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# 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

Osamu Tomita,<sup>a,b</sup> Bunsho Ohtani<sup>b</sup> and Ryu Abe<sup>\*a,c</sup>

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Particles of tungsten oxide loaded with nanoparticulate platinum (Pt/WO<sub>3</sub>) photocatalytically produced phenol from benzene with high selectivity (e.g., 74% at 69% of benzene conversion) in water containing molecular O<sub>2</sub>; the selectivity for phenol were much higher than those on conventional titanium oxide (TiO<sub>2</sub>) photocatalysts (both the unmodified and Pt-loaded) that generated CO<sub>2</sub> as a main product. Results confirmed that photoexcited electrons in the Pt/WO<sub>3</sub> photocatalysts mainly generated H<sub>2</sub>O<sub>2</sub> from molecular O<sub>2</sub> through a two-electron reduction; the H<sub>2</sub>O<sub>2</sub> generated did not significantly contribute to the undesirable peroxidation of phenol produced. In contrast, the oxygen radical species, such as •O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>, generated on TiO<sub>2</sub> photocatalysts partially contributed to the successive oxidation of phenol and other intermediates to reduce the selectivity toward phenol. More importantly, the reactions using <sup>18</sup>O-labeled O<sub>2</sub> and H<sub>2</sub>O clearly revealed that the holes generated on Pt/WO<sub>3</sub> react primarily with H<sub>2</sub>O 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 TiO<sub>2</sub> photocatalysts reacts directly with benzene molecules, which are adsorbed on the surface of TiO<sub>2</sub> 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 TiO<sub>2</sub>. The two unique features of Pt/WO<sub>3</sub>, the absence of reactive oxygen radical species from O<sub>2</sub> 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.<sup>1-3</sup> The high reduction and oxidation potentials of photoexcited electrons and holes, respectively, generated on semiconductor particles such as TiO<sub>2</sub> can promote various chemical reactions, even endothermic reactions. Another advantage of photocatalytic organic syntheses is the availability of molecular oxygen (O<sub>2</sub>) or water (H<sub>2</sub>O) 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 O<sub>2</sub> is an efficient electron acceptor (*i.e.*, oxidant) for the photoexcited electron generated on TiO<sub>2</sub> photocatalysts, where the holes generated can directly oxidize the organic substances adsorbed, and can indirectly oxidize through formation of •OH radicals from H<sub>2</sub>O molecules adsorbed on the surface; the •OH radicals generated subsequently oxidize the organic substances to produce desired products.<sup>2, 4-11</sup> However, TiO<sub>2</sub> photocatalysts generally exhibit high activity for non-

selective and complete oxidation of organic compounds in the presence of ambient O<sub>2</sub>, yielding CO<sub>2</sub> and highly oxidized products.<sup>2, 12-18</sup> 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 TiO<sub>2</sub> photocatalysts in the presence of molecular O<sub>2</sub> has been reported.<sup>19, 20</sup> 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.<sup>21, 22</sup> Some oxygen radical species, such as •O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub> generated from O<sub>2</sub> molecules *via* reaction with photoexcited electrons, are thought to contribute to the oxidation of organic substances to some extent.<sup>23-30</sup> Some research groups have reported highly selective organic synthesis using TiO<sub>2</sub>-related photocatalysts in the absence of molecular O<sub>2</sub>.<sup>31-34</sup> For example, Shiraishi *et al.* demonstrated highly selective synthesis of benzimidazoles from *ortho*-phenylenediamine and ethanol using Pt-loaded TiO<sub>2</sub> photocatalyst (Pt/TiO<sub>2</sub>) under UV light irradiation.<sup>31</sup> Yoshida *et al.* reported direct hydroxylation of benzene to phenols using Pt/TiO<sub>2</sub> 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 O<sub>2</sub>.<sup>32</sup> In these reactions on Pt/TiO<sub>2</sub> photocatalysts, protons (H<sup>+</sup>) were used as an electron acceptor instead of molecular O<sub>2</sub>, accompanied by production of H<sub>2</sub> 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<sup>+</sup> as an electron acceptor compared to O<sub>2</sub>. Furthermore, the potential of H<sup>+</sup> reduction requires a highly negative conduction band minimum (CBM) of the semiconductor, and therefore limits the applicable semiconductor materials to TiO<sub>2</sub>. The use of TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 (WO<sub>3</sub>) 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 TiO<sub>2</sub> under UV light.<sup>35</sup> Although WO<sub>3</sub> generally has been regarded as a photocatalyst inactive for oxidation of organic compounds with molecular O<sub>2</sub> due to insufficient CBM for reduction of O<sub>2</sub>, the loading of nanoparticulate Pt cocatalyst significantly increases the probability of multi-electron reduction of O<sub>2</sub> by photoexcited electrons, enhancing the oxidation of organic substances by the holes remaining in the valence band. The photoexcited electrons in Pt-loaded WO<sub>3</sub> (Pt/WO<sub>3</sub>) were suggested to produce mainly H<sub>2</sub>O<sub>2</sub> *via* two-electron reduction. These findings led to the application of the Pt/WO<sub>3</sub> photocatalyst to organic synthesis reactions because it is activated under visible light but does not generate oxygen radicals such as •O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>, 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/WO<sub>3</sub> photocatalysts recently have been shown to possess activity for direct production of phenol from benzene using O<sub>2</sub> and water as reactants under UV or visible light.<sup>36</sup> Selectivity toward phenol on Pt/WO<sub>3</sub> photocatalysts was much greater than that on Pt/TiO<sub>2</sub> (or unmodified TiO<sub>2</sub>) 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/WO<sub>3</sub> photocatalysts in detail compared to that on TiO<sub>2</sub> (including Pt-loaded TiO<sub>2</sub>) to find the contributing factors. Results revealed that the holes generated in the WO<sub>3</sub> photocatalysts possess distinctly different reactivity from those in TiO<sub>2</sub> 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 WO<sub>3</sub> powders, such as WO<sub>3</sub>-K (triclinic and monoclinic, 4.8 m<sup>2</sup> g<sup>-1</sup>, Kojundo Chemical Laboratory), WO<sub>3</sub>-Y (monoclinic, 2.2 m<sup>2</sup> g<sup>-1</sup>, Yamanaka Chemical Industries), and WO<sub>3</sub>-S (monoclinic, 1.6 m<sup>2</sup> g<sup>-1</sup>, Soekawa Chemicals), were used. The fine particulate WO<sub>3</sub> sample, referred to as WO<sub>3</sub>-K (triclinic, 10 m<sup>2</sup> g<sup>-1</sup>), was obtained by separation from large aggregates by mean of centrifugation of the purchased WO<sub>3</sub>-K samples as previously reported.<sup>35</sup> The TiO<sub>2</sub> powders, such as TiO<sub>2</sub>-P [anatase and rutile, P 25, 55 m<sup>2</sup> g<sup>-1</sup>, Degussa (Evonik)], TiO<sub>2</sub>-A (anatase, 10 m<sup>2</sup> g<sup>-1</sup>, Merck), and TiO<sub>2</sub>-R (rutile, 4.0 m<sup>2</sup> g<sup>-1</sup>, 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 H<sub>2</sub>PtCl<sub>6</sub> as a Pt precursor. The WO<sub>3</sub> samples were irradiated with visible light; the TiO<sub>2</sub> 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.<sup>35</sup>

