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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/WO₃) 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/WO₃ photocatalysts was much higher than those on platinum-loaded titanium(IV) oxide (Pt/TiO₂) 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 (O₂) 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 (O₂ 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 (TiO₂) photocatalysts suspended in a water-benzene mixture in the presence of molecular O₂,⁵⁻¹⁰ 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 O₂, to Pt-loaded TiO₂ 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 O₂.¹¹

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/WO₃), which was recently developed as a highly efficient visible-light-responsive photocatalyst,¹² in an aqueous solution containing benzene and O₂ under the irradiation of ultraviolet or visible light irradiation. The Pt/WO₃ photocatalysts showed much higher selectivity for phenol production than platinized (or bare) TiO₂ photocatalysts. The different reactivity between WO₃ and TiO₂ photocatalysts toward benzene oxidation is discussed.

Commercially available WO₃ powders such as WO₃-K (Kojundo Chemical Laboratory, monoclinic, 2.2 m²·g⁻¹), WO₃-Y (Yamanaka Chemical Industries, monoclinic, 2.2 m²·g⁻¹), and WO₃-S (Soekawa Chemicals, monoclinic, 1.6 m²·g⁻¹) were used. Since the WO₃-K sample consists of mixture of fine and large aggregated particles, fine particulate WO₃ with a particle size of 50–200 nm was separated from WO₃-K by the method reported previously,¹² which will be denoted as WO₃-K (10 m²·g⁻¹) hereafter. TiO₂ powders such as TiO₂-P25 (Degussa (Evonik) P 25, 59 m²·g⁻¹), TiO₂-M (Merck, anatase, 11 m²·g⁻¹), and TiO₂-J (JRC-TIO-8 donated from the Catalysis Society of Japan, anatase, 338 m²·g⁻¹) were also used for comparison. The modification of photocatalysts with nanoparticulate Pt metal cocatalysts (0.1wt%) was accomplished by photodeposition from hexachloroplatinic acid (H₂PtCl₆·6H₂O) 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 (CO₂) in the gas phase was analyzed by gas chromatography.

Figure 1 shows the time-course curves of photocatalytic reactions over Pt/WO₃-K and Pt/TiO₂-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).

Figure 1. Time courses of photocatalytic oxidation of benzene over (a) Pt/WO₃-K and (b) Pt/TiO₂-P25 in aerated aqueous solutions of benzene (18.8 μmol) under ultraviolet and visible light (300 < λ < 500 nm).

Table 1. Photocatalytic oxidation of benzene by WO₃ and TiO₂ photocatalysts^a

Entry	Sample	Conditions	Conversion (%) ^(b) (Irradiation time)	Selectivity (%) ^(c)						Amount of CO ₂ /mmol
				Phenol	Di-hydroxylated	Resorcinol	Catechol	p-Benzoquinone	Other	
1	Pt/WO ₃ -K	λ > 300	O ₂	22.2 (60)	79.3	1.9	0	1.2	4.0	< 0.1
		λ > 400	O ₂	68.9 (240)	73.7	2.3	0.7	0	8.8	1.4
2	Pt/WO ₃ -K	λ > 300	O ₂	26.6 (60)	83.8	1.4	0	1.2	2.8	< 0.1
		λ > 400	O ₂	52.5 (240)	75.1	1.4	0	2.9	1.2	0.6
3	WO ₃ -K	λ > 300	O ₂	16.4 (240)	84.6	1.6	0	3.3	1.1	< 0.1
4	Pt/WO ₃ -Y	λ > 300	O ₂	40.6 (60)	58.8	1.2	0	1.3	1.1	< 0.1
5	Pt/WO ₃ -S	λ > 300	O ₂	32.4 (60)	48.7	1.2	0	2.0	1.2	0.6
6	Pt/TiO ₂ -P25	λ > 300	O ₂	38.0 (60)	25.9	0	0	0.6	1.1	4.1
		λ > 400	O ₂	59.1 (240)	21.8	0	< 0.1	0.8	0.1	13.6
7	Pt/TiO ₂ -P25	λ > 300	Ar	13.3 (60)	60.8	0	0	0.9	0	0.4
		λ > 400	Ar	33.8 (240)	34.0	0	0.1	0.7	0	0.3
8	TiO ₂ -P25	λ > 300	O ₂	82.5 (240)	20.6	< 0.1	0	0.8	0.1	13.4
9	Pt/TiO ₂ -M	λ > 300	O ₂	43.0 (60)	31.0	2.8	0	1.9	0	0.8
10	Pt/TiO ₂ -J	λ > 300	O ₂	48.9 (60)	26.5	0	1.3	0.1	0	1.2
		λ > 400	Ar	11.5 (15)	63.0	0	0	0.7	0	< 0.1
11	Pt/TiO ₂ -J	λ > 300	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 : H₂O 7.5 mL, Light source : 300 W Xe lamp, (b) Conversion : (C_{benzene,0} - C_{benzene,t})/C_{benzene,0} × 10², (c) Selectivity : C_{products,t}/(C_{benzene,0} - C_{benzene,t}) × 10²

