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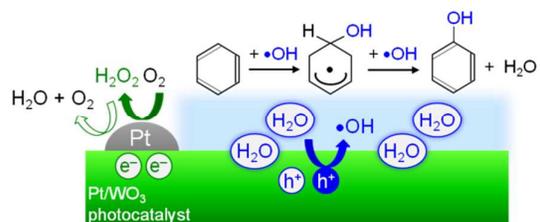


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Highly selective phenol production from benzene proceeded on Pt/WO_3 photocatalysts due to the unique reactivity of holes generating hydroxyl radicals.

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ARTICLE TYPE

Highly selective phenol production from benzene on platinum-loaded tungsten oxide photocatalyst with water and molecular oxygen: Selective oxidation of water by holes for generating hydroxyl radical as predominant source of hydroxyl group

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Particles of tungsten oxide loaded with nanoparticulate platinum (Pt/WO₃) photocatalytically produced phenol from benzene with high selectivity (e.g., 74% at 69% of benzene conversion) in water containing molecular O₂; the selectivity for phenol were much higher than those on conventional titanium oxide (TiO₂) photocatalysts (both the unmodified and Pt-loaded) that generated CO₂ as a main product. Results confirmed that photoexcited electrons in the Pt/WO₃ photocatalysts mainly generated H₂O₂ from molecular O₂ through a two-electron reduction; the H₂O₂ generated did not significantly contribute to the undesirable peroxidation of phenol produced. In contrast, the oxygen radical species, such as •O₂⁻ or •HO₂, generated on TiO₂ photocatalysts partially contributed to the successive oxidation of phenol and other intermediates to reduce the selectivity toward phenol. More importantly, the reactions using ¹⁸O-labeled O₂ and H₂O clearly revealed that the holes generated on Pt/WO₃ react primarily with H₂O molecules, even in the presence of benzene in aqueous solution, selectively generating •OH radicals that subsequently react with benzene to produce phenol. In contrast, a portion of holes generated on TiO₂ photocatalysts reacts directly with benzene molecules, which are adsorbed on the surface of TiO₂ by strong interaction with surface hydroxyl groups. This direct oxidation of substances by holes undoubtedly enhanced non-selective oxidation, consequently lowering selectivity for phenol by TiO₂. The two unique features of Pt/WO₃, the absence of reactive oxygen radical species from O₂ and the ability to selectively oxidize water to form •OH, are the most likely reasons for the highly selective phenol production.

1. Introduction

Chemical syntheses using semiconductor photocatalysts can be environmentally benign processes that possess great potential for reducing energy consumption in industrial production of useful chemicals by using light energy.¹⁻³ The high reduction and oxidation potentials of photoexcited electrons and holes, respectively, generated on semiconductor particles such as TiO₂ can promote various chemical reactions, even endothermic reactions. Another advantage of photocatalytic organic syntheses is the availability of molecular oxygen (O₂) or water (H₂O) as abundant and harmless reductants or oxidants, instead of conventional, expensive reductants and oxidants that generally generate non-recyclable wastes requiring separation from the products. Molecular O₂ is an efficient electron acceptor (*i.e.*, oxidant) for the photoexcited electron generated on TiO₂ photocatalysts, where the holes generated can directly oxidize the organic substances adsorbed, and can indirectly oxidize through formation of •OH radicals from H₂O molecules adsorbed on the surface; the •OH radicals generated subsequently oxidize the organic substances to produce desired products.^{2, 4-11} However, TiO₂ photocatalysts generally exhibit high activity for non-

selective and complete oxidation of organic compounds in the presence of ambient O₂, yielding CO₂ and highly oxidized products.^{2, 12-18} This property is very useful for mineralization of toxic organic compounds, but is detrimental to the development of highly selective organic synthetic systems. Only a limited number of highly selective organic synthesis using conventional TiO₂ photocatalysts in the presence of molecular O₂ has been reported.^{19, 20} The low selectivity for the desired products is due to the competitive nature of successive oxidations of products, as well as the raw materials and intermediates through undesirable pathways.^{21, 22} Some oxygen radical species, such as •O₂⁻ or •HO₂ generated from O₂ molecules *via* reaction with photoexcited electrons, are thought to contribute to the oxidation of organic substances to some extent.²³⁻³⁰ Some research groups have reported highly selective organic synthesis using TiO₂-related photocatalysts in the absence of molecular O₂.³¹⁻³⁴ For example, Shiraishi *et al.* demonstrated highly selective synthesis of benzimidazoles from *ortho*-phenylenediamine and ethanol using Pt-loaded TiO₂ photocatalyst (Pt/TiO₂) under UV light irradiation.³¹ Yoshida *et al.* reported direct hydroxylation of benzene to phenols using Pt/TiO₂ suspended in water containing a high concentration of substances such as benzene (*e.g.*, 1:1 v/v),

in which selectivity for hydroxylation of benzenes was greatly improved because the reaction was conducted in the absence of molecular O₂.³² In these reactions on Pt/TiO₂ photocatalysts, protons (H⁺) were used as an electron acceptor instead of molecular O₂, accompanied by production of H₂ on Pt cocatalysts. Although these reports might indicate the potential of highly selective organic synthesis through the use of photocatalysts, reaction efficiencies generally decreased significantly due to the reduced ability of H⁺ as an electron acceptor compared to O₂. Furthermore, the potential of H⁺ reduction requires a highly negative conduction band minimum (CBM) of the semiconductor, and therefore limits the applicable semiconductor materials to TiO₂. The use of TiO₂ photocatalysts is limited in practical applications by their wide bandgaps (*ca.* 3.2 eV for anatase, *ca.* 3.0 eV for rutile) that require UV light irradiation for excitation. The energy efficiencies in artificial UV light sources, such as high-pressure Hg lamps or UV-LEDs, are low and insufficient for achieving cost-effective chemical synthesis using TiO₂ photocatalysts. Thus, using visible light is desired for the lower cost provided by efficient visible light sources such as blue-LEDs as well as for the possibility of using natural sunlight.

Previous studies have demonstrated that particles of tungsten oxide (WO₃) loaded with nanoparticulate platinum (Pt) exhibit photocatalytic activity sufficient for oxidation of various organic compounds under visible light; the activity was similar to that of TiO₂ under UV light.³⁵ Although WO₃ generally has been regarded as a photocatalyst inactive for oxidation of organic compounds with molecular O₂ due to insufficient CBM for reduction of O₂, the loading of nanoparticulate Pt cocatalyst significantly increases the probability of multi-electron reduction of O₂ by photoexcited electrons, enhancing the oxidation of organic substances by the holes remaining in the valence band. The photoexcited electrons in Pt-loaded WO₃ (Pt/WO₃) were suggested to produce mainly H₂O₂ *via* two-electron reduction. These findings led to the application of the Pt/WO₃ photocatalyst to organic synthesis reactions because it is activated under visible light but does not generate oxygen radicals such as •O₂⁻ or •HO₂, which may enhance the peroxidation of products. The direct hydroxylation of benzene to phenol was selected as the target reaction because it is one of the most challenging chemical reactions. The present industrial synthesis of phenol, the major source of phenol resins, is based on the cumene method—a multi-step process that requires a large amount of energy. Therefore, direct, one-step synthesis of phenol from benzene is a desirable process and has been studied extensively. The Pt/WO₃ photocatalysts recently have been shown to possess activity for direct production of phenol from benzene using O₂ and water as reactants under UV or visible light.³⁶ Selectivity toward phenol on Pt/WO₃ photocatalysts was much greater than that on Pt/TiO₂ (or unmodified TiO₂) photocatalyst; however, reasons for the differences in reactivity and selectivity of the two photocatalysis systems are not known.