### 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 TiO<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> produced during photocatalytic oxidation of an organic substrate was analyzed by iodometry.<sup>37</sup> 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<sup>-1</sup> aq. potassium hydrogen phthalate (C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>) and 1 mL of 400 mmol L<sup>-1</sup> aq. potassium iodide (KI) were added. The H<sub>2</sub>O<sub>2</sub> was allowed to react with I<sup>-</sup> under acidic conditions (H<sub>2</sub>O<sub>2</sub> + 3I<sup>-</sup> + 2H<sup>+</sup> → I<sub>3</sub><sup>-</sup> + 2H<sub>2</sub>O). The amount of H<sub>2</sub>O<sub>2</sub> was determined by the maximum intensity of absorption attributed to I<sub>3</sub><sup>-</sup> at approximately 350 nm, measured using a UV-Vis spectrophotometer (Shimadzu UV-1800).

For tracer studies, either H<sub>2</sub><sup>18</sup>O (98 atom%, Taiyo Nippon Sanso Corp.) or <sup>18</sup>O<sub>2</sub> (98 atom%, Taiyo Nippon Sanso Corp.) gas was used as the oxygen isotope source. Then, 50 mg of photocatalyst suspended in 1 mL H<sub>2</sub><sup>18</sup>O (in air) or H<sub>2</sub><sup>16</sup>O (in <sup>18</sup>O<sub>2</sub>) was used. In the case of reactions in H<sub>2</sub><sup>18</sup>O solvent with <sup>18</sup>O<sub>2</sub> gas, the solution was purged with Ar gas and subsequently with <sup>18</sup>O<sub>2</sub> gas to make the partial pressure of O<sub>2</sub> in the reaction system similar to that in air; the amount of N<sub>2</sub> 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<sup>-1</sup>). 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 <sup>18</sup>O-labeled phenol was determined using GC-MS (Shimadzu, GCMS-2010/PARVUM2).

#### 2.4. IR measurements

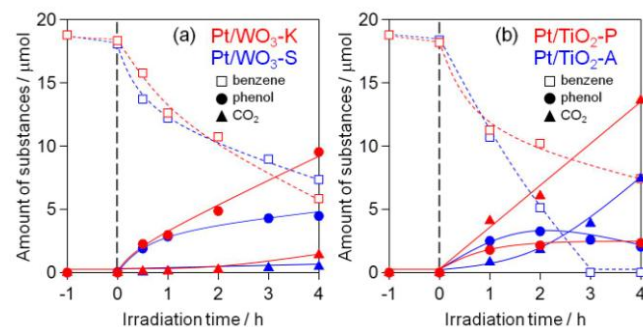
FT-IR spectra of the adsorbed benzene on each sample were recorded with a Fourier-transform infrared spectrometer (Jasco FT-4200). The sample pellet was introduced into an IR cell equipped with CaF<sub>2</sub> windows. Prior to the measurements, the sample was heated in vacuum. After cooling, benzene 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/WO<sub>3</sub> and Pt/TiO<sub>2</sub> photocatalysts

Figure 1 shows the time course of photocatalytic hydroxylation and oxidation of benzene on Pt-loaded WO<sub>3</sub> and Pt-loaded TiO<sub>2</sub> 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<sup>-1</sup>) sufficiently lower than the maximum soluble value of benzene in water (22.3 mmol L<sup>-1</sup>), in order to accurately quantify the reduced amount of benzene during each reaction.<sup>38</sup> 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/WO<sub>3</sub> and Pt/TiO<sub>2</sub> systems.

Phenol and CO<sub>2</sub> were the predominant products in the Pt/WO<sub>3</sub>



**Figure 1.** Time course of photocatalytic oxidation of benzene over (a) Pt/WO<sub>3</sub> and (b) Pt/TiO<sub>2</sub> photocatalysts in aerated aqueous solutions of benzene (18.8 μmol) under ultraviolet and visible light irradiation (300 < λ < 500 nm).

and Pt/TiO<sub>2</sub> systems, respectively. For Pt/WO<sub>3</sub>-K (Fig. 1a), phenol was produced at an almost steady rate under irradiation along with small amounts of di-hydroxylated benzenes (not plotted) and CO<sub>2</sub>.

**Table 1.** Conversion and phenol selectivity for hydroxylation of benzene<sup>a</sup>

Entry	Photocatalyst	Conversion (%) <sup>b</sup> (Irradiation time / h)	Selectivity (%) <sup>c</sup>					Amount of CO <sub>2</sub> / μmol
			Phenol	Catechol	Resorcinol	Hydroquinone	Benzoquinone	
1	Pt/WO <sub>3</sub> -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 <sub>3</sub> -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 <sub>3</sub> -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 <sub>3</sub> -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 <sup>d</sup>	Pt/WO <sub>3</sub> -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 <sub>2</sub> -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 <sub>2</sub> -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 <sub>2</sub> -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 <sub>2</sub> -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 <sub>2</sub> -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 <sub>2</sub> -R	68.3 (4)	16.1	1.6	0	6.7	0	12.5

<sup>a</sup>Initial amount of benzene : 18.8 μmol, solvent : H<sub>2</sub>O 7.5 mL, light source : 300 W Xe lamp, <sup>b</sup>Conversion : (C<sub>benzene,0</sub> - C<sub>benzene,t</sub>) / C<sub>benzene,0</sub> × 10<sup>2</sup>, <sup>c</sup>Selectivity : C<sub>products,t</sub> / (C<sub>benzene,0</sub> - C<sub>benzene,t</sub>) × 10<sup>2</sup>, <sup>d</sup>Under 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 CO<sub>2</sub> is difficult to determine due to uncertainty in the stoichiometry between the decrease in benzene and generation of CO<sub>2</sub>, the amount of CO<sub>2</sub> generated is listed in Table 1. Selectivity for phenol by the Pt/WO<sub>3</sub>-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 CO<sub>2</sub> 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 CO<sub>2</sub> became detectable (*ca.* 1.4 μmol). The Pt/WO<sub>3</sub>-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 CO<sub>2</sub>. Other Pt/WO<sub>3</sub> samples also generated phenol as the main product with relatively high selectivity and a negligibly small amount of CO<sub>2</sub> (Figs. 1a and S1a, and Table 1) in the initial period (1 h), while the Pt/WO<sub>3</sub>-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/WO<sub>3</sub> photocatalysts, specifically on Pt/WO<sub>3</sub>-K sample, is lower than that of hydroxylation of benzene, affording high selectivity for phenol.