As seen in Fig. 1-a, phenol was produced with almost constant rate over Pt/WO₃-K photocatalyst after 30 min of irradiation along with the consumption of benzene. Small amounts of di-hydroxylated benzenes such as catechol or hydroquinone were also produced (see entry 1 in Table 1). Although appreciable generation of CO₂ (ca. 1.4 μmol) was observed in gas phase after the prolonged irradiation (240 min), the amount of CO₂ produce was much smaller than that of phenol (ca. 9.5 μmol). The production of phenol was also observed over the Pt/TiO₂-P25 as seen in Fig. 1-b, while the phenol production was saturated within 60 min of irradiation accompanied by significant increase of CO₂ generation, suggesting that the once-produced phenol was subsequently oxidized over the photocatalyst.¹³⁻¹⁷

As summarized in Table 1, photocatalytic reaction over Pt/WO₃-K resulted in highly selective phenol production with 79% of selectivity at 22% of benzene conversion in initial period (30 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 CO₂. Visible light irradiation (λ > 400 nm) afforded better phenol selectivity (entries 2) on Pt/WO₃-K photocatalyst compared to the case of full arc irradiation (entries 1). Other Pt/WO₃ samples also showed relatively high selectivity for phenol production above 48 % (entries 4 and 5). On the other hand, all the Pt/TiO₂ photocatalysts showed much lower selectivity for phenol production below 31% in the presence of O₂ even at low conversions of benzene (entries 6, 9 and 10). In all cases H₂ production was negligible, indicating that almost all of the photoexcited electrons were consumed to reduce molecular O₂, not water (or H⁺). It should be noted that the Pt/WO₃-K and the Pt/TiO₂-M, which have similar surface

Figure 2. Time courses of photocatalytic reaction over (a) Pt/WO₃-K and (b) Pt/TiO₂-P25 in aerated aqueous solutions containing both benzene (18.8 μmol) and phenol (18.8 μmol) under ultraviolet and visible light (300 < λ < 500 nm).

areas (ca. 10 m²·g⁻¹), showed apparently different reactivity. Thus, the factor dominating the reactivity undoubtedly rests on the difference in the composition (WO₃ or TiO₂) but not on the surface areas. As expected by the photoabsorption property of TiO₂, visible light irradiation did not yield any appreciable products over Pt/TiO₂ photocatalysts.

