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Direct Synthesis of Phenol from Benzene over Platinum-loaded Tungsten(VI) Oxide Photocatalysts with Water and Molecular Oxygen

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Tungsten(VI) oxide loaded with nanoparticulate platinum (Pt/WO_3) was demonstrated for the first time to exhibit photocatalytic activity for direct synthesis of phenol from benzene using water and molecular oxygen as reactants under ultraviolet or visible light irradiation; the selectivity for phenol (e.g., 74% at 69% of benzene conversion) on Pt/WO_3 photocatalysts was much higher than those on platinum-loaded titanium(IV) oxide (Pt/TiO_2) photocatalysts.

Hydroxylated aromatic compounds are the most important raw materials in chemical industry. For example, phenol is the major source of phenol resins, which are utilized in many commodities throughout the world. However, its industrial production still requires multistep reaction processes, namely cumene method, which consumes considerably large energy and yields a by-product, acetone.[1] Direct synthesis of phenol from benzene in a one-step reaction, especially using environmentally benign oxidants such as molecular oxygen (O_2) or water, is highly desirable, and thus have been extensively studied.[2–4] However, there have been few catalytic process that enables high benzene conversion with high phenol selectivity by using such environmentally benign oxidants (O_2 and/or water). Photocatalysis on semiconductor materials may be one of the candidates for such clean and direct synthesis of phenol from benzene. Although several research groups have reported direct synthesis of phenol from benzene using titanium(IV) oxide (TiO_2) photocatalysts suspended in a water–benzene mixture in the presence of molecular O_2,[5–10] the selectivity for phenol was generally low mainly due to the occurrence of subsequent peroxidation on photocatalyst. Yoshida et al. have demonstrated that the selectivity for phenol can be significantly improved by applying deaerated condition, i.e., the absence of O_2, to Pt-loaded TiO_2 photocatalyst system, however, the efficiency was not so high possibly due to the lower capability of water (or proton) to capture the photoexcited electrons compared to O_2.[11]

In the present study, we report highly selective phenol production (ca. 74% at 69% of benzene conversion) on a Pt-loaded tungsten(VI) oxide (Pt/WO_3), which was recently developed as a highly efficient visible-light-responsive photocatalyst,[12] in an aqueous solution containing benzene and O_2 under the ultraviolet or visible light irradiation. The Pt/WO_3 photocatalysts showed much higher selectivity for phenol production than platinized (or bare) TiO_2 photocatalysts. The different reactivity between WO_3 and TiO_2 photocatalysts toward benzene oxidation is discussed.

Commercially available WO_3 powders such as WO_3-K (Kojundo Chemical Laboratory, monoclinic, $2.2\,m^2\,g^{-1}$), WO_3-Y (Yamanaka Chemical Industries, monoclinic, $2.2\,m^2\,g^{-1}$), and WO_3-S (Soekawa Chemicals, monoclinic, $1.6\,m^2\,g^{-1}$) were used. Since the WO_3-K sample consists of mixture of fine and large aggregated particles, fine particulate WO_3 with a particle size of 50–200 nm was separated from WO_3-K by the method reported previously,[12] which will be denoted as WO_3-K ($10\,m^2\,g^{-1}$) hereafter. TiO_2 powders such as TiO_2-P25 (Degussa (Evonik) P 25, $59\,m^2\,g^{-1}$), TiO_2-M (Merck, anatase, $11\,m^2\,g^{-1}$), and TiO_2-J (JRC-TIO-8 donated from the Catalysis Society of Japan, anatase, $338\,m^2\,g^{-1}$) were also used for comparison. The modification of photocatalysts with nanoparticulate Pt metal cocatalysts (0.1 wt %) was accomplished by photodeposition from hexachloroplatinic acid ($H_2[PtCl_6]\cdot 6H_2O$) according to the method reported previously, which affords a highly uniform dispersion of platinum particles (average size, 5 nm) on the photocatalyst surface.[12] Photocatalytic oxidation (hydroxylation) of benzene was carried out in a Pyrex reaction cell with internal volume of 15 mL containing a suspension of the photocatalyst powder (50 mg) in an aerated aqueous benzene solution (2.5 mmol L^{-1}, 7.5 mL) with continuous stirring using a magnetic stirrer. The reaction temperature was kept at 279 K by circulating cooling water around the cell. Sample aliquots were withdrawn from the reactor cell after each irradiation and filtered through a PVDF filter to remove photocatalyst particles. Quantitative analysis of solution was carried out using a high-performance liquid chromatograph (Shimadzu, LC-10AT VP) equipped with a C-18 column (Shodex, ODP2 HP4E) and a photodiode-array detector. Generation of carbon dioxide (CO_2) in the gas phase was analyzed by gas chromatography.