The present study examined the reaction mechanism of highly selective phenol production from benzene on Pt/WO₃ photocatalysts in detail compared to that on TiO₂ (including Pt-loaded TiO₂) to find the contributing factors. Results revealed that the holes generated in the WO₃ photocatalysts possess distinctly different reactivity from those in TiO₂ toward oxidation

and hydroxylation of benzene, regardless of their similar oxidation potentials, enabling highly selective phenol production from benzene in water.

2. Experimental Section

2.1. Samples

Commercially available WO₃ powders, such as WO₃-K (triclinic and monoclinic, 4.8 m² g⁻¹, Kojundo Chemical Laboratory), WO₃-Y (monoclinic, 2.2 m² g⁻¹, Yamanaka Chemical Industries), and WO₃-S (monoclinic, 1.6 m² g⁻¹, Soekawa Chemicals), were used. The fine particulate WO₃ sample, referred to as WO₃-K (triclinic, 10 m² g⁻¹), was obtained by separation from large aggregates by mean of centrifugation of the purchased WO₃-K samples as previously reported.³⁵ The TiO₂ powders, such as TiO₂-P [anatase and rutile, P 25, 55 m² g⁻¹, Degussa (Evonik)], TiO₂-A (anatase, 10 m² g⁻¹, Merck), and TiO₂-R (rutile, 4.0 m² g⁻¹, Aldrich), were used.

2.2. Platinum loading using the photodeposition method

Samples loaded with Pt nanoparticles were prepared as follows. The sample powder was stirred in an aqueous methanol solution (10 vol%) containing the required amount of H₂PtCl₆ as a Pt precursor. The WO₃ samples were irradiated with visible light; the TiO₂ samples were irradiated with UV and visible light. After washing several times with distilled water, the sample was dried in air at 353 K for 12 h. The diameters of Pt nanoparticles loaded were confirmed to be 3 ~ 10 nm as demonstrated in the previous study.³⁵

2.3. Photocatalytic reaction

Photocatalytic reaction of benzene was conducted in a Pyrex reaction cell (15 mL) in an aerated aqueous benzene solution (water volume: 7.5 mL; initial benzene amount: 18.8 μmol) with continuous stirring at 279 K. The source for both the ultraviolet and visible light was a 300-W Xenon lamp so that results could be compared with those for TiO₂ photocatalysts (300 < λ < 500 nm). Sample aliquots were withdrawn from the reactor cell after each irradiation and filtered through a PVDF filter (Mini-Uni Prep™) to remove photocatalyst particles. Product analysis was performed using a high performance liquid chromatograph equipped with a C-18 column and photodiode-array detector (Shimadzu, SPD-M20A). Generation of carbon dioxide in the gas phase was analyzed using a gas chromatograph (Shimadzu, GC-14B) equipped with a flame-ionization detector.

The amount of H₂O₂ produced during photocatalytic oxidation of an organic substrate was analyzed by iodometry.³⁷ The photocatalyst (10 mg) suspended in 10 mL water was placed in a Pyrex test tube (30 mL) in the presence of ambient oxygen. The initial amount of acetic acid (as hole scavenger) was 300 μmol. After irradiation of the photocatalyst suspension, 2 mL of solution was removed with a syringe and the photocatalyst separated from the solution using a syringe PVDF filter (Millex®W). Then 1 mL of 100 mmol L⁻¹ aq. potassium hydrogen phthalate (C₈H₅KO₄) and 1 mL of 400 mmol L⁻¹ aq. potassium iodide (KI) were added. The H₂O₂ was allowed to react with I⁻ under acidic conditions (H₂O₂ + 3I⁻ + 2H⁺ → I₃⁻ + 2H₂O). The amount of H₂O₂ was determined by the maximum intensity of absorption attributed to I₃⁻ at approximately 350 nm, measured using a UV-Vis spectrophotometer (Shimadzu UV-1800).

For tracer studies, either H₂¹⁸O (98 atom%, Taiyo Nippon Sanso Corp.) or ¹⁸O₂ (98 atom%, Taiyo Nippon Sanso Corp.) gas was used as the oxygen isotope source. Then, 50 mg of photocatalyst suspended in 1 mL H₂¹⁸O (in air) or H₂¹⁶O (in ¹⁸O₂) was used. In the case of reactions in H₂¹⁸O solvent with ¹⁸O₂ gas, the solution was purged with Ar gas and subsequently with ¹⁸O₂ gas to make the partial pressure of O₂ in the reaction system similar to that in air; the amount of N₂ gas was under the detection limit in each reaction. The initial amount of benzene used to investigate the hydroxylation process of benzene to phenol was 500 μmol (500 mmol L⁻¹). After the photocatalyst suspended in solution had been irradiated, a portion (20 μL) was extracted by syringe, added to diethyl ether (300 μL) containing the internal standard, and shaken in a tube mixer. The amount of ¹⁸O-labeled phenol was determined using GC-MS (Shimadzu, GCMS-2010/PARVUM2).

2.4. IR measurements

FT-IR spectra of the adsorbed benzene on each sample were recorded with a Fourier-transform infrared spectrometer (Jasco FT-4200). The sample pellet was introduced into an IR cell equipped with CaF₂ windows. Prior to the measurements, the sample was heated in vacuum. After cooling, benzene vapor was introduced into the cell and then evacuated in the gas phase. The spectra obtained after adsorption of benzene were subtracted from the corresponding spectra before adsorption.

3. Results and Discussion

3.1. Hydroxylation of benzene over various Pt/WO₃ and Pt/TiO₂ photocatalysts

Figure 1 shows the time course of photocatalytic hydroxylation and oxidation of benzene on Pt-loaded WO₃ and Pt-loaded TiO₂ samples in water (7.5 mL) containing saturated air and a small amount of benzene (*ca.* 18.8 μmol). Reactions were started with the benzene concentration (2.5 mmol L⁻¹) sufficiently lower than the maximum soluble value of benzene in water (22.3 mmol L⁻¹), in order to accurately quantify the reduced amount of benzene during each reaction.³⁸ Upon irradiation with UV and visible light, the amount of benzene decreased, while the rate and the order of reaction varied among the samples. Selectivity for each product was distinctly different for the Pt/WO₃ and Pt/TiO₂ systems.

Phenol and CO₂ were the predominant products in the Pt/WO₃

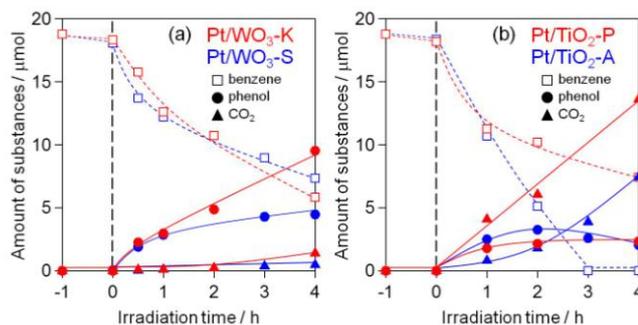


Figure 1. Time course of photocatalytic oxidation of benzene over (a) Pt/WO₃ and (b) Pt/TiO₂ photocatalysts in aerated aqueous solutions of benzene (18.8 μmol) under ultraviolet and visible light irradiation (300 < λ < 500 nm).

and Pt/TiO₂ systems, respectively. For Pt/WO₃-K (Fig. 1a), phenol was produced at an almost steady rate under irradiation along with small amounts of di-hydroxylated benzenes (not plotted) and CO₂.

