_2	0.076	0.006	0.518	0.600	2.6	86	1.0
1b	TiO_2 (air-tight)	0.001	0.001	0.055	0.057	0.3	96	0.1
1c	$TiO_2 + Fe^{3+}$	0.094	Trace	0.893	0.987	4.5	91	1.7
1d	$TiO_2 + H_2O_2$	0.400	0.027	0.944	1.371	4.7	69	1.8
1e	$TiO_2 + Fe^{3+} + H_2O_2$	0.180	0.032	1.847	2.062	9.2	90	3.6
1f	$TiO_2 + Ag^+$	0.043	0.022	0.679	0.764	3.4	89	1.3
1g	$TiO_2 + Ag^+ + Fe^{3+}$	0.108	0.019	0.852	0.979	4.3	87	1.6

[a] TiO_2 = 25 mg; benzene:H_2O:CH_3CN = 50 μL:24 mL:1 mL; $[benzene]_0$ = 20 mM; $[Fe^{3+}]$ = 1.47 mM; $[H_2O_2]$ = 9.4 mM; $[Ag^+]$ = 0.98 mM; no pH adjustment; open to air except for 1b; illuminated for 4 h. Dissolved O_2 is present as a base electron acceptor in all cases.

[b] HQ: hydroquinone; CT: catechol; PhOH: phenol; total: HQ + CT + PhOH

[c] $Y_P = [PhOH]/[benzene]_0$.

[d] $S_P = [PhOH]/[total]$.

[e] Relative phenol yield (RY_P) with respect to the phenol yield of 1a ($RY_P = [PhOH]/[PhOH]_{1a}$).

Table 2
Hydroxylation of benzene in surface-modified TiO_2 suspensions

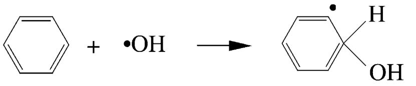
Entry #	Conditions[a]	Product (mM)				Y_P (%)	S_P (%)	RY_P
		HQ	CT	PhOH	Total			
1a	TiO_2	0.076	0.006	0.518	0.600	2.6	86	1.0
2a	Pt/TiO_2	0.040	Trace	0.883	0.923	4.4	96	1.7
2b	$Pt/TiO_2 + Fe^{3+}$	0.082	0.005	1.025	1.112	5.1	92	2.0
2c	$Pt/TiO_2 + H_2O_2$	0.213	0.002	0.440	0.684	2.2	64	0.85
2d	$Pt/TiO_2 + N_2O(g)$	Trace	Trace	0.395	0.395	2.0	100	0.76
2e	$Pt/TiO_2 + N_2O(g)/O_2(g)$	0.469	Trace	0.997	1.466	5.0	68	1.9
2f	Pd/TiO_2	0.033	Trace	0.656	0.689	3.3	95	1.3
2g	$Pd/TiO_2 + H_2O_2$	0.060	0.002	0.664	0.744	3.3	89	1.3
2h	TiO_2/SiO_2	0.096	0.053	0.602	0.751	3.0	80	1.2
2i	$TiO_2/SiO_2 + H_2O_2$	0.042	0.048	0.504	0.594	2.5	85	0.97
2j	F-TiO_2	0.320	0.221	1.134	1.675	5.7	68	2.2
2k	F-$TiO_2 + H_2O_2$	0.062	0.018	0.650	0.787	3.3	83	1.3
2l	TiO_2 (rutile)	Trace	Trace	0.268	0.268	1.3	100	0.52
2m	Pt/TiO_2 (rutile)	Trace	–	0.056	0.056	0.3	100	0.11

[a] Photocatalyst = 25 mg; benzene:H_2O:CH_3CN = 50 μL:24 mL:1 mL; $[\text{benzene}]_0$ = 20 mM; $[Fe^{3+}]$ = 1.47 mM; $[H_2O_2]$ = 9.4 mM; no pH adjustment except for 2j and 2k in which pH was set to 3.5; open to air except for 2d and 2e; illuminated for 4 h.