In contrast, CO<sub>2</sub> was predominantly generated on Pt/TiO<sub>2</sub>-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 CO<sub>2</sub>. The production of CO<sub>2</sub> 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/TiO<sub>2</sub>-P, even at short irradiation times (1 h) with relatively low conversion of benzene (Table 1, entry 6). The use of other Pt/TiO<sub>2</sub> samples also resulted in predominant production of CO<sub>2</sub>, along with much lower selectivity for phenol (Figs. 1b and S1, Table 1) than that of Pt/WO<sub>3</sub>. However, the time courses for CO<sub>2</sub> and phenol production were different from that using Pt/TiO<sub>2</sub>-P. For example, use of Pt/TiO<sub>2</sub>-A (Fig. 1b) generated predominantly phenol during the initial period, followed by generation of CO<sub>2</sub> along with a gradual decrease in phenol amount, indicating successive oxidation of the phenol produced. Similar reactivity was observed for the Pt/TiO<sub>2</sub>-R sample with the pure rutile phase (Fig. S1). Selectivity for phenol on these Pt/TiO<sub>2</sub> photocatalysts (Table 1, entries 6-8) was much lower than that on Pt/WO<sub>3</sub> photocatalysts. Note that the Pt/WO<sub>3</sub>-K and the Pt/TiO<sub>2</sub>-A samples, which have similar surface areas (*ca.* 10 m<sup>2</sup> g<sup>-1</sup>), possessed different reactivities. Thus, the factor dominating reactivity is related to the difference in the composition (WO<sub>3</sub> or TiO<sub>2</sub>), not on the surface area.

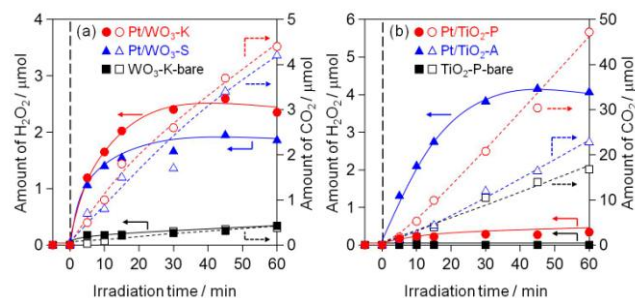
These results indicate that the rates of successive oxidation of phenol on Pt/WO<sub>3</sub> photocatalysts are much lower than those on Pt/TiO<sub>2</sub> photocatalysts, enabling Pt/WO<sub>3</sub> to produce phenol with high selectivity. Another advantage of the Pt/WO<sub>3</sub> photocatalysts is 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/WO<sub>3</sub>-K photocatalyst, with a comparable reaction rate. For Pt/TiO<sub>2</sub>-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 TiO<sub>2</sub> anatase, visible light irradiation of Pt/TiO<sub>2</sub>-A did not yield any appreciable products (Fig. S2).

### 3.2. Influence of oxygen-reduced species on phenol selectivity by Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> photocatalysts

The Pt/WO<sub>3</sub> photocatalysts exhibited significantly greater selectivity for phenol production than did the Pt/TiO<sub>2</sub> 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 O<sub>2</sub> reduced species (H<sub>2</sub>O<sub>2</sub>, •O<sub>2</sub><sup>-</sup>, or •HO<sub>2</sub>), generated during the reductive process by photoexcited electrons, in the oxidation of benzene or intermediates. The conduction band minimum (CBM) of WO<sub>3</sub> semiconductor (*ca.* +0.5V vs. SHE) was much lower than the potentials of O<sub>2</sub> reduction *via* the one-electron process [O<sub>2</sub> + e<sup>-</sup> → •O<sub>2</sub><sup>-</sup>, E<sup>0</sup>(O<sub>2</sub>/•O<sub>2</sub><sup>-</sup>) = -0.28 V; or O<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → •HO<sub>2</sub>, E<sup>0</sup>(O<sub>2</sub>/•HO<sub>2</sub>) = -0.05 V vs. SHE], resulting in rapid recombination between photoexcited electrons and holes in WO<sub>3</sub> photocatalysts even in the presence of a sufficient amount of O<sub>2</sub>. Unmodified WO<sub>3</sub> 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 WO<sub>3</sub> 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 O<sub>2</sub> [O<sub>2</sub> + 2e<sup>-</sup> + 2H<sup>+</sup> → H<sub>2</sub>O<sub>2</sub>, E<sup>0</sup>(O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>) = +0.68 V; or O<sub>2</sub> + 4e<sup>-</sup> + 4H<sup>+</sup> → 2H<sub>2</sub>O, E<sup>0</sup>(O<sub>2</sub>/H<sub>2</sub>O) = +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 WO<sub>3</sub>. The small amount of Pt loading (0.1 wt.%) also was effective for enhancing the rate of hydroxylation and oxidation of benzene on Pt/WO<sub>3</sub>-K photocatalysts, strongly suggesting the occurrence of multi-electron reduction of O<sub>2</sub> 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 CO<sub>2</sub>, while the reaction rate was increased.

In contrast, TiO<sub>2</sub> semiconductors possess much more negative CBM (anatase: *ca.* -0.2 V, rutile: *ca.* +0.05 V vs. SHE) than that of WO<sub>3</sub>. These values, especially that of anatase, are considered sufficient for progress of O<sub>2</sub> reduction *via* a single-electron process by assuming a shift in the CBM potentials of TiO<sub>2</sub> under near neutral pH conditions.<sup>39</sup> Most TiO<sub>2</sub> 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 TiO<sub>2</sub>-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 TiO<sub>2</sub> surface, even with Pt loading, *via* single-electron processes producing radical species of O<sub>2</sub> (*e.g.*, •O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>). As shown in Fig. S3, selectivity for phenol on TiO<sub>2</sub> photocatalysts was minimally affected by Pt loading amount, while the conversion of benzene on Pt/TiO<sub>2</sub>-A increased significantly with Pt loading amount. Thus, an amount of 0.1 wt.% Pt loading in the TiO<sub>2</sub> system was a reasonable value for comparison with the Pt/WO<sub>3</sub> system.