Figure 1 shows the time-course curves of photocatalytic reactions over Pt/WO_3-K and Pt/TiO_2-P25 in aqueous solutions of benzene (2.5 mmol L^{-1}, 7.5 mL) in the presence of molecular oxygen under the full arc irradiation with a 300-W xenon lamp ($\lambda > 300$ nm). As seen in Figure 1a, phenol was produced with almost constant rate over Pt/WO_3-K photocatalyst after 30 min

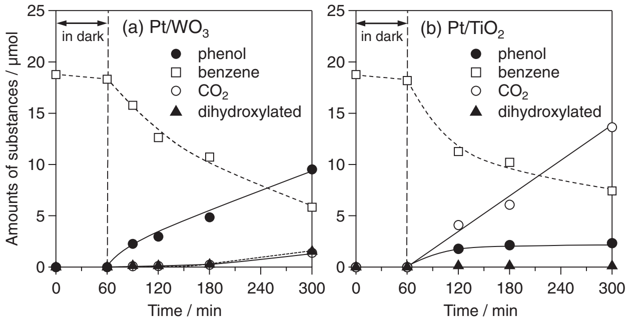
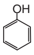
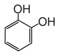
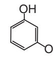
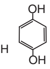
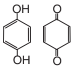


Figure 1. Time courses of photocatalytic oxidation of benzene over (a) Pt/WO_3-K and (b) Pt/TiO_2-P25 in aerated aqueous solutions of benzene (18.8 µmol) under ultraviolet and visible light ($300 < \lambda < 500$ nm).

Table 1. Photocatalytic oxidation of benzene by WO_3 and TiO_2 photocatalysts[a]

Entry	Sample	Conditions		Conversion/%[b] (Time/min)	Selectivity/%[c]					Amount of CO_2/μmol
										
1	Pt/WO_3-K	$\lambda > 300$ nm	O_2	22.2 (60)	79.3	1.9	0	1.2	4.0	<0.1
		$\lambda > 300$ nm	O_2	68.9 (240)	73.7	2.3	0.7	0	8.8	1.4
2	Pt/WO_3-K	$\lambda > 400$ nm	O_2	26.6 (60)	83.8	1.4	0	1.2	2.8	<0.1
		$\lambda > 400$ nm	O_2	52.5 (240)	75.1	1.4	0	2.9	1.2	0.6
3	WO_3-K	$\lambda > 300$ nm	O_2	16.4 (240)	84.6	1.6	0	3.3	1.1	<0.1
4	Pt/WO_3-Y	$\lambda > 300$ nm	O_2	40.6 (60)	58.8	1.2	0	1.3	1.1	<0.1
5	Pt/WO_3-S	$\lambda > 300$ nm	O_2	32.4 (60)	48.7	1.2	0	2.0	1.2	0.6
6	Pt/TiO_2-P25	$\lambda > 300$ nm	O_2	38.0 (60)	25.9	0	0	0.6	1.1	4.1
		$\lambda > 300$ nm	O_2	59.1 (240)	21.8	0	<0.1	0.8	0.1	13.6
7	Pt/TiO_2-P25	$\lambda > 300$ nm	Ar	13.3 (60)	60.8	0	0	0.9	0	0.4
		$\lambda > 300$ nm	Ar	33.8 (240)	34.0	0	0.1	0.7	0	0.3
8	TiO_2-P25	$\lambda > 300$ nm	O_2	82.5 (240)	20.6	<0.1	0	0.8	0.1	13.4
9	Pt/TiO_2-M	$\lambda > 300$ nm	O_2	43.0 (60)	31.0	2.8	0	1.9	0	0.8
10	Pt/TiO_2-J	$\lambda > 300$ nm	O_2	48.9 (60)	26.5	0	1.3	0.1	0	1.2
11	Pt/TiO_2-J	$\lambda > 300$ nm	Ar	11.5 (15)	63.0	0	0	0.7	0	<0.1
		$\lambda > 300$ nm	Ar	38.6 (60)	35.4	0	0.2	0.7	0	0.1