Table 1. Conversion and phenol selectivity for hydroxylation of benzene^a

| Entry | Photocatalyst | Conversion (%) ^b (Irradiation time / h) | Selectivity (%) ^c | | | | | Amount of CO ₂ / μmol |
|----------------|------------------------|---|------------------------------|----------|------------|--------------|--------------|----------------------------------|
| | | | Phenol | Catechol | Resorcinol | Hydroquinone | Benzoquinone | |
| 1 | Pt/WO ₃ -K | 22.2 (1) | 79.3 | 1.9 | 0 | 1.2 | 4.0 | <0.1 |
| | | 68.9 (4) | 73.7 | 2.3 | 0.7 | 0 | 8.8 | 1.4 |
| 2 | Pt/WO ₃ -Y | 40.6 (1) | 58.8 | 1.2 | 0 | 1.3 | 1.1 | <0.1 |
| | | 63.6 (4) | 57.1 | 1.4 | 0 | 2.2 | 0.5 | 0.4 |
| 3 | Pt/WO ₃ -S | 32.4 (1) | 48.7 | 1.2 | 0 | 2.0 | 1.2 | 0.6 |
| | | 59.2 (4) | 41.7 | 1.2 | 0 | 2.1 | 0.0 | 1.1 |
| 4 | WO ₃ -K | 16.4 (4) | 84.6 | 1.6 | 0 | 3.3 | 1.1 | <0.1 |
| | | 26.6 (1) | 83.8 | 1.4 | 0 | 1.2 | 2.8 | <0.1 |
| 5 ^d | Pt/WO ₃ -K | 52.5 (4) | 75.1 | 1.4 | 0 | 2.9 | 1.2 | 0.6 |
| | | 38.0 (1) | 25.9 | 0 | 0 | 0.6 | 1.1 | 4.1 |
| 6 | Pt/TiO ₂ -P | 59.1 (4) | 21.8 | 0 | <0.1 | 0.8 | 0.1 | 13.6 |
| | | 43.0 (1) | 31.0 | 2.8 | 0 | 1.9 | 0 | 0.8 |
| 7 | Pt/TiO ₂ -A | 99.0 (4) | 10.9 | 4.2 | 0.3 | 2.1 | 0 | 7.5 |
| | | 24.1 (1) | 36.9 | 3.2 | 0 | 9.1 | 1.7 | 1.5 |
| 8 | Pt/TiO ₂ -R | 76.8 (4) | 11.9 | 2.6 | 0.1 | 5.9 | 1.7 | 3.7 |
| | | 51.6 (1) | 22.7 | 0 | 0 | 1.4 | 0.2 | 4.7 |
| 9 | TiO ₂ -P | 82.5 (4) | 20.6 | <0.1 | 0 | 0.8 | 0.1 | 13.4 |
| | | 37.8 (1) | 23.6 | 3.4 | 0 | 3.0 | 0 | 0.4 |
| 10 | TiO ₂ -A | 84.5 (4) | 14.5 | 5.7 | 0.1 | 2.8 | 0 | 4.9 |
| | | 34.1 (1) | 24.8 | 1.6 | 0 | 11.5 | 0 | 1.8 |
| 11 | TiO ₂ -R | 68.3 (4) | 16.1 | 1.6 | 0 | 6.7 | 0 | 12.5 |

^aInitial amount of benzene : 18.8 μmol, solvent : H₂O 7.5 mL, light source : 300 W Xe lamp, ^bConversion : (C_{benzene,0} - C_{benzene,t}) / C_{benzene,0} × 10², ^cSelectivity : C_{products,t} / (C_{benzene,0} - C_{benzene,t}) × 10², ^dUnder visible light irradiation (400 < λ < 500 nm).

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Table 1 summarizes the selectivity for each product, calculated on the basis of the decrease in benzene. Because selectivity for CO₂ is difficult to determine due to uncertainty in the stoichiometry between the decrease in benzene and generation of CO₂, the amount of CO₂ generated is listed in Table 1. Selectivity for phenol by the Pt/WO₃-K photocatalyst (entry 1) initially (1 h) was *ca.* 79%, with a benzene conversion of 22%, along with appreciable production of catechol (1.9%), hydroquinone (1.2%), and *p*-benzoquinone (4.0%). The generation of CO₂ was below the detection limit (< 0.1 μmol). Even with high benzene conversion (64%) after a long period of irradiation (4 h), selectivity for phenol was high (74%), while the amount of CO₂ became detectable (*ca.* 1.4 μmol). The Pt/WO₃-K photocatalyst had high selectivity for hydroxylated benzene or quinone throughout the reaction period (*ca.* 86.4% and 85.5% after 1 and 4 h of irradiation, respectively). The products without an aromatic ring were not quantified because quantification by HPLC was difficult, even with a photodiode array detector. Therefore, the unidentified fraction (*ca.* 14%) reflected the cleaved intermediates, including oxidized CO₂. Other Pt/WO₃ samples also generated phenol as the main product with relatively high selectivity and a negligibly small amount of CO₂ (Figs. 1a and S1a, and Table 1) in the initial period (1 h), while the Pt/WO₃-S sample showed significantly lower selectivity (*ca.* 42%) after 4-h irradiation. These findings strongly suggest that the rate of successive oxidation of phenol on Pt/WO₃ photocatalysts, specifically on Pt/WO₃-K sample, is lower than that of hydroxylation of benzene, affording high selectivity for phenol.

In contrast, CO₂ was predominantly generated on Pt/TiO₂-P (Fig. 1b) at a steady rate during the initial period along with an appreciable amount of phenol. The amount of phenol nearly reached saturation after 1 h of photo-irradiation, indicating

successive oxidation of the phenol once produced to give cleaved intermediates and CO₂. The production of CO₂ during the initial period strongly suggests a direct oxidation pathway of benzene without the formation of any hydroxylated intermediates such as phenol. Selectivity for phenol was quite low (26%) on Pt/TiO₂-P, even at short irradiation times (1 h) with relatively low conversion of benzene (Table 1, entry 6). The use of other Pt/TiO₂ samples also resulted in predominant production of CO₂, along with much lower selectivity for phenol (Figs. 1b and S1, Table 1) than that of Pt/WO₃. However, the time courses for CO₂ and phenol production were different from that using Pt/TiO₂-P. For example, use of Pt/TiO₂-A (Fig. 1b) generated predominantly phenol during the initial period, followed by generation of CO₂ along with a gradual decrease in phenol amount, indicating successive oxidation of the phenol produced. Similar reactivity was observed for the Pt/TiO₂-R sample with the pure rutile phase (Fig. S1). Selectivity for phenol on these Pt/TiO₂ photocatalysts (Table 1, entries 6-8) was much lower than that on Pt/WO₃ photocatalysts. Note that the Pt/WO₃-K and the Pt/TiO₂-A samples, which have similar surface areas (*ca.* 10 m² g⁻¹), possessed different reactivities. Thus, the factor dominating reactivity is related to the difference in the composition (WO₃ or TiO₂), not on the surface area.