**Figure 2.** Time course curves of H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> generation over (a) WO<sub>3</sub> and (b) TiO<sub>2</sub> photocatalysts suspended in AcOH solution under ultraviolet and visible light irradiation (300 <  $\lambda$  < 500 nm).

Products generated from molecular O<sub>2</sub> during the reduction on WO<sub>3</sub> and TiO<sub>2</sub> were evaluated using the photocatalytic oxidation of acetic acid in aqueous solution containing O<sub>2</sub>. Figure 2 shows time courses for H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> production over WO<sub>3</sub> and TiO<sub>2</sub> photocatalysts suspended in aqueous acetic acid (AcOH) under both ultraviolet and visible light irradiation (300 <  $\lambda$  < 500 nm).

(Time courses for other samples are shown in Fig. S4.) Under irradiation, both H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> were simultaneously generated on unmodified and Pt-loaded WO<sub>3</sub> samples, while the rates were much greater with the Pt-loaded samples. Saturation of H<sub>2</sub>O<sub>2</sub> on Pt/WO<sub>3</sub> samples was undoubtedly due to the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> into H<sub>2</sub>O and O<sub>2</sub> on Pt particles, with a possible contribution of photocatalysis by electrons or holes. Assuming that CO<sub>2</sub> generation occurred only by photogenerated holes (CH<sub>3</sub>COOH + 2H<sub>2</sub>O + 8H<sup>+</sup> → 2CO<sub>2</sub> + 8H<sup>+</sup>), combining this process with H<sub>2</sub>O<sub>2</sub> generation (O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>) should result in generation of H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> with the ideal stoichiometric ratio of 2:1 (CH<sub>3</sub>COOH + 2H<sub>2</sub>O + 4O<sub>2</sub> → 4H<sub>2</sub>O<sub>2</sub> + 2CO<sub>2</sub>). As summarized in Table 2, the ratio of amount of H<sub>2</sub>O<sub>2</sub> generated to that of CO<sub>2</sub> was close to the stoichiometric value, both on unmodified and Pt-loaded WO<sub>3</sub>-K samples (2.4 and 2.1), indicating that most of the photoexcited electrons on WO<sub>3</sub>-K were consumed *via* the two-electron reduction of O<sub>2</sub>, producing H<sub>2</sub>O<sub>2</sub>. Other Pt/WO<sub>3</sub> samples also showed appreciable generation of H<sub>2</sub>O<sub>2</sub> with CO<sub>2</sub>, while the rates of H<sub>2</sub>O<sub>2</sub> production were lower than the stoichiometric value expected from the CO<sub>2</sub> generation. This deviation is likely due to the catalytic and/or photocatalytic decomposition of H<sub>2</sub>O<sub>2</sub>, and possibly the four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O on Pt cocatalyst.

**Table 2.** Initial production rate of H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> over WO<sub>3</sub> and TiO<sub>2</sub> photocatalysts suspended in aq. AcOH.<sup>a</sup>

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

<sup>a</sup>Initial amount of AcOH : 300 μmol, amount of solvent (H<sub>2</sub>O) : 10 mL light source : 300 W Xe lamp (300 < λ < 500 nm), calculated on the amount of products after 5 min, <sup>b</sup>Calculated on the amount of products after 10 min.

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

Comparison of the results shown in Tables 1 and 2 indicate a connection between selectivity for H<sub>2</sub>O<sub>2</sub> generation from aq. AcOH and selectivity for phenol from benzene. The TiO<sub>2</sub> samples with low selectivity for H<sub>2</sub>O<sub>2</sub> production (*e.g.*, unmodified TiO<sub>2</sub>-P, Pt/TiO<sub>2</sub>-P) that indicated high selectivity for oxygen radical species (•O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>) tended to exhibit low

selectivity for phenol production from benzene. However, samples with high selectivity for H<sub>2</sub>O<sub>2</sub> generation (*e.g.*, Pt/TiO<sub>2</sub>-A, Pt/TiO<sub>2</sub>-R) exhibited appreciably higher selectivity for phenol. These findings suggest that the oxygen radical species (•O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>) generated on TiO<sub>2</sub> 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 (•O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>) should be greater than that of non-radical H<sub>2</sub>O<sub>2</sub>. Some studies have suggested that the •O<sub>2</sub><sup>-</sup> species generated during photocatalysis on TiO<sub>2</sub> enhanced the cleavage of aromatic rings.<sup>30</sup> However, the generation of reactive oxygen radical species is suppressed on the Pt-WO<sub>3</sub> systems by the lower CBM, which forces reduction of O<sub>2</sub> molecules into H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O *via* a multi-electron process.

These results have prompted the hypothesis that the high selectivity for phenol on Pt/WO<sub>3</sub> is due to the absence of reactive oxygen radical species (•O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>), 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 O<sub>2</sub>, which are summarized in Table 3. For the Pt/WO<sub>3</sub> system, reactions were conducted in the presence of Ag<sup>+</sup> as an electron acceptor instead of O<sub>2</sub>, because it possesses an appropriate potential [+0.799 V vs. SHE] for efficient scavenging of photoexcited electrons generated in WO<sub>3</sub>. Since the addition of AgNO<sub>3</sub> (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/WO<sub>3</sub>-K samples was reduced by decreasing pH value (Fig. S5). Therefore, results for Pt/WO<sub>3</sub>-K samples in the presence of O<sub>2</sub> (*i.e.*, in the absence of Ag<sup>+</sup>) at different pH values are included in Table 3 for comparison.

**Table 3.** Hydroxylation of benzene over WO<sub>3</sub> photocatalysts in the absence of molecular O<sub>2</sub>.<sup>a</sup>

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

<sup>a</sup> Initial amount of benzene : 18.8 μmol, initial amount of Ag<sup>+</sup> ion : 18.8 μmol, amount of solvent (H<sub>2</sub>O) : 7.5 mL, light source : 300 W Xe lamp (300 < λ < 500 nm)