[a] Initial concentration of benzene: 2.5 mmol L^{-1}, Solvent: H_2O 7.5 mL, Light source: 300 W Xe lamp. [b] Conversion: $(C_{\mathrm{benzene},0} - C_{\mathrm{benzene},t})/C_{\mathrm{benzene},0} \times 10^2$. [c] Selectivity: $C_{\mathrm{products},t}/(C_{\mathrm{benzene},0} - C_{\mathrm{benzene},t}) \times 10^2$.

of irradiation along with the consumption of benzene. Small amounts of dihydroxylated benzenes such as catechol or hydroquinone were also produced (Entry 1 in Table 1). Although appreciable generation of CO_2 (ca. 1.4 μmol) was observed in gas phase after the prolonged irradiation (240 min), the amount of CO_2 produce was much smaller than that of phenol (ca. 9.5 μmol). The production of phenol was also observed over the Pt/TiO_2-P25 as seen in Figure 1b, while the phenol production was saturated within 60 min of irradiation accompanied by significant increase of CO_2 generation, suggesting that the once-produced phenol was subsequently oxidized over the photocatalyst.[13–17]

As summarized in Table 1, the photocatalytic reaction over Pt/WO_3-K resulted in highly selective phenol production with 79% of selectivity at 22% of benzene conversion in initial period (60 min). Even after the long time irradiation of 240 min, a high selectivity of 74% was still obtained at 69% of benzene conversion (Entry 1) along with the production of catechol (2.3%), resorcinol (0.7%), and *p*-benzoquinone (8.8%), resulting in 85.5% of selectivity for hydroxylated benzene or quinone products from benzene. It should be noted here that the products without aromatic ring could not be quantified in the present study. Therefore, other unidentified parts (ca. 14%) are certainly corresponding to the various intermediate compounds produced through the cleavage of aromatic ring, as well as to the final oxidative product CO_2. Visible light irradiation ($\lambda > 400$ nm) afforded better phenol selectivity (Entry 2) on Pt/WO_3-K photocatalyst compared to the case of full arc irradiation (Entry 1). Other Pt/WO_3 samples also showed relatively high selectivity for phenol production above 48% (Entries 4 and 5). On the other hand, all the Pt/TiO_2 photocatalysts showed much lower selectivity for phenol production below 31% in the presence of O_2 even at low conversions of benzene (Entries 6, 9, and 10). In all cases H_2 production was negligible, indicating that almost all of the photoexcited electrons were consumed to reduce molecular O_2, not water (or H^+). It should be noted that the Pt/WO_3-K and the Pt/TiO_2-M, which have similar surface areas (ca. 10 $m^2 g^{-1}$), showed apparently different reactivity. Thus, the factor dominating the reactivity undoubtedly rests on the difference in the composition (WO_3 or TiO_2) but not on the surface areas. As expected by the photoabsorption property of TiO_2, visible light irradiation did not yield any appreciable products over Pt/TiO_2 photocatalysts.