the hydroxylation yield (1c, 1f). Fe^{3+} and dissolved O_2 have been reported to be not only CB electron acceptors (reaction (4)) [12,15,16,19,26–28] but also good oxidants of HCHD radicals (reaction (6)). However, Ag^+ does not seem to oxidize HCHD radicals. A range of Ag^+ concentrations (0.02–4.90 mM) were used (optimal at 0.98 mM) but they were not as efficient as Fe^{3+} (1.47 mM) in enhancing Y_P. The fact that Fe^{3+} is more efficient than Ag^+ in inducing hydroxylation implies that reaction (6) is critical in determining the overall yield:

$$e_{cb}^- + O_2 \rightarrow O_2^- \tag{3}$$

$$e_{cb}^- + Fe^{3+}(\text{or}Ag^+) \rightarrow Fe^{2+}(\text{or}Ag^0) \tag{4}$$



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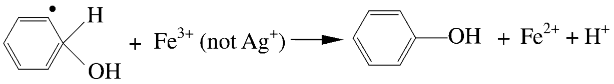

(6)

The addition of H_2O_2 also significantly increased the phenol yield by ca. 1.8 times (1d) because H_2O_2 generates additional OH radicals via reacting with a CB electron (reaction (7)) [29]. The OH radical generation from the direct photolysis of H_2O_2 ($H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$) should be negligible under the present irradiation condition ($\lambda > 300$ nm):

$$H_2O_2 + e_{cb}^- \rightarrow {}^{\bullet}OH + OH^- \tag{7}$$

However, in this case, the selectivity was markedly reduced from 86% to 69%. The OH radicals generated from reaction (7) are thought to be more mobile than those produced at the site of surface hydroxyl groups ($\equiv Ti{-}OH + h^+ \rightarrow \equiv Ti{-}OH^{\bullet +}$) and are more likely to induce di-hydroxylation of benzene with reducing the selectivity. On the other hand, the addition of both Fe^{3+} and H_2O_2 to TiO_2 suspension (1e) increased the yield even more compared with the systems of Fe^{3+} added alone (1c) or H_2O_2 added alone (1d). When Fe^{3+} and H_2O_2 are present together in the TiO_2 suspension, the photo-Fenton reaction should occur and contribute to the overall hydroxylation process. We carried out the phenol synthesis using a homogeneous photo-Fenton reaction ($Fe^{3+} + H_2O_2$) in the absence of TiO_2 (with other experimental conditions to be the same as 1e) and found that this homogeneous system produced more phenol than 1e. Therefore, a part of phenol production in 1e could be ascribed to the photo-Fenton reaction. However, the quantitative comparison between the heterogeneous and homogeneous systems is very difficult because the strong light scattering effect by the suspended TiO_2 particles should be taken into account.

3.2. Effect of TiO_2 surface modifications

Table 2 summarizes the effects of TiO_2 surface modification on the hydroxylation of benzene. Pt/TiO_2 (2a) exhibited an enhanced yield (1.7 times) and selectivity (96%). Noble metal deposits on TiO_2 surface often enhance the photocatalytic reactivity because they trap CB electrons with reducing charge pair recombination and promoting interfacial electron transfer [20,23,24,27,30]. Pt is generally the most effective among noble metals such as Au, Pd, and Ag. The kind of dissolved gas as an electron acceptor influences the photocatalytic conversion process and the electron transfer to dissolved gas can be accelerated when TiO_2 surface is platinized. Fig. 2 shows the effect of dissolved gas on the phenol production yield in Pt/TiO_2 suspension. Compared to O_2 alone (2a) or N_2O alone (2d), using the mixed gas (O_2/N_2O) (2e) showed a higher activity for hydroxylation. N_2O has a capability to scavenge CB electrons trapped on ZnO [31,32] and TiO_2 [33,34]. It has been recently reported that the electron accepting ability of N_2O is greatly enhanced on Pt/TiO_2 surface [20]. The

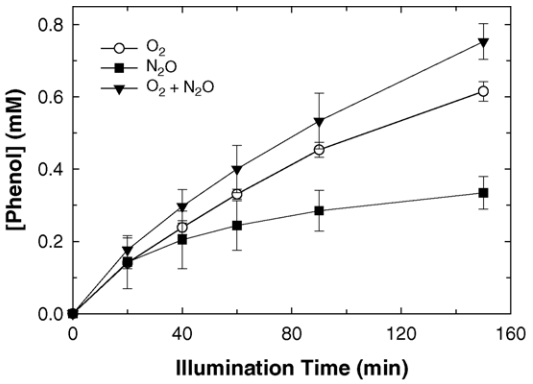

Fig. 2. Effect of O_2, N_2O, and $O_2 + N_2O$ (50/50 vol.% mixing ratio) gas purging on the photocatalytic production of phenol in Pt/TiO_2 suspension. $[Pt/TiO_2] = 1$ g/L; [benzene] = ca. 20 mM; $[CH_3CN] = 4$ vol.%.