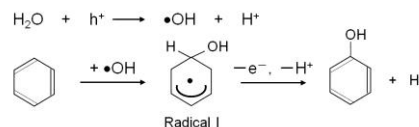
Interestingly, selectivity for phenol by the Pt/WO<sub>3</sub> system was minimally affected by the presence of O<sub>2</sub>; similar values for phenol selectivity were obtained with or without O<sub>2</sub>, even at different reaction times (*i.e.*, at different levels of benzene conversion). These findings strongly suggest that the H<sub>2</sub>O<sub>2</sub>

generated by the Pt/WO<sub>3</sub> system *via* reduction of O<sub>2</sub> did not significantly contribute to the undesirable peroxidation of phenol. These results also imply that the existence of O<sub>2</sub> in the reaction media, whether it is reduced or not, has no impact on phenol selectivity. In contrast, the existence of O<sub>2</sub> significantly decreased selectivity of phenol by the Pt/TiO<sub>2</sub> system. For the Pt/TiO<sub>2</sub> system, reactions were initiated in deaerated water containing only benzene, without adding any electron acceptor, because the CBM of TiO<sub>2</sub>, especially that of anatase, is sufficient for reduction of water (or H<sup>+</sup>) to H<sub>2</sub> (generation of H<sub>2</sub> was confirmed for all the Pt/TiO<sub>2</sub> samples). As summarized in Table 3, selectivity toward phenol by the Pt/TiO<sub>2</sub> samples was improved significantly by conducting the reactions in the absence of O<sub>2</sub>, while the conversions at same reaction time lower compared to those with O<sub>2</sub> (see Table 1) primarily due to the lower reaction rate of photoexcited electron with H<sup>+</sup> than that with O<sub>2</sub>. For example, phenol selectivity on Pt/TiO<sub>2</sub>-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/TiO<sub>2</sub> photocatalyst in a deaerated solution of benzene and water (1:1 by vol.).<sup>32</sup> The same tendency was observed on unmodified TiO<sub>2</sub>-P in the presence of an Ag<sup>+</sup> 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 O<sub>2</sub> from solution. These findings strongly support the hypothesis that the oxygen radical species (•O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>) generated on TiO<sub>2</sub> contributed to oxidative decomposition of the substrate including phenol, consequently lowering selectivity for phenol. However, selectivity for phenol in the Pt/TiO<sub>2</sub> system decreased significantly upon prolonged reaction time, even in the absence of O<sub>2</sub> (Table 3, entries 4-6), in contrast to results for the Pt/WO<sub>3</sub> system. These results suggest that factors other than the reactive oxygen radical species contribute to the difference in reactivity between Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> (including unmodified TiO<sub>2</sub>) 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 WO<sub>3</sub> and TiO<sub>2</sub> systems, the reaction mechanism for each system was investigated in detail using <sup>18</sup>O-labeled O<sub>2</sub> and H<sub>2</sub>O.

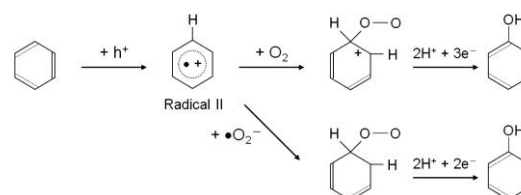
### 3.3. Determination of oxygen sources for phenol production from benzene on Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> systems using <sup>18</sup>O-labeled O<sub>2</sub> and H<sub>2</sub>O

In general, photocatalytic hydroxylation of benzene to phenols is considered to proceed through two different routes as illustrated in Schemes 1 and 2.<sup>2, 40-44</sup> The first route (Scheme 1) is initiated by photocatalytic generation of hydroxyl radicals (•OH) from H<sub>2</sub>O 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 H<sub>2</sub>O 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.*,<sup>43</sup> 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 O<sub>2</sub> or •O<sub>2</sub><sup>-</sup> molecules to give peroxidized species. The peroxidized species then are transformed into phenol molecules accompanied by proton (H<sup>+</sup>)-coupled reduction with photoexcited electrons (e<sup>-</sup>), as shown in Scheme 2. In this case, the phenol molecules produced must contain O atoms originating from the molecular O<sub>2</sub> dissolved in the solution. To clarify the dominant route operating in phenol production on Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> systems, reactions were conducted using a stable oxygen isotope (<sup>18</sup>O-enriched water: H<sub>2</sub><sup>18</sup>O, or <sup>18</sup>O<sub>2</sub>).