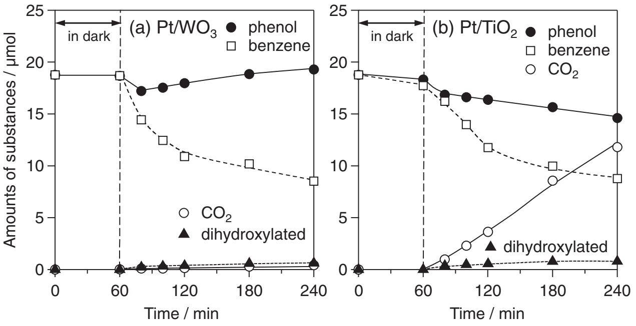


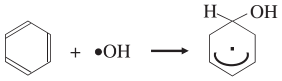
Figure 2. Time courses of photocatalytic reaction over (a) Pt/WO_3-K and (b) Pt/TiO_2-P25 in aerated aqueous solutions containing both benzene (18.8 μmol) and phenol (18.8 μmol) under ultraviolet and visible light ($300 < \lambda < 500$ nm).

These results suggested that the rates of subsequent oxidations of phenol on Pt/WO_3 photocatalysts are much lower than those on Pt/TiO_2 photocatalysts, enabling the high selectivity of phenol to be obtained in Pt/WO_3 photocatalyst systems. To examine this, the photocatalytic reactions were carried out in the coexistence of benzene and phenol. As shown in Figure 2a, the amount of phenol was first decreased and then increased with steady rate over Pt/WO_3-K photocatalyst along with decrease of benzene. This indicates that the rate of phenol production on Pt/WO_3-K is higher than that of subsequent oxidation of phenol, possibly due to the preferential reaction of benzene over phenol on Pt/WO_3-K photocatalyst. On the other hand, both benzene and phenol decreased on the Pt/TiO_2-P25 photocatalyst, while benzene decreased much faster than phenol (Figure 2b). The CO_2 generation on Pt/TiO_2-P25 was observed from the beginning of the photoirradiation with much higher rate compared to that of dihydroxylated products, indicating that both the phenol and dihydroxylated products are readily oxidized with cleavage of the aromatic ring producing various oxidized intermediates and CO_2. The faster decrease of benzene suggests another possible reaction pathway on Pt/TiO_2-P25; benzene molecules are directly oxidized into CO_2 without forming any hydroxylated benzenes. When the photocatalytic oxidation of benzene was carried out in the absence of water, i.e., in dehydrated acetonitrile, no hydroxylated product was obtained on Pt/WO_3-K nor Pt/TiO_2-P25 photocatalysts, indicating that the hydroxyl groups were originated from water molecules. It has been reported that hydroxyl radicals (•OH) are produced through the reaction of photogenerated holes with water molecules adsorbed on the photocatalyst surface.[18,19]

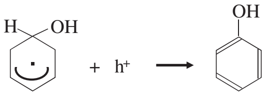
$$\text{photocatalyst} + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$h^+ + H_2O \rightarrow H^+ + {\bullet}OH \tag{2}$$

The hydroxyl radical certainly reacts with benzene (or phenol) to generate hydroxylated benzene radical, which are then oxidized by a hole on a photocatalyst surface and deprotonated producing phenol (or dihydroxylated benzenes), as shown below.[20]



(3)



(4)