These results indicate that the rates of successive oxidation of phenol on Pt/WO₃ photocatalysts are much lower than those on Pt/TiO₂ photocatalysts, enabling Pt/WO₃ to produce phenol with high selectivity. Another advantage of the Pt/WO₃ photocatalysts is the ability to use it with visible light irradiation. As shown in Table 1, visible light irradiation ($\lambda > 400$ nm) afforded better phenol selectivity (entry 5) than did full arc irradiation (entry 1) on Pt/WO₃-K photocatalyst, with a comparable reaction rate. For Pt/TiO₂-P with mixed anatase and rutile phase, an appreciable decrease in benzene amount was observed (Fig. S2) certainly due to reaction on the rutile phase that can absorb light up to *ca.* 410 nm, while the rate was much lower than that under UV light irradiation (Fig. 1). As expected based on the photoabsorption properties of TiO₂ anatase, visible light irradiation of Pt/TiO₂-A did not yield any appreciable products (Fig. S2).

3.2. Influence of oxygen-reduced species on phenol selectivity by Pt/WO₃ and Pt/TiO₂ photocatalysts

The Pt/WO₃ photocatalysts exhibited significantly greater selectivity for phenol production than did the Pt/TiO₂ system, which showed high activity for oxidative degradation of benzene and other intermediates including phenols. A possible reason for the difference in reactivity between the two systems could be a difference in level of participation of the O₂ reduced species (H₂O₂, •O₂⁻, or •HO₂), generated during the reductive process by photoexcited electrons, in the oxidation of benzene or intermediates. The conduction band minimum (CBM) of WO₃ semiconductor (*ca.* +0.5V vs. SHE) was much lower than the potentials of O₂ reduction *via* the one-electron process [O₂ + e⁻ → •O₂⁻, E⁰(O₂/•O₂⁻) = -0.28 V; or O₂ + H⁺ + e⁻ → •HO₂, E⁰(O₂/•HO₂) = -0.05 V vs. SHE], resulting in rapid recombination between photoexcited electrons and holes in WO₃ photocatalysts even in the presence of a sufficient amount of O₂. Unmodified WO₃ samples indeed exhibited a low rate of benzene oxidation and hydroxylation, but the selectivity toward phenol

was adequate (Table 1, entry 4). However, loading of highly dispersed Pt nanoparticles on WO₃ was shown to significantly enhance the rate of oxidative decomposition of aliphatic compounds, such as acetaldehyde, under visible light. This enhancement is due to promotion of multi-electron reduction of O₂ [O₂ + 2e⁻ + 2H⁺ → H₂O₂, E⁰(O₂/H₂O₂) = +0.68 V; or O₂ + 4e⁻ + 4H⁺ → 2H₂O, E⁰(O₂/H₂O) = +1.23 V vs. SHE] on Pt cocatalysts; these reactions are able to proceed thermodynamically, even through the photoexcited electrons generated in the conduction band of WO₃. The small amount of Pt loading (0.1 wt.%) also was effective for enhancing the rate of hydroxylation and oxidation of benzene on Pt/WO₃-K photocatalysts, strongly suggesting the occurrence of multi-electron reduction of O₂ on Pt cocatalyst in the present system. As shown in Fig. S3, the optimum amount of Pt loading for phenol production was *ca.* 0.1 wt.%; greater amounts resulted in lower selectivity for phenol and increased generation of CO₂, while the reaction rate was increased.

In contrast, TiO₂ semiconductors possess much more negative CBM (anatase: *ca.* -0.2 V, rutile: *ca.* +0.05 V vs. SHE) than that of WO₃. These values, especially that of anatase, are considered sufficient for progress of O₂ reduction *via* a single-electron process by assuming a shift in the CBM potentials of TiO₂ under near neutral pH conditions.³⁹ Most TiO₂ photocatalysts, especially those with anatase, exhibit sufficiently high activity for oxidative degradation of various organic compounds even without a cocatalyst such as Pt. In the present system, unmodified TiO₂-P photocatalyst exhibited greater conversion of benzene than that loaded with 0.1 wt.% of Pt (see Table 1 and Fig. S3), implying that most of the photoexcited electrons were consumed on the TiO₂ surface, even with Pt loading, *via* single-electron processes producing radical species of O₂ (*e.g.*, •O₂⁻ or •HO₂). As shown in Fig. S3, selectivity for phenol on TiO₂ photocatalysts was minimally affected by Pt loading amount, while the conversion of benzene on Pt/TiO₂-A increased significantly with Pt loading amount. Thus, an amount of 0.1 wt.% Pt loading in the TiO₂ system was a reasonable value for comparison with the Pt/WO₃ system.

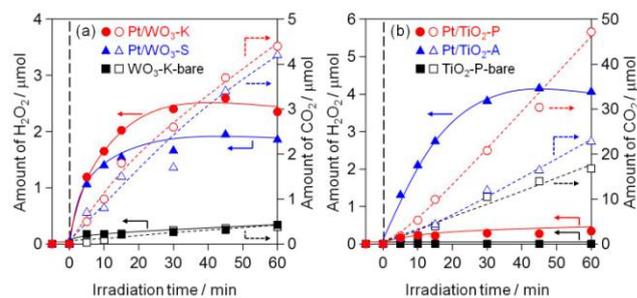


Figure 2. Time course curves of H₂O₂ and CO₂ generation over (a) WO₃ and (b) TiO₂ photocatalysts suspended in AcOH solution under ultraviolet and visible light irradiation (300 < λ < 500 nm).

Products generated from molecular O₂ during the reduction on WO₃ and TiO₂ were evaluated using the photocatalytic oxidation of acetic acid in aqueous solution containing O₂. Figure 2 shows time courses for H₂O₂ and CO₂ production over WO₃ and TiO₂ photocatalysts suspended in aqueous acetic acid (AcOH) under both ultraviolet and visible light irradiation (300 < λ < 500 nm).

(Time courses for other samples are shown in Fig. S4.) Under irradiation, both H₂O₂ and CO₂ were simultaneously generated on unmodified and Pt-loaded WO₃ samples, while the rates were much greater with the Pt-loaded samples. Saturation of H₂O₂ on Pt/WO₃ samples was undoubtedly due to the catalytic decomposition of H₂O₂ into H₂O and O₂ on Pt particles, with a possible contribution of photocatalysis by electrons or holes. Assuming that CO₂ generation occurred only by photogenerated holes (CH₃COOH + 2H₂O + 8H⁺ → 2CO₂ + 8H⁺), combining this process with H₂O₂ generation (O₂ + 2H⁺ + 2e⁻ → H₂O₂) should result in generation of H₂O₂ and CO₂ with the ideal stoichiometric ratio of 2:1 (CH₃COOH + 2H₂O + 4O₂ → 4H₂O₂ + 2CO₂). As summarized in Table 2, the ratio of amount of H₂O₂ generated to that of CO₂ was close to the stoichiometric value, both on unmodified and Pt-loaded WO₃-K samples (2.4 and 2.1), indicating that most of the photoexcited electrons on WO₃-K were consumed *via* the two-electron reduction of O₂, producing H₂O₂. Other Pt/WO₃ samples also showed appreciable generation of H₂O₂ with CO₂, while the rates of H₂O₂ production were lower than the stoichiometric value expected from the CO₂ generation. This deviation is likely due to the catalytic and/or photocatalytic decomposition of H₂O₂, and possibly the four-electron reduction of O₂ to H₂O on Pt cocatalyst.