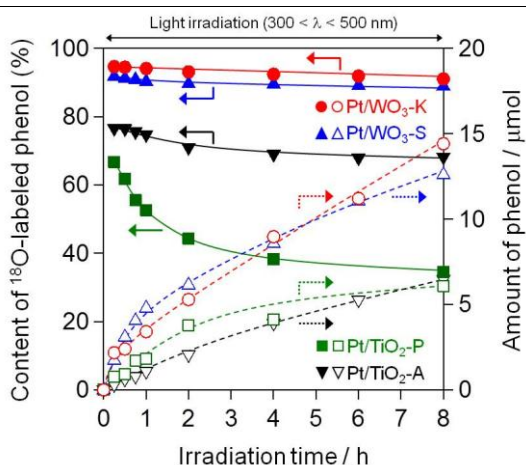


**Scheme 1.** Proposed reaction for phenol production over photocatalysts *via* hydroxyl radical.

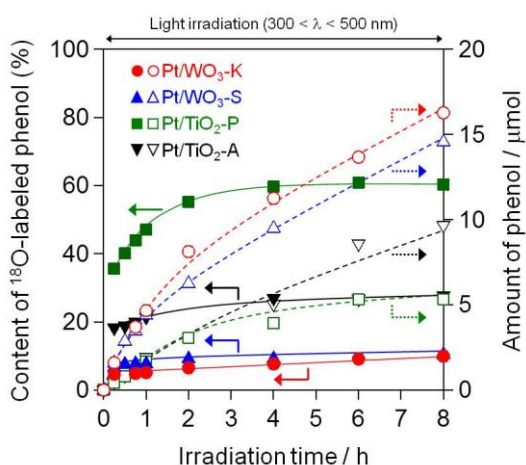


**Scheme 2.** Proposed reaction for phenol production over photocatalysts *via* oxygen molecule and oxygen radical.

Figures 3 and S7 show time courses for production of phenol from benzene by photocatalysis using four Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> samples, conducted in <sup>18</sup>O-enriched water (1.0 mL, 98% H<sub>2</sub><sup>18</sup>O) containing benzene and molecular O<sub>2</sub> (<sup>16</sup>O<sub>2</sub>). Total amount of phenol produced and percentage of phenol containing <sup>18</sup>O 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/WO<sub>3</sub>-K produced phenol at a nearly steady rate; percentage of <sup>18</sup>O-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 <sup>18</sup>O-labeled phenol throughout the reaction indicated that phenol production on Pt/WO<sub>3</sub>-K proceeded primarily *via* a reaction pathway involving hydroxyl radicals (•OH) from H<sub>2</sub><sup>18</sup>O molecules, which were the source of <sup>18</sup>O in the phenol produced (Scheme 1). The slight decrease in percentage of <sup>18</sup>O-labeled phenol during the reaction was probably due to the increased amount of H<sub>2</sub><sup>16</sup>O molecules, which were generated directly by four-electron reduction of <sup>16</sup>O<sub>2</sub> or indirectly by catalytic decomposition of H<sub>2</sub><sup>16</sup>O<sub>2</sub> on Pt; the H<sub>2</sub><sup>16</sup>O 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 H<sub>2</sub><sup>16</sup>O solvent containing labeled <sup>18</sup>O<sub>2</sub> 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 H<sub>2</sub><sup>16</sup>O-H<sub>2</sub><sup>18</sup>O (1:1) containing unlabeled <sup>16</sup>O<sub>2</sub>, the percentage of <sup>18</sup>O-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/WO<sub>3</sub> and Pt/TiO<sub>2</sub> samples. Reactions were conducted in <sup>18</sup>O-enriched water (98% H<sub>2</sub><sup>18</sup>O) containing benzene and normal molecular <sup>16</sup>O<sub>2</sub>.



**Figure 4.** Time course of photocatalyzed production of phenol from benzene on Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> samples. Reactions were conducted in normal water (H<sub>2</sub><sup>16</sup>O) containing benzene and molecular <sup>18</sup>O<sub>2</sub>.

**Table 4.** Direct hydroxylation of benzene in H<sub>2</sub><sup>18</sup>O in the presence of <sup>16</sup>O<sub>2</sub>

Entry	Photocatalyst	Reaction Condition	Content of labeled phenol (%) (Amount of phenol produced / μmol)	
			15 min	8 h
1	Pt/WO <sub>3</sub> -K	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O	94.7 (2.2)	91.1 (14.4)
2	Pt/WO <sub>3</sub> -Y	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O	92.7 (1.0)	88.6 (11.9)
3	Pt/WO <sub>3</sub> -S	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O	92.5 (1.7)	88.9 (12.6)
4	Pt/TiO <sub>2</sub> -P	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O	66.8 (0.8)	34.5 (6.1)
5	Pt/TiO <sub>2</sub> -A	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O	76.6 (0.3)	68.2 (6.5)
6	Pt/TiO <sub>2</sub> -R	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O	74.5 (0.1)	47.3 (1.2)
7	Pt/WO <sub>3</sub> -K	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O : H <sub>2</sub> <sup>16</sup> O = 1 : 1	46.3 (1.2)	43.9 (14.9)
8	Pt/TiO <sub>2</sub> -P	<sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O : H <sub>2</sub> <sup>16</sup> O = 1 : 1	31.6 (0.4)	16.7 (5.9)
9	Pt/WO <sub>3</sub> -K	<sup>18</sup> O <sub>2</sub> , H <sub>2</sub> <sup>16</sup> O	4.6 (1.6)	9.9 (16.3)
10	Pt/WO <sub>3</sub> -Y	<sup>18</sup> O <sub>2</sub> , H <sub>2</sub> <sup>16</sup> O	6.9 (1.4)	8.6 (13.2)
11	Pt/WO <sub>3</sub> -S	<sup>18</sup> O <sub>2</sub> , H <sub>2</sub> <sup>16</sup> O	6.7 (1.6)	10.4 (14.6)
12	Pt/TiO <sub>2</sub> -P	<sup>18</sup> O <sub>2</sub> , H <sub>2</sub> <sup>16</sup> O	35.7 (0.4)	60.4 (5.3)
13	Pt/TiO <sub>2</sub> -A	<sup>18</sup> O <sub>2</sub> , H <sub>2</sub> <sup>16</sup> O	18.2 (0.5)	27.7 (9.7)
14	Pt/TiO <sub>2</sub> -R	<sup>18</sup> O <sub>2</sub> , H <sub>2</sub> <sup>16</sup> 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 H<sub>2</sub>O on the Pt/WO<sub>3</sub>-K photocatalyst. Other Pt/WO<sub>3</sub> photocatalysts also preferentially generated phenol that contained O atoms originating from H<sub>2</sub>O molecules (Figs. S7 and S8; Table 4, entries 2, 3, 10, 11), indicating that phenol production on Pt/WO<sub>3</sub> proceeded through •OH generation from H<sub>2</sub>O (Scheme 1). As shown in Fig. S9, phenol production on Pt/WO<sub>3</sub>-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/TiO<sub>2</sub> system produced appreciable amounts of phenol containing O atoms originating from O<sub>2</sub>, along with others derived from H<sub>2</sub>O, indicating that phenol production proceeded through a reaction pathway involving O<sub>2</sub> molecules (Scheme 2) in parallel with a pathway involving H<sub>2</sub>O (Scheme 1). For example, photoirradiation of Pt/TiO<sub>2</sub>-P in H<sub>2</sub><sup>18</sup>O with <sup>16</sup>O<sub>2</sub> 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 O<sub>2</sub> molecules became more dominant as the reaction progressed. Reaction in H<sub>2</sub><sup>16</sup>O with labeled <sup>18</sup>O<sub>2</sub> also yielded a mixture of phenol molecules containing <sup>16</sup>O or <sup>18</sup>O (Fig. 4; Table 4, entry 12), in which the percentage of <sup>18</sup>O-labeled phenol molecules increased from 36 to 60% as the reaction proceeded. Phenol production on Pt/TiO<sub>2</sub>-P was suppressed slightly by addition of 2-propanol, an •OH scavenger (Fig. S9). Thus, phenol production on Pt/TiO<sub>2</sub>-P proceeded simultaneously via two different pathways (Schemes 1 and 2), while the contribution of the pathway involving O<sub>2</sub> gradually becomes dominant after prolonged irradiation time. Other Pt/TiO<sub>2</sub> photocatalysts, regardless of crystal phase (anatase or rutile), also produced a significant percentage of phenol molecules containing O atoms originating from O<sub>2</sub> (Figs. 3, 4, S6, S7; Table 4, entries 5, 6, 13, 14), while the change in percentage of <sup>18</sup>O-labeled phenol during the reaction differed significantly between Pt/TiO<sub>2</sub>-A and Pt/TiO<sub>2</sub>-R.

These results revealed that the Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> systems possessed different reactivity toward oxidations as well as toward reductions. The holes generated on Pt/WO<sub>3</sub> photocatalysts reacted primarily with H<sub>2</sub>O 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/TiO<sub>2</sub> photocatalysts reacted directly with benzene molecules adsorbed on the TiO<sub>2</sub> surfaces, not only with H<sub>2</sub>O, to generate cationic radical benzene species, which subsequently reacted with O<sub>2</sub> (or •O<sub>2</sub><sup>-</sup>) and protons to produce phenol.