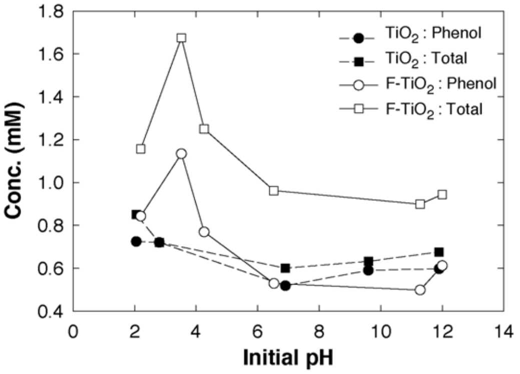

Fig. 3. pH dependence of the photocatalytic production of phenol and total hydroxylated benzenes in $F\text{-}TiO_2$ suspension. $[TiO_2] = 1$ g/L; [NaF] = 10 mM; [benzene] = ca. 20 mM; $[CH_3CN] = 4$ vol.%.

reaction of N_2O and CB electrons can lead to the generation of OH radicals (reactions (8) and (9)) with increasing the total hydroxylation yield:

$$N_2O + e^-_{cb}(Pt) \rightarrow N_2O^{\bullet -}(Pt) \qquad (8)$$

$$N_2O^{\bullet -}(Pt) + H_2O \rightarrow N_2 + HO^{\bullet} + HO^- \qquad (9)$$

Three volumetric mixing ratios ($O_2/N_2O = 2$, 1, or 0.5) were tested and the 1:1 mixing ratio was found to be optimal. The co-presence of O_2 seems to be beneficial in the phenol production and hydroxylation reactions because O_2 is not only a CB electron acceptor but also an oxidant of HCHD radicals (second step in reaction (1)). However, in terms of the selectivity, the co-presence of O_2 had a negative effect: the selectivity in $Pt/TiO_2 + N_2O$ system (2d) was 100% while that in $Pt/TiO_2 + N_2O/O_2$ system (2e) was reduced to 68%.

Surface fluorinated TiO_2 ($F\text{-}TiO_2$) was also used for the hydroxylation of benzene because it has been reported that $F\text{-}TiO_2$ produces more free (mobile) OH radicals than pure TiO_2 [21,22,35]. $F\text{-}TiO_2$ can be prepared through a simple ligand exchange between fluoride anions and surface hydroxyl groups on TiO_2 (reaction (10)). The surface fluorides should not be reactive with VB holes under UV irradiation and the OH radicals generated on $F\text{-}TiO_2$ have weak surface affinity and easily desorb into the solution phase (reaction (11)), whereas most OH radicals generated on naked TiO_2 surface remain adsorbed:

$$\equiv Ti{-}OH + F^- \rightarrow \equiv Ti{-}F + HO^- \qquad (10)$$

$$\equiv Ti{-}F + H_2O + h\nu \rightarrow \equiv Ti{-}F + HO^{\bullet} + H^+ \qquad (11)$$

As a result, surface fluorination of TiO_2 enhances the OH radical-mediated reaction but inhibits the hole transfer-mediated reaction on the contrary because the substrate adsorption or complexation is prohibited on fluorinated surface [22]. As shown in Table 2, both the phenol production and total hydroxylation were significantly enhanced with $F\text{-}TiO_2$ (2j) but the selectivity was reduced on the contrary. As mentioned earlier, mobile OH radicals seem to favor the di-hydroxylation of benzene with reducing the selectivity. Fig. 3 shows that the hydroxylation yield strongly depends on pH (optimal around pH 3–4) with $F\text{-}TiO_2$ whereas the hydroxylation with pure TiO_2 shows a weak pH dependence. This is due to the fact that the surface fluorination (reaction (10)) is strongly favored at acidic condition and does not take place at basic pH [21]. On the other hand, the presence of surface $\equiv$Ti–F species seems to stabilize CB electrons at surface trap sites [22] and hence the hydroxylation can be favored if the reductive back reaction (reaction (2)) is retarded on $F\text{-}TiO_2$. In addition, the surface of $F\text{-}TiO_2$ particle is rather hydrophobic and the