Table 2. Initial production rate of H₂O₂ and CO₂ over WO₃ and TiO₂ photocatalysts suspended in aq. AcOH.^a

| Entry | Photocatalyst | Amount of H ₂ O ₂ production / μmol | Amount of CO ₂ production / μmol | Ratio of amount of H ₂ O ₂ to CO ₂ |
|-----------------|------------------------|---|---|---|
| 1 | Pt/WO ₃ -K | 1.2 | 0.5 | 2.4 |
| 2 | Pt/WO ₃ -Y | 1.1 | 0.7 | 1.4 |
| 3 | Pt/WO ₃ -S | 0.6 | 0.5 | 1.1 |
| 4 | Pt/TiO ₂ -P | 0.2 | 1.8 | 0.1 |
| 5 | Pt/TiO ₂ -A | 1.3 | 1.2 | 1.1 |
| 6 ^b | Pt/TiO ₂ -R | 0.9 | 1.0 | 0.9 |
| 7 ^b | WO ₃ -K | 0.2 | 0.1 | 2.1 |
| 8 | TiO ₂ -P | 0 | 1.2 | 0 |
| 9 | TiO ₂ -A | 0.2 | 0.7 | 0.3 |
| 10 ^b | TiO ₂ -R | 0.1 | 0.1 | 1.2 |

^aInitial amount of AcOH : 300 μmol, amount of solvent (H₂O) : 10 mL light source : 300 W Xe lamp (300 < λ < 500 nm), calculated on the amount of products after 5 min, ^bCalculated on the amount of products after 10 min.

In contrast, the generation of H₂O₂ on TiO₂-P was negligibly low, independent of Pt loading, despite the high rates of CO₂ generation (Fig 2 and Table 2, entries 4, 8). These results indicate that photoexcited electrons on the TiO₂-P photocatalyst were consumed mainly *via* one-electron processes producing radical species (•O₂⁻ or •HO₂), although four-electron reduction of O₂ to form H₂O on the Pt-loaded sample also was possible. On other TiO₂-A and TiO₂-R samples, H₂O₂ generation was appreciable, especially after Pt loading, indicating enhanced two-electron reduction of O₂ on Pt cocatalyst.

Comparison of the results shown in Tables 1 and 2 indicate a connection between selectivity for H₂O₂ generation from aq. AcOH and selectivity for phenol from benzene. The TiO₂ samples with low selectivity for H₂O₂ production (*e.g.*, unmodified TiO₂-P, Pt/TiO₂-P) that indicated high selectivity for oxygen radical species (•O₂⁻ or •HO₂) tended to exhibit low

selectivity for phenol production from benzene. However, samples with high selectivity for H₂O₂ generation (*e.g.*, Pt/TiO₂-A, Pt/TiO₂-R) exhibited appreciably higher selectivity for phenol. These findings suggest that the oxygen radical species (•O₂⁻ or •HO₂) generated on TiO₂ samples contributed to oxidative decomposition of the substrates and consequently lowered selectivity for phenol. Although the contribution of these oxygen radical species toward oxidation of organic compounds is not well understood, the oxidative reactivity of radical species (•O₂⁻ or •HO₂) should be greater than that of non-radical H₂O₂. Some studies have suggested that the •O₂⁻ species generated during photocatalysis on TiO₂ enhanced the cleavage of aromatic rings.³⁰ However, the generation of reactive oxygen radical species is suppressed on the Pt-WO₃ systems by the lower CBM, which forces reduction of O₂ molecules into H₂O₂ or H₂O *via* a multi-electron process.

These results have prompted the hypothesis that the high selectivity for phenol on Pt/WO₃ is due to the absence of reactive oxygen radical species (•O₂⁻ or •HO₂), which enhances oxidative decomposition of the phenol or other intermediates produced. This hypothesis is supported by the results from photocatalytic oxidation and hydroxylation of benzene in the absence of molecular O₂, which are summarized in Table 3. For the Pt/WO₃ system, reactions were conducted in the presence of Ag⁺ as an electron acceptor instead of O₂, because it possess an appropriate potential [+0.799 V vs. SHE] for efficient scavenging of photoexcited electrons generated in WO₃. Since the addition of AgNO₃ (18.8 μmol) makes the aqueous solution acidic (pH ~5), the influence of pH on phenol selectivity needs to be considered. Phenol selectivity of the Pt/WO₃-K samples was reduced by decreasing pH value (Fig. S5). Therefore, results for Pt/WO₃-K samples in the presence of O₂ (*i.e.*, in the absence of Ag⁺) at different pH values are included in Table 3 for comparison.

Table 3. Hydroxylation of benzene over WO₃ photocatalysts in the absence of molecular O₂.^a

| Entry | Reaction conditions | Photocatalyst | Conversion (%) (Irradiation time / h) | Phenol selectivity (%) |
|--------|-----------------------|--------------------------|---------------------------------------|------------------------|
| Ref. 1 | O ₂ , pH=6 | Pt/WO ₃ -K | 22.2 (1) | 79.3 |
| Ref. 2 | O ₂ , pH=5 | Pt/WO ₃ -K | 18.9 (1) | 55.4 |
| 1 | Ag ⁺ , Ar | Pt/WO ₃ -K | 27.5 (1) | 54.0 |
| | | | 53.0 (3) | 51.5 |
| 2 | Ag ⁺ , Ar | Pt/WO ₃ -Y | 40.8 (1) | 50.1 |
| | | | 72.3 (3) | 50.3 |
| 3 | Ag ⁺ , Ar | Pt/WO ₃ -S | 46.9 (1) | 48.2 |
| | | | 71.1 (3) | 51.5 |
| 4 | H ⁺ , Ar | Pt/TiO ₂ -P | 13.3 (1) | 60.8 |
| | | | 33.8 (4) | 34.0 |
| 5 | H ⁺ , Ar | Pt/TiO ₂ -A | 10.8 (0.3) | 51.9 |
| | | | 27.4 (4) | 26.1 |
| 6 | H ⁺ , Ar | Pt/TiO ₂ -R | 11.6 (1) | 41.8 |
| | | | 25.8 (4) | 27.2 |
| 7 | Ag ⁺ , Ar | TiO ₂ -P-bare | 19.8 (0.5) | 50.5 |

^a Initial amount of benzene : 18.8 μmol, initial amount of Ag⁺ ion : 18.8 μmol, amount of solvent (H₂O) : 7.5 mL, light source : 300 W Xe lamp (300 < λ < 500 nm)

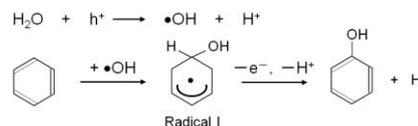
Interestingly, selectivity for phenol by the Pt/WO₃ system was minimally affected by the presence of O₂; similar values for phenol selectivity were obtained with or without O₂, even at different reaction times (*i.e.*, at different levels of benzene conversion). These findings strongly suggest that the H₂O₂