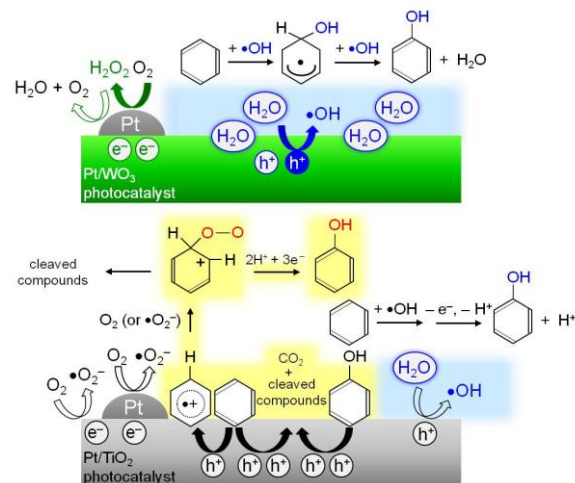
### 3.4. Reaction mechanisms for phenol production on Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub>

The holes generated in WO<sub>3</sub> and TiO<sub>2</sub> demonstrate distinctly different reactivity toward hydroxylation and oxidation of benzene in water. Since the oxidative potential of the holes generated in WO<sub>3</sub> and TiO<sub>2</sub> are essentially the same due to similarities in their valence band maximums,<sup>45, 46</sup> 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 WO<sub>3</sub>-K (10 m<sup>2</sup> g<sup>-1</sup>) and TiO<sub>2</sub>-A (10 m<sup>2</sup> g<sup>-1</sup>) 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 WO<sub>3</sub>-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 WO<sub>3</sub>-K particles. In contrast, intense IR band corresponding to benzene molecules adsorbed on TiO<sub>2</sub>-A were observed at wavenumbers (1440–1540 cm<sup>-1</sup>) slightly lower than those of benzene molecules in the gas phase. In addition, the IR band derived from surface hydroxyl groups of TiO<sub>2</sub>-A, originally observed at approximately 3500–3800 cm<sup>-1</sup>, decreased after benzene adsorption. This result indicated that the benzene molecules were strongly adsorbed to the TiO<sub>2</sub>-A surface through interactions with surface hydroxyl groups, whereas benzene molecules were only physically adsorbed onto the WO<sub>3</sub> 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<sub>3</sub> and Pt/TiO<sub>2</sub> systems as illustrated in Fig. 5. Since only small amount of benzene molecules were physically adsorbed on the WO<sub>3</sub> surface, the photo-generated holes in the WO<sub>3</sub> photocatalyst react primarily with H<sub>2</sub>O molecules, even in the presence of benzene molecules in the aqueous solution, yielding •OH radicals that subsequently react with benzene to produce phenol with high selectivity. At the same time, the photoexcited electrons on Pt/WO<sub>3</sub> photocatalysts react with molecular O<sub>2</sub> to generate mainly H<sub>2</sub>O<sub>2</sub> on the Pt cocatalyst. The H<sub>2</sub>O<sub>2</sub> generated is readily decomposed into H<sub>2</sub>O and O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (or •O<sub>2</sub><sup>-</sup>) 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<sub>2</sub> for phenol. The adsorption of benzene molecules on the surface of TiO<sub>2</sub> undoubtedly increases the possibility of direct oxidation of benzene into cleaved intermediates leading to CO<sub>2</sub> as the final product due to the holes. This direct decomposition pathway is supported by the noticeable production of CO<sub>2</sub> in the initial period of photoirradiation on Pt/TiO<sub>2</sub>-P as seen in Fig. 1. Additionally, the photoexcited electrons on TiO<sub>2</sub> reduce O<sub>2</sub> into radical species such as •O<sub>2</sub><sup>-</sup> or •HO<sub>2</sub>, which subsequently contribute to the oxidative decomposition of benzene and its intermediates. Both the direct oxidation of substrates (*e.g.*, phenol) on the TiO<sub>2</sub> surface and

oxidation by oxygen radical species are the main reasons for reduced phenol selectivity on TiO<sub>2</sub>. In contrast, these two oxidation pathways are inhibited by WO<sub>3</sub> system, enabling the Pt/WO<sub>3</sub> photocatalysts to produce phenol with high selectivity in the presence of H<sub>2</sub>O and O<sub>2</sub>.



**Figure 5.** Proposed reaction mechanisms for phenol production over Pt/WO<sub>3</sub> and Pt/TiO<sub>2</sub> photocatalysts.

The main property of Pt/WO<sub>3</sub> photocatalysts that enables highly selective phenol production is the selective generation of •OH radicals, even in the presence of organic substances such as benzene in water. When reaction on Pt/WO<sub>3</sub> was initiated with 10-fold greater concentration of benzene (25 mmol L<sup>-1</sup>), the amount of phenol produced only increased by *ca.* 16% (see Fig. S11). Note that the results of <sup>18</sup>O-labeled reactions with a much higher concentration of benzene (500 mmol L<sup>-1</sup>) indicated the preferential oxidation of water molecules on Pt/WO<sub>3</sub> photocatalysts. These results confirmed that the surface of WO<sub>3</sub> has properties that promote preferential oxidation of water molecules, even in the presence of significantly high concentration of benzene molecules, generating •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<sub>3</sub> and TiO<sub>2</sub> for adsorption of benzene and its intermediates. However, the Pt/WO<sub>3</sub>-K and the Pt/TiO<sub>2</sub>-A samples, which have similar surface areas (*ca.* 10 m<sup>2</sup> g<sup>-1</sup>), had different reactivities. A series of WO<sub>3</sub> 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 <sup>18</sup>O<sub>2</sub>. 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<sub>3</sub> and TiO<sub>2</sub> systems for the oxidative process. Although the dominant property enabling the WO<sub>3</sub> system to produce phenol with high selectivity remains unclear and needs clarification, the unique properties of WO<sub>3</sub> photocatalysts for achieving highly selective phenol production in the presence of molecular O<sub>2</sub> probably promote practically useful organic syntheses using photocatalysis.



## 4. Conclusions

Highly selective phenol synthesis directly from benzene was demonstrated using Pt-loaded WO<sub>3</sub> photocatalysts in water containing molecular oxygen. Results revealed that the surface of WO<sub>3</sub>, which is different from that of conventional TiO<sub>2</sub>, 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/WO<sub>3</sub> photocatalysts in water in the presence of O<sub>2</sub>; the •OH radicals generated can then be used for organic synthetic reactions in water if the reactant possesses low affinity toward the surface of WO<sub>3</sub>. Both the efficiency and selectivity in the present system will be improved when the nature and the reaction mechanism on WO<sub>3</sub> 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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## Notes and references

<sup>a</sup> Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. Fax: +81-75383-2479; Tel: +81-75383-2479; E-mail: ryu-abe@scl.kyoto-u.ac.jp

<sup>b</sup> Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan. Fax: +81-11706-9133; Tel: +81-11706-9132; E-mail: ohtani@cat.hokudai.ac.jp

<sup>c</sup> JSPS-NEXT Program, Koujijimachi, Chiyoda-ku, Tokyo 102-0083, Japan.