Table 3

Hydroxylation of benzene with TiO_2 alone, POM alone, or TiO_2 + POM

Entry #	Conditions[a]	Products (mM)				Y_P (%)	S_P (%)	RY_P
		HQ	CT	PhOH	Total			
1a	TiO_2	0.076	0.006	0.518	0.600	2.6	86	1.0
3a	$PMo_{12}O_{40}^{3-}$	–	–	0.444	0.444	2.2	100	0.86
3b	$SiW_{12}O_{40}^{4-}$	Trace	–	0.231	0.231	1.2	100	0.46
3c	$PW_{12}O_{40}^{3-}$	0.148	0.135	0.590	0.871	3.0	68	1.1
3d	$PW_{12}O_{40}^{3-} + Fe^{3+}$	Trace	0.009	0.743	0.752	3.7	99	1.4
3e	$PW_{12}O_{40}^{3-} + H_2O_2$	0.028	0.039	0.477	0.607	2.4	79	0.92
3f	$PW_{12}O_{40}^{3-} + Fe^{3+} + H_2O_2$	–	–	0.051	0.187	0.3	27	0.10
3g	$TiO_2 + PW_{12}O_{40}^{3-}$	0.696	0.250	2.180	3.128	11	70	4.2
3h	$TiO_2 + PW_{12}O_{40}^{3-} + H_2O_2$	0.060	0.288	1.524	1.999	7.6	76	2.9

[a] $TiO_2 = 25$ mg; [POM] = 2.0 mM (3a–3f) or 0.5 mM (3g and 3h); pH = 1.5; benzene:H_2O:CH_3CN = 50 μL:24 mL:1 mL; $[benzene]_0 = 20$ mM; $[Fe^{3+}] = 1.47$ mM; $[H_2O_2] = 9.4$ mM; open to air; illuminated for 4 h.

hydrophobic interaction between the fluorinated surface and benzene can be enhanced. The addition of H_2O_2 (ca. 9 mM) in Pt/TiO_2 or F-TiO_2 suspensions lowered the phenol yield (2c, 2k, 2m) whereas the H_2O_2 addition enhanced the phenol yield in naked TiO_2 suspension (1d). This implies that reaction (7) that generates OH radicals from H_2O_2 is not favored with F-TiO_2 and Pt/TiO_2. This is consistent with a recent observation that the interfacial electron transfer on F-TiO_2 is much slower than that on naked TiO_2 [22]. On Pt/TiO_2, two-electron reduction (reaction (12)) seems to be favored:

$$H_2O_2 + 2e^-_{cb} + 2H^+ \rightarrow 2H_2O \quad (12)$$

Other reactions using Pd/TiO_2, TiO_2/SiO_2, and rutile TiO_2 are also listed in Table 2. Pd/TiO_2 behaved quite similarly as Pt/TiO_2. The silica loading on TiO_2 had little influence on the phenol yield and selectivity (2h). The addition of H_2O_2 in TiO_2/SiO_2 suspension slightly lowered the phenol yield (2i). It is interesting to note that the selectivity with rutile (2l, 2m) was 100% although the yield was low.

3.3. *Phenol production using polyoxometalates*

As one of homogeneous photocatalysts, polyoxometalate (POM) has been widely investigated [36]. UV ($\lambda < 350$ nm) excitation of POM induces a ligand-to-metal charge transfer (LMCT), and the charge-transferred excited state POM* has a highly oxidizing power (ca. 2.5 V versus NHE) that is strong enough to oxidize a variety of organic compounds. POM is very similar to the heterogeneous TiO_2 photocatalyst in its light absorption and electrochemical band-edge positions [37,38]. POM* reacts with water to generate OH radicals (reaction (13)), which can hydroxylate benzene:

$$POM^* + H_2O \rightarrow POM^- + H^+ + {}^{\bullet}OH \quad (13)$$

We used three kinds of POM ($PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$, $PMo_{12}O_{40}{}^{3-}$) as a photocatalyst and compared their phenol production yields in Table 3 and Fig. 4. The yield is in the order of $PW_{12}O_{40}{}^{3-} > PMo_{12}O_{40}{}^{3-} > SiW_{12}O_{40}{}^{4-}$, which is similar to the reactivity order in other photocatalytic reactions [39]. However, the selectivity of $PW_{12}O_{40}{}^{3-}$ was much lower than the other two. POM is also known as an efficient electron shuttle between CB and O_2 in UV-illuminated TiO_2 suspension (reactions (14) and (15)) and hence enhances the overall reactivity of TiO_2 photocatalysis [27]:

$$POM + e^-_{cb} \rightarrow POM^- \quad (14)$$

$$POM^- + O_2 \rightarrow POM + O_2^- \quad (15)$$

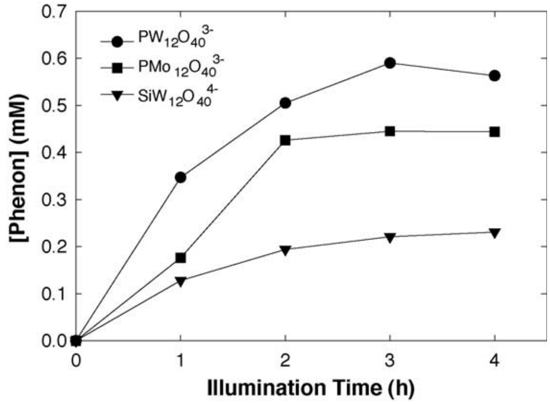

Fig. 4. Photocatalytic production of phenol in aqueous POM solution. [POM] = 2.0 mM; [benzene] = ca. 20 mM; [CH_3CN] = 4 vol.%; pH = 1.5.

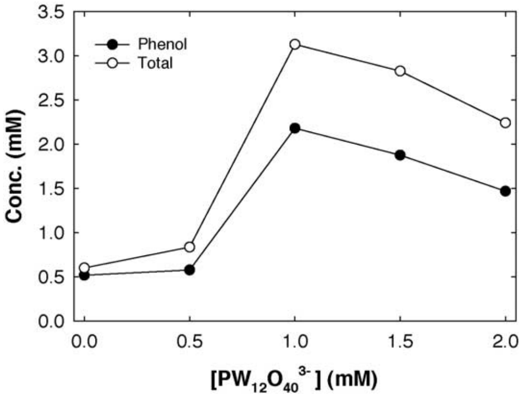

Fig. 5. Effect of $PW_{12}O_{40}{}^{3-}$ concentration on the photocatalytic production of phenol and total hydroxlyated benzene in $PW_{12}O_{40}{}^{3-}$ + TiO_2 suspension. [TiO_2] = 1 g/L; [benzene] = ca. 20 mM; [CH_3CN] = 4 vol.%; pH = 1.5.

As shown in Fig. 5, the addition of $PW_{12}O_{40}{}^{3-}$ in TiO_2 suspension greatly enhanced the hydroxylation reaction. At an optimal concentration of $PW_{12}O_{40}{}^{3-}$, the yield of phenol production increased by four times (3g in Table 3), which can be attributed to dual roles of POM as both a photocatalyst and an electron shuttle in TiO_2 suspension. The system of $TiO_2 + PW_{12}O_{40}{}^{3-}$ showed the highest phenol yield among all photocatalytic synthesis tested in this work.

4. Conclusions

Photocatalytic synthesis of phenol from benzene under various conditions can be summarized as follows: (1) the role of CB electron acceptors was critical in determining the overall conversion yield; (2) platinum deposition and surface fluorination of TiO_2 markedly enhanced the phenol yield, which indicates that TiO_2 surface plays an important role in photocatalytic hydroxylation of benzene; (3) POM as a homogeneous photocatalyst was comparable to TiO_2 in the phenol yield and the combined system of POM + TiO_2 highly enhanced the production of phenol because of the dual roles of POM as both a photocatalyst and an electron shuttle. The highest phenol production yield obtained in this study (i.e., $Y_P \approx 11\%$ in the TiO_2 + POM system) is about double yield of the conventional cumene process. As for the selectivity of phenol production from benzene (S_P), it was higher than 85% in most cases and reached 100% in a few cases. In general, when S_P was high, Y_P was low and vice versa. The phenol should be recovered from the final mixture solution by a simple distillation: the boiling point of phenol is 182 °C and those of other di-hydroxylated by-products were higher by more than 60 °C. The photocatalytic synthetic process is operated at ambient temperature and pressure, needs no complex equipments, and can utilize solar light, which makes this process energy-efficient and environmentally benign.

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