generated by the Pt/WO₃ system *via* reduction of O₂ did not significantly contribute to the undesirable peroxidation of phenol. These results also imply that the existence of O₂ in the reaction media, whether it is reduced or not, has no impact on phenol selectivity. In contrast, the existence of O₂ significantly decreased selectivity of phenol by the Pt/TiO₂ system. For the Pt/TiO₂ system, reactions were initiated in deaerated water containing only benzene, without adding any electron acceptor, because the CBM of TiO₂, especially that of anatase, is sufficient for reduction of water (or H⁺) to H₂ (generation of H₂ was confirmed for all the Pt/TiO₂ samples). As summarized in Table 3, selectivity toward phenol by the Pt/TiO₂ samples was improved significantly by conducting the reactions in the absence of O₂, while the conversions at same reaction time lower compared to those with O₂ (see Table 1) primarily due to the lower reaction rate of photoexcited electron with H⁺ than that with O₂. For example, phenol selectivity on Pt/TiO₂-P was improved significantly from 26 to 61% during the initial period (Table 1, entry 6; Table 3, entry 4). Yoshida *et al.* also demonstrated improved phenol selectivity using Pt/TiO₂ photocatalyst in a deaerated solution of benzene and water (1:1 by vol.).³² The same tendency was observed on unmodified TiO₂-P in the presence of an Ag⁺ electron acceptor (Table 3, entry 7); selectivity for phenol was improved from *ca.* 23% (Table 1, entry 9) to 50% at 30 min of reaction by removing O₂ from solution. These findings strongly support the hypothesis that the oxygen radical species (•O₂⁻ or •HO₂) generated on TiO₂ contributed to oxidative decomposition of the substrate including phenol, consequently lowering selectivity for phenol. However, selectivity for phenol in the Pt/TiO₂ system decreased significantly upon prolonged reaction time, even in the absence of O₂ (Table 3, entries 4-6), in contrast to results for the Pt/WO₃ system. These results suggest that factors other than the reactive oxygen radical species contribute to the difference in reactivity between Pt/WO₃ and Pt/TiO₂ (including unmodified TiO₂) for hydroxylation and oxidation of benzene. The most likely cause is the difference in reactivity of the holes generated in each photocatalyst system. To clarify the reasons for the reactivity differences, specifically the difference in selectivity of holes for phenol production on the WO₃ and TiO₂ systems, the reaction mechanism for each system was investigated in detail using ¹⁸O-labeled O₂ and H₂O.

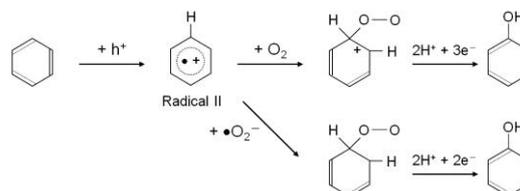
3.3. Determination of oxygen sources for phenol production from benzene on Pt/WO₃ and Pt/TiO₂ systems using ¹⁸O-labeled O₂ and H₂O

In general, photocatalytic hydroxylation of benzene to phenols is considered to proceed through two different routes as illustrated in Schemes 1 and 2.^{2, 40-44} The first route (Scheme 1) is initiated by photocatalytic generation of hydroxyl radicals (•OH) from H₂O molecules and/or surface hydroxyl groups of the semiconductor, which then react with benzene molecules to yield benzene radical species (Radical I). The benzene radical species then reacts with another •OH in solution or a hole on the semiconductor to produce a phenol. If phenol production proceeds through this route, the O atoms originally contained in the H₂O molecules of the solvent must be introduced into the phenol. The route shown in Scheme 2, which has been suggested recently by Matsumura *et al.*,⁴³ is initiated by direct oxidation of

benzene molecules on the semiconductor surface with photo-generated holes, giving cationic radical species of benzene (Radical II). The cationic radical species then are attacked by O₂ or •O₂⁻ molecules to give peroxidized species. The peroxidized species then are transformed into phenol molecules accompanied by proton (H⁺)-coupled reduction with photoexcited electrons (e⁻), as shown in Scheme 2. In this case, the phenol molecules produced must contain O atoms originating from the molecular O₂ dissolved in the solution. To clarify the dominant route operating in phenol production on Pt/WO₃ and Pt/TiO₂ systems, reactions were conducted using a stable oxygen isotope (¹⁸O-enriched water: H₂¹⁸O, or ¹⁸O₂).



Scheme 1. Proposed reaction for phenol production over photocatalysts *via* hydroxyl radical.



Scheme 2. Proposed reaction for phenol production over photocatalysts *via* oxygen molecule and oxygen radical.

Figures 3 and S7 show time courses for production of phenol from benzene by photocatalysis using four Pt/WO₃ and Pt/TiO₂ samples, conducted in ¹⁸O-enriched water (1.0 mL, 98% H₂¹⁸O) containing benzene and molecular O₂ (¹⁶O₂). Total amount of phenol produced and percentage of phenol containing ¹⁸O were plotted against irradiation time. A larger amount of benzene (500 μmol) was added to the water for these reactions compared to that for reactions shown in Fig. 1, to minimize successive peroxidation of phenol. Photoirradiation of Pt/WO₃-K produced phenol at a nearly steady rate; percentage of ¹⁸O-labeled phenol was greater than 90% throughout the reaction, while the percentage decreased slightly from 95% (15 min) to 91% (8 h) during the reaction (Table 4, entry 1). The high percentage of ¹⁸O-labeled phenol throughout the reaction indicated that phenol production on Pt/WO₃-K proceeded primarily *via* a reaction pathway involving hydroxyl radicals (•OH) from H₂¹⁸O molecules, which were the source of ¹⁸O in the phenol produced (Scheme 1). The slight decrease in percentage of ¹⁸O-labeled phenol during the reaction was probably due to the increased amount of H₂¹⁶O molecules, which were generated directly by four-electron reduction of ¹⁶O₂ or indirectly by catalytic decomposition of H₂¹⁶O₂ on Pt; the H₂¹⁶O molecules produced subsequently were used as a source of O atoms for phenol through formation of •OH radicals. As shown in Fig. 4, reaction in unlabeled H₂¹⁶O solvent containing labeled ¹⁸O₂ molecules resulted in preferential production of unlabeled phenol molecules (*ca.* 95% at 15 min and 90% at 8 h). When the reaction was conducted in H₂¹⁶O-H₂¹⁸O (1:1) containing unlabeled ¹⁶O₂, the percentage of ¹⁸O-labeled phenol was slightly less than 50% throughout the reaction (Fig. S6; Table 4, entry 7).

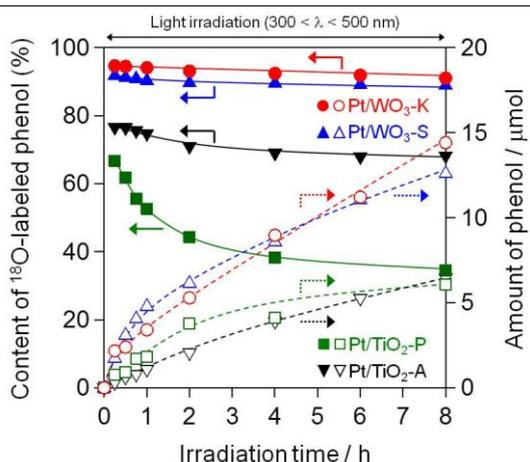


Figure 3. Time course of photocatalyzed production of phenol from benzene on Pt/WO₃ and Pt/TiO₂ samples. Reactions were conducted in ¹⁸O-enriched water (98% H₂¹⁸O) containing benzene and normal molecular ¹⁶O₂.

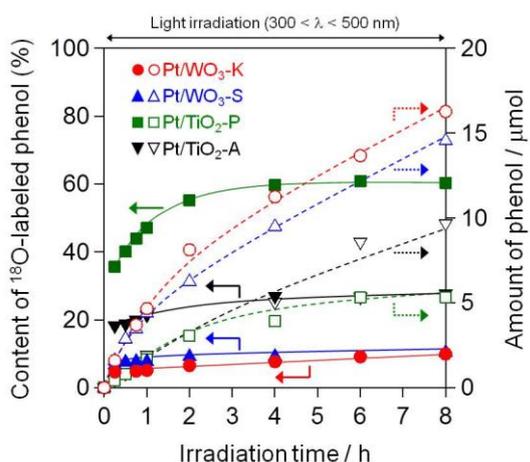


Figure 4. Time course of photocatalyzed production of phenol from benzene on Pt/WO₃ and Pt/TiO₂ samples. Reactions were conducted in normal water (H₂¹⁶O) containing benzene and molecular ¹⁸O₂.