These results suggested that the rates of subsequent oxidations of phenol on Pt/WO₃ photocatalysts are much lower than those on Pt/TiO₂ photocatalysts, enabling the high selectivity of phenol to be obtained in Pt/WO₃ photocatalyst systems. To examine this, the photocatalytic reactions were carried out in the co-existence of benzene and phenol. As shown in Fig. 2-a, the amount of phenol was first decreased and then increased with steady rate over Pt/WO₃-K photocatalyst along with decrease of benzene. This indicates that the rate of phenol production on Pt/WO₃-K is higher than that of subsequent oxidation of phenol, possibly due to the preferential reaction of benzene over phenol on Pt/WO₃-K photocatalyst. On the other hand, both benzene and phenol decreased on the Pt/TiO₂-P25 photocatalyst, while benzene decreased much faster than phenol. The CO₂ generation on Pt/TiO₂-P25 was observed from the beginning of the photoradiation with much higher rate compared to that of di-hydroxylated products, indicating that both the phenol and di-hydroxylated products are readily oxidized with cleavage of the aromatic ring producing various oxidized intermediates and CO₂. The faster decrease of benzene suggests another possible reaction pathway on Pt/TiO₂-P25; benzene molecules are directly oxidized into CO₂ 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/WO₃-K nor Pt/TiO₂-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

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 di-hydroxylated benzenes), as shown below.²⁰

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/TiO₂-P25 photocatalyst was irradiated in the presence of O_2 , while no CO_2 gas was generated on Pt/WO₃-K in a same time scale of irradiation (~ 120 min). This result indicates the presence of reaction pathway of direct oxidation of benzene on Pt/TiO₂-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/TiO₂-P25 photocatalyst even in aqueous solution, resulting in the significant generation of CO_2 from the initial period (see Fig. 1-b). On the other hand, the holes generated on Pt/WO₃ photocatalysts possibly react with water preferentially over benzene, resulting in the preferential generation of $\bullet\text{OH}$ 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 WO₃ and TiO₂ photocatalysts. It is well known that bare WO₃ is not an efficient photocatalyst for oxidation of organic compounds in the presence of O_2 because the conduction band (CB) bottom (ca. $+0.5 \text{ V}_{\text{NHE}}$) potential is insufficient for the reduction of O_2 [$E^0(\text{O}_2/\text{O}_2\bullet^-) = -0.33 \text{ V}_{\text{NHE}}$ and $E^0(\text{O}_2/\text{HO}_2\bullet) = -0.05 \text{ V}_{\text{NHE}}$] in a one-electron process. The incapability of O_2 to scavenge the electrons in CB of WO₃ results in the fast recombination and the lower photocatalytic activity. Indeed, bare WO₃ photocatalyst showed much lower conversion for the photocatalytic reaction with benzene (entry 3) compared to that on Pt/WO₃, while the selectivity for phenol production was high. We have recently demonstrated that Pt-loaded WO₃ exhibits high photocatalytic activity for decomposition of various aliphatic compounds due to the promotion of multi-electron 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 [$E^0(\text{O}_2/\text{H}_2\text{O}_2) = +0.55 \text{ V}_{\text{NHE}}$]. 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, TiO₂ photocatalysts possess sufficiently negative CB bottom for one-electron reduction of O_2 . Therefore TiO₂ can reduce O_2 even without Pt cocatalyst resulting in efficient oxidation of organic compounds by holes. Interestingly, bare TiO₂-P25 showed higher rate for benzene oxidation than Pt/TiO₂-P25 (see entries 6 and 8), implying that most of the photoexcited electrons were consumed on the TiO₂ surface, not on Pt, via single electron processes producing radical species of O_2 (e.g., $\text{O}_2\bullet^-$ or $\text{HO}_2\bullet$). It has been suggested that the presence of O_2 enhances the oxidation of organic compounds in some TiO₂ 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/TiO₂-P25 in the absence of O_2 (entry 7), in which an appreciable amount of H_2 was produced during the photoradiation, 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 WO₃ and TiO₂ photocatalysts. However, the selectivity for phenol drastically decreased in prolonged reactions on the Pt/TiO₂ photocatalyst even in the absence of O_2 (entries 7, 11), indicating that the different behavior of O_2 is not the sole reason for the different reactivity between WO₃ and TiO₂ 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/WO₃ photocatalysts.

In conclusion, it was first demonstrated that Pt/WO₃ 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/WO₃ photocatalysts was much higher than those on Pt/TiO₂ (or TiO₂) photocatalysts. These results demonstrate the potential of Pt/WO₃ 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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References and Notes

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