Interestingly, stoichiometric amount of CO_2 to the decreased benzene was found to generate from benzene–acetonitrile solution with a relatively high rate when Pt/TiO_2-P25 photocatalyst was irradiated in the presence of O_2, while no CO_2 gas was generated on Pt/WO_3-K in a same time scale of irradiation ($\approx$120 min). This result indicates the presence of reaction pathway of direct oxidation of benzene on Pt/TiO_2-P25 surface by photogenerated holes into CO_2 without forming any hydroxylated benzenes. It appears that the direct oxidation of benzene occurs preferentially on Pt/TiO_2-P25 photocatalyst even in aqueous solution, resulting in the significant generation of CO_2 from the initial period (Figure 1b). On the other hand, the holes generated on Pt/WO_3 photocatalysts possibly react with water preferentially over benzene, resulting in the preferential generation of •OH that can produce phenol from benzene without cleavage of aromatic ring. The different participation of molecular oxygen (O_2) to the reactions seems to be another reason for the different reactivity between WO_3 and TiO_2 photocatalysts. It is well known that bare WO_3 is not an efficient photocatalyst for oxidation of organic compounds in the presence of O_2 because the conduction band (CB) bottom (ca. $+0.5\,V_{NHE}$) potential is insufficient for the reduction of O_2 [$E^0(O_2/O_2^{\bullet -}) = -0.33\,V_{NHE}$ and $E^0(O_2/HO_2\bullet) = -0.05\,V_{NHE}$] in a one-electron process. The incapability of O_2 to scavenge the electrons in CB of WO_3 results in the fast recombination and the lower photocatalytic activity. Indeed, bare WO_3 photocatalyst showed much lower conversion for the photocatalytic reaction with benzene (Entry 3) compared to that on Pt/WO_3, while the selectivity for phenol production was high. We have recently demonstrated that Pt-loaded WO_3 exhibits high photocatalytic activity for decomposition of various aliphatic compounds due to the promotion of multielectron reduction of O_2 on the Pt cocatalysts.[12] It was also confirmed that the reduction product of O_2 was mainly hydrogen peroxide (H_2O_2) generated via two-electron process [$E^0(O_2/H_2O_2) = +0.55\,V_{NHE}$]. Negligible reaction occurred by the simple mixture of benzene and H_2O_2 in water, indicating that the H_2O_2 itself cannot participate to the oxidation (hydroxylation) of benzene. On the other hand, TiO_2 photocatalysts possess sufficiently negative CB bottom for one-electron reduction of O_2. Therefore TiO_2 can reduce O_2 even without Pt cocatalyst resulting in efficient oxidation of organic compounds by holes. Interestingly, bare TiO_2-P25 showed higher rate for benzene oxidation than Pt/TiO_2-P25 (Entries 6 and 8), implying that most of the photoexcited electrons were consumed on the TiO_2 surface, not on Pt, via single electron processes producing radical species of O_2 (e.g., $O_2^{\bullet -}$ or $HO_2\bullet$). It has been suggested that the presence of O_2 enhances the oxidation of organic compounds in some TiO_2 photocatalysis systems via radical chain reaction mechanism.[21] It therefore appears that such radical species of O_2 also enhances the oxidative decomposition, especially the cleavage of aromatic ring, of benzene, resulting in low selectivity of phenols. Indeed, the reaction of Pt/TiO_2-P25 in the absence of O_2 (Entry 7), in which an appreciable amount of H_2 was produced during the photoirradiation, showed much higher selectivity for phenol (60.7% at 13.3% of conversion) than that in the presence of O_2, while the reaction rate was lowered considerably due to the lower capability of H_2O (or H^+) to capture the photoexcited electrons compared to that of O_2. These results strongly suggest that the different behavior of O_2 in the reactions is one of the reasons for the different reactivity in benzene oxidation between WO_3 and TiO_2 photocatalysts. However, the selectivity for phenol drastically decreased in prolonged reactions on the Pt/TiO_2 photocatalyst even in the absence of O_2 (Entries 7 and 11), indicating that the different behavior of O_2 is not the sole reason for the different reactivity between WO_3 and TiO_2 photocatalysts. As suggested above, the different reactivity of holes toward benzene and water certainly may contribute to the different reactivity. Further investigation is now under way to clarify the reaction mechanism for hydroxylation of benzene on Pt/WO_3 photocatalysts.

In conclusion, it was first demonstrated that Pt/WO_3 photocatalysts showed activity for direct production of phenol from benzene using water and O_2 as reactants under UV or visible light. The selectivity for phenol on Pt/WO_3 photocatalysts was much higher than those on Pt/TiO_2 (or TiO_2) photocatalysts. These results demonstrate the potential of Pt/WO_3 photocatalysts for highly selective organic synthesis with environmentally benign oxidants such as water and/or O_2 using abundant visible light included in solar radiation.

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