Table 4. Direct hydroxylation of benzene in H₂¹⁸O in the presence of ¹⁶O₂

| Entry | Photocatalyst | Reaction Condition | Content of labeled phenol (%) (Amount of phenol produced / μmol) | |
|-------|------------------------|--|---|-------------|
| | | | 15 min | 8 h |
| 1 | Pt/WO ₃ -K | ¹⁶ O ₂ , H ₂ ¹⁸ O | 94.7 (2.2) | 91.1 (14.4) |
| 2 | Pt/WO ₃ -Y | ¹⁶ O ₂ , H ₂ ¹⁸ O | 92.7 (1.0) | 88.6 (11.9) |
| 3 | Pt/WO ₃ -S | ¹⁶ O ₂ , H ₂ ¹⁸ O | 92.5 (1.7) | 88.9 (12.6) |
| 4 | Pt/TiO ₂ -P | ¹⁶ O ₂ , H ₂ ¹⁸ O | 66.8 (0.8) | 34.5 (6.1) |
| 5 | Pt/TiO ₂ -A | ¹⁶ O ₂ , H ₂ ¹⁸ O | 76.6 (0.3) | 68.2 (6.5) |
| 6 | Pt/TiO ₂ -R | ¹⁶ O ₂ , H ₂ ¹⁸ O | 74.5 (0.1) | 47.3 (1.2) |
| 7 | Pt/WO ₃ -K | ¹⁶ O ₂ , H ₂ ¹⁸ O : H ₂ ¹⁶ O = 1 : 1 | 46.3 (1.2) | 43.9 (14.9) |
| 8 | Pt/TiO ₂ -P | ¹⁶ O ₂ , H ₂ ¹⁸ O : H ₂ ¹⁶ O = 1 : 1 | 31.6 (0.4) | 16.7 (5.9) |
| 9 | Pt/WO ₃ -K | ¹⁸ O ₂ , H ₂ ¹⁶ O | 4.6 (1.6) | 9.9 (16.3) |
| 10 | Pt/WO ₃ -Y | ¹⁸ O ₂ , H ₂ ¹⁶ O | 6.9 (1.4) | 8.6 (13.2) |
| 11 | Pt/WO ₃ -S | ¹⁸ O ₂ , H ₂ ¹⁶ O | 6.7 (1.6) | 10.4 (14.6) |
| 12 | Pt/TiO ₂ -P | ¹⁸ O ₂ , H ₂ ¹⁶ O | 35.7 (0.4) | 60.4 (5.3) |
| 13 | Pt/TiO ₂ -A | ¹⁸ O ₂ , H ₂ ¹⁶ O | 18.2 (0.5) | 27.7 (9.7) |
| 14 | Pt/TiO ₂ -R | ¹⁸ O ₂ , H ₂ ¹⁶ O | 25.8 (0.1) | 53.2 (1.5) |

Initial concentration of benzene : 500 μmol, amount of solvent : 1.0 mL
light source : 300 W Xe lamp (300 < λ < 500 nm)

These findings confirm preferential introduction of O atoms from H₂O on the Pt/WO₃-K photocatalyst. Other Pt/WO₃ photocatalysts also preferentially generated phenol that contained O atoms originating from H₂O molecules (Figs. S7 and S8; Table 4, entries 2, 3, 10, 11), indicating that phenol production on Pt/WO₃ proceeded through •OH generation from H₂O (Scheme 1). As shown in Fig. S9, phenol production on Pt/WO₃-K was drastically suppressed by addition of a small amount of 2-propanol (188 μmol, 10 times greater than benzene), which is an efficient •OH scavenger. This adds additional evidence for the reaction scheme involving •OH radicals.

In contrast, the Pt/TiO₂ system produced appreciable amounts of phenol containing O atoms originating from O₂, along with others derived from H₂O, indicating that phenol production proceeded through a reaction pathway involving O₂ molecules (Scheme 2) in parallel with a pathway involving H₂O (Scheme 1). For example, photoirradiation of Pt/TiO₂-P in H₂¹⁸O with ¹⁶O₂ yielded a significant percentage of unlabeled phenol (ca. 33% at 15 min); the percentage was less than that of labeled phenol (Fig. 3; Table 4, entry 4). Interestingly, the percentage of unlabeled phenol increased with irradiation time (ca. 65% at 8 h), indicating that the contribution of the reaction pathway involving O₂ molecules became more dominant as the reaction progressed. Reaction in H₂¹⁶O with labeled ¹⁸O₂ also yielded a mixture of phenol molecules containing ¹⁶O or ¹⁸O (Fig. 4; Table 4, entry 12), in which the percentage of ¹⁸O-labeled phenol molecules increased from 36 to 60% as the reaction proceeded. Phenol production on Pt/TiO₂-P was suppressed slightly by addition of 2-propanol, an •OH scavenger (Fig. S9). Thus, phenol production on Pt/TiO₂-P proceeded simultaneously via two different pathways (Schemes 1 and 2), while the contribution of the pathway involving O₂ gradually becomes dominant after prolonged irradiation time. Other Pt/TiO₂ photocatalysts, regardless of crystal phase (anatase or rutile), also produced a significant percentage of phenol molecules containing O atoms originating from O₂ (Figs. 3, 4, S6, S7; Table 4, entries 5, 6, 13, 14), while the change in percentage of ¹⁸O-labeled phenol during the reaction differed significantly between Pt/TiO₂-A and Pt/TiO₂-R.

These results revealed that the Pt/WO₃ and Pt/TiO₂ systems possessed different reactivity toward oxidations as well as toward reductions. The holes generated on Pt/WO₃ photocatalysts reacted primarily with H₂O molecules, even in the presence of benzene in the aqueous solution, selectively generating •OH radicals that subsequently reacted with benzene to produce phenol. However, a portion of the holes generated on Pt/TiO₂ photocatalysts reacted directly with benzene molecules adsorbed on the TiO₂ surfaces, not only with H₂O, to generate cationic radical benzene species, which subsequently reacted with O₂ (or •O₂⁻) and protons to produce phenol.

3.4. Reaction mechanisms for phenol production on Pt/WO₃ and Pt/TiO₂

The holes generated in WO₃ and TiO₂ demonstrate distinctly different reactivity toward hydroxylation and oxidation of benzene in water. Since the oxidative potential of the holes generated in WO₃ and TiO₂ are essentially the same due to similarities in their valence band maximums,^{45, 46} the different

levels of reactivity for oxidation was likely due to the different adsorption states of benzene molecules on the surface of the photocatalyst in water. The adsorption state of benzene molecules from the gas phase onto the surface of the photocatalyst was investigated using FT-IR, while it is an indirect method for investigating the adsorbed states of benzene in aqueous solutions. The spectra before adsorption of benzene on $\text{WO}_3\text{-K}$ ($10\text{ m}^2\text{ g}^{-1}$) and $\text{TiO}_2\text{-A}$ ($10\text{ m}^2\text{ g}^{-1}$) was subtracted from the corresponding spectra after adsorption. The spectrum of benzene in the gas phase also is shown for comparison. As shown in Fig. S10, only weak peaks corresponding to adsorbed benzene molecules were observed on $\text{WO}_3\text{-K}$ sample at wavenumbers similar to those of benzene molecules in the gas phase, indicating that only a small number of benzene molecules adsorbed physically on the surface of $\text{WO}_3\text{-K}$ particles. In contrast, intense IR band corresponding to benzene molecules adsorbed on $\text{TiO}_2\text{-A}$ were observed at wavenumbers ($1440\text{--}1540\text{ cm}^{-1}$) slightly lower than those of benzene molecules in the gas phase. In addition, the IR band derived from surface hydroxyl groups of $\text{TiO}_2\text{-A}$, originally observed at approximately $3500\text{--}3800\text{ cm}^{-1}$, decreased after benzene adsorption. This result indicated that the benzene molecules were strongly adsorbed to the $\text{TiO}_2\text{-A}$ surface through interactions with surface hydroxyl groups, whereas benzene molecules were only physically adsorbed onto the WO_3 surface through weak interactions.

These results shown above led to the proposed reaction mechanism for direct hydroxylation of benzene to phenol in the Pt/WO_3 and Pt/TiO_2 systems as illustrated in Fig. 5. Since only small amount of benzene molecules were physically adsorbed on the WO_3 surface, the photo-generated holes in the WO_3 photocatalyst react primarily with H_2O molecules, even in the presence of benzene molecules in the aqueous solution, yielding $\bullet\text{OH}$ radicals that subsequently react with benzene to produce phenol with high selectivity. At the same time, the photoexcited electrons on Pt/WO_3 photocatalysts react with molecular O_2 to generate mainly H_2O_2 on the Pt cocatalyst. The H_2O_2 generated is readily decomposed into H_2O and O_2 on the Pt cocatalyst and therefore has little impact on the hydroxylation and oxidation of benzene. In contrast, a considerable number of holes generated on Pt/TiO_2 photocatalysts react directly with benzene molecules that are strongly adsorbed on the surface *via* interactions with surface hydroxyl groups, generating cationic radical benzene species. These radicals subsequently react with O_2 (or $\bullet\text{O}_2^-$) to give peroxy radicals that then reductively react with photoexcited electrons and protons to produce phenol. Since these peroxy radicals are generally unstable and spontaneously decompose, the formation of peroxy radicals might be a reason for the low selectivity of TiO_2 for phenol. The adsorption of benzene molecules on the surface of TiO_2 undoubtedly increases the possibility of direct oxidation of benzene into cleaved intermediates leading to CO_2 as the final product due to the holes. This direct decomposition pathway is supported by the noticeable production of CO_2 in the initial period of photoirradiation on $\text{Pt}/\text{TiO}_2\text{-P}$ as seen in Fig. 1. Additionally, the photoexcited electrons on TiO_2 reduce O_2 into radical species such as $\bullet\text{O}_2^-$ or $\bullet\text{HO}_2$, which subsequently contribute to the oxidative decomposition of benzene and its intermediates. Both the direct oxidation of substrates (*e.g.*, phenol) on the TiO_2 surface and

oxidation by oxygen radical species are the main reasons for reduced phenol selectivity on TiO_2 . In contrast, these two oxidation pathways are inhibited by WO_3 system, enabling the Pt/WO_3 photocatalysts to produce phenol with high selectivity in the presence of H_2O and O_2 .

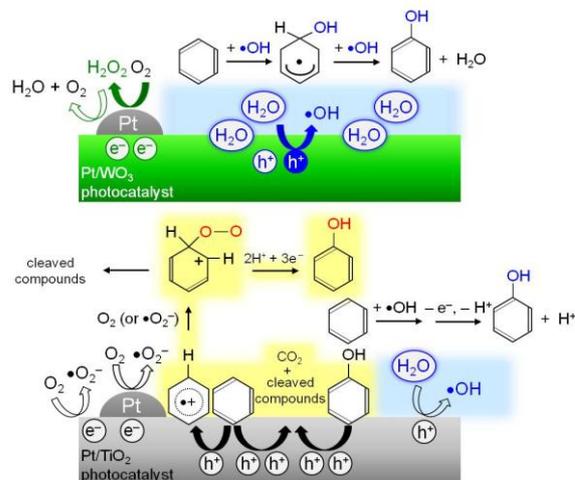


Figure 5. Proposed reaction mechanisms for phenol production over Pt/WO_3 and Pt/TiO_2 photocatalysts.

The main property of Pt/WO_3 photocatalysts that enables highly selective phenol production is the selective generation of $\bullet\text{OH}$ radicals, even in the presence of organic substances such as benzene in water. When reaction on Pt/WO_3 was initiated with 10-fold greater concentration of benzene (25 mmol L^{-1}), the amount of phenol produced only increased by *ca.* 16% (see Fig. S11). Note that the results of ^{18}O -labeled reactions with a much higher concentration of benzene (500 mmol L^{-1}) indicated the preferential oxidation of water molecules on Pt/WO_3 photocatalysts. These results confirmed that the surface of WO_3 has properties that promote preferential oxidation of water molecules, even in the presence of significantly high concentration of benzene molecules, generating $\bullet\text{OH}$ radicals that are effective for selective phenol synthesis.

The specific surface area and the difference in the density of hydroxyl groups on the sample surface were considered as reasons for the differences in properties between WO_3 and TiO_2 for adsorption of benzene and its intermediates. However, the $\text{Pt}/\text{WO}_3\text{-K}$ and the $\text{Pt}/\text{TiO}_2\text{-A}$ samples, which have similar surface areas (*ca.* $10\text{ m}^2\text{ g}^{-1}$), had different reactivities. A series of WO_3 samples with different densities of hydroxyl groups as well as the surface areas, was prepared by calcination of tungstic acid at various temperatures (XRD patterns: Fig. S12; IR spectra: Fig. S13), and employed as photocatalysts in the reactions with isotopically labeled $^{18}\text{O}_2$. As shown in Table S1, the percentage of labeled phenol produced for each sample was similar, indicating that the density of surface hydroxyl groups was not the main cause of reactivity differences between WO_3 and TiO_2 systems for the oxidative process. Although the dominant property enabling the WO_3 system to produce phenol with high selectivity remains unclear and needs clarification, the unique properties of WO_3 photocatalysts for achieving highly selective phenol production in the presence of molecular O_2 probably promote practically useful organic syntheses using photocatalysis.

4. Conclusions

Highly selective phenol synthesis directly from benzene was demonstrated using Pt-loaded WO₃ photocatalysts in water containing molecular oxygen. Results revealed that the surface of WO₃, which is different from that of conventional TiO₂, enables preferential oxidation of water molecules even in the presence of considerably high concentration of benzene molecules in water, to selectively generate •OH radicals that promote selective phenol production. This finding indicates that the •OH radicals can be continuously generated by simple photoirradiation (utilizing visible light) of Pt/WO₃ photocatalysts in water in the presence of O₂; the •OH radicals generated can then be used for organic synthetic reactions in water if the reactant possesses low affinity toward the surface of WO₃. Both the efficiency and selectivity in the present system will be improved when the nature and the reaction mechanism on WO₃ photocatalyst is better understood. The present study demonstrates the possibility of environmentally benign photocatalytic processes with potential for reducing energy consumption of fine chemical production by harnessing the energy of artificial or natural sunlight.

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† Electronic Supplementary Information (ESI) available: Results on hydroxylation and oxidation of benzene on various photocatalyst under different conditions such as, photocatalysts loaded with different amount of Pt cocatalyst, irradiated in the aqueous solution with different pH values or different benzene concentrations, irradiated in the copresence of benzene and 2-propanol, are shown. IR spectra of photocatalyst samples after benzene adsorption, XRD pattern and raw IR spectra of WO₃ samples prepared from tungstic acid (WO₃-TA), and the results on the hydroxylation of benzene using oxygen stable isotope on WO₃-TA are also shown. See DOI: 10.1039/b0000000x/

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