† 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 WO<sub>3</sub> samples prepared from tungstic acid (WO<sub>3</sub>-TA), and the results on the hydroxylation of benzene using oxygen stable isotope on WO<sub>3</sub>-TA are also shown. See DOI: 10.1039/b000000x/

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## *Supporting Information*

### **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**

Osamu Tomita,<sup>a,b</sup> Bunsho Ohtani<sup>b</sup> and Ryu Abe<sup>\*a,c</sup>

<sup>\*</sup>*Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

<sup>†</sup>*Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan*

<sup>‡</sup>*JSPS-NEXT Program, Koujimachi, Chiyoda-ku, Tokyo 102-0083, Japan*

*E-mail: [ryu-abe@scl.kyoto-u.ac.jp](mailto:ryu-abe@scl.kyoto-u.ac.jp)*

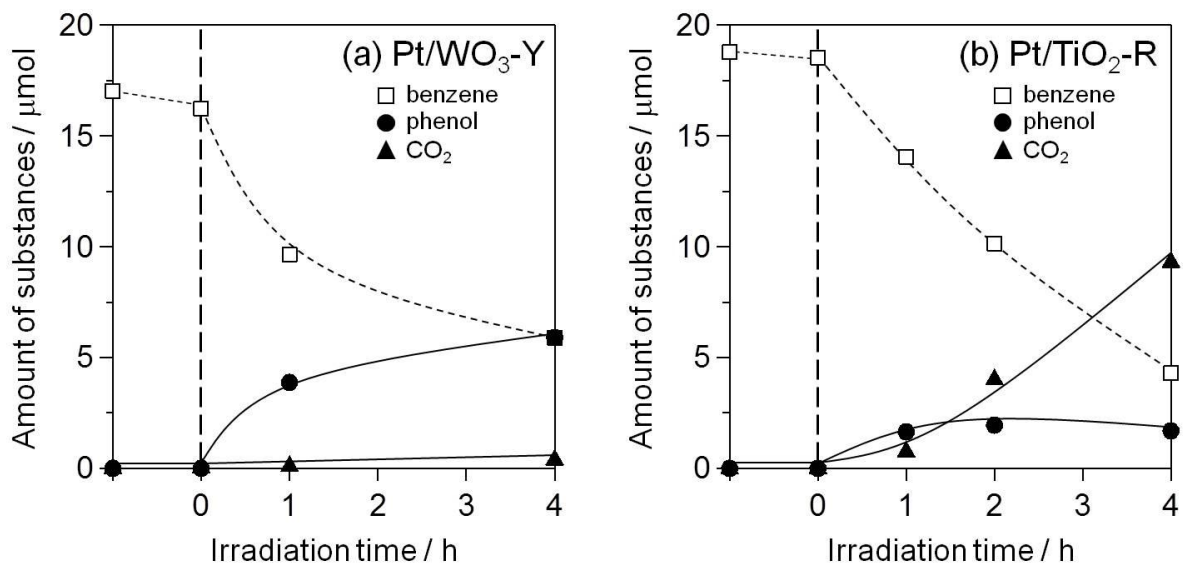


Figure S1. Time course of hydroxylation and oxidation of benzene over (a) Pt/WO<sub>3</sub>-Y and (b) Pt/TiO<sub>2</sub>-R photocatalysts in aerated aqueous solutions of benzene (18.8  $\mu\text{mol}$ ) under ultraviolet and visible light irradiation ( $300 < \lambda < 500 \text{ nm}$ ).

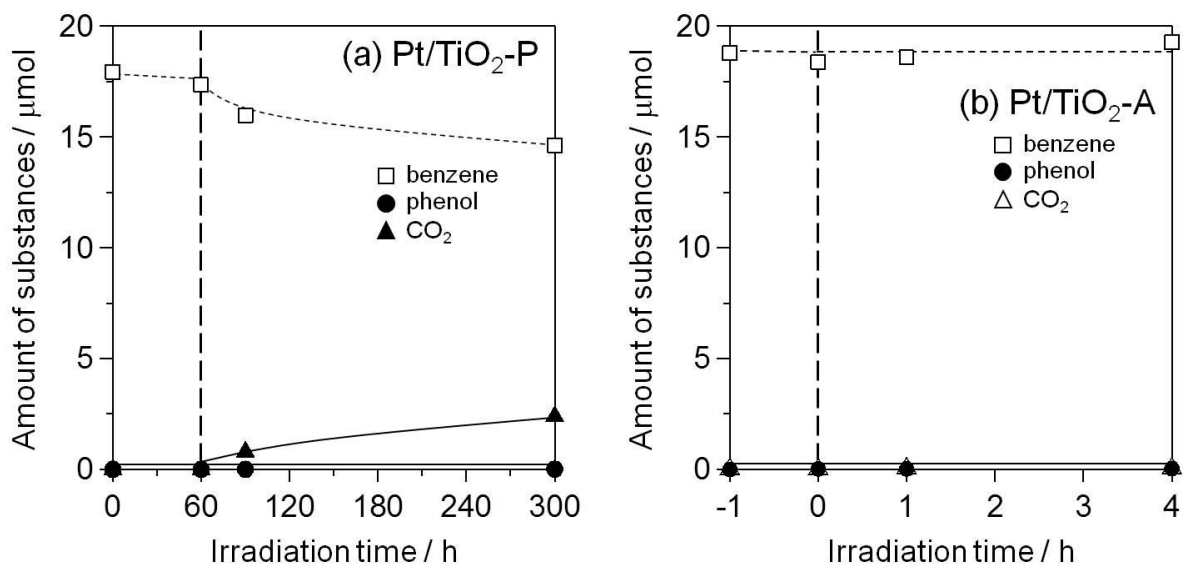


Figure S2. Time course of photocatalytic oxidation of benzene over (a) Pt/TiO<sub>2</sub>-P and (b) Pt/TiO<sub>2</sub>-A photocatalysts in aerated aqueous solutions of benzene (18.8  $\mu\text{mol}$ ) under visible light irradiation ( $400 < \lambda < 500 \text{ nm}$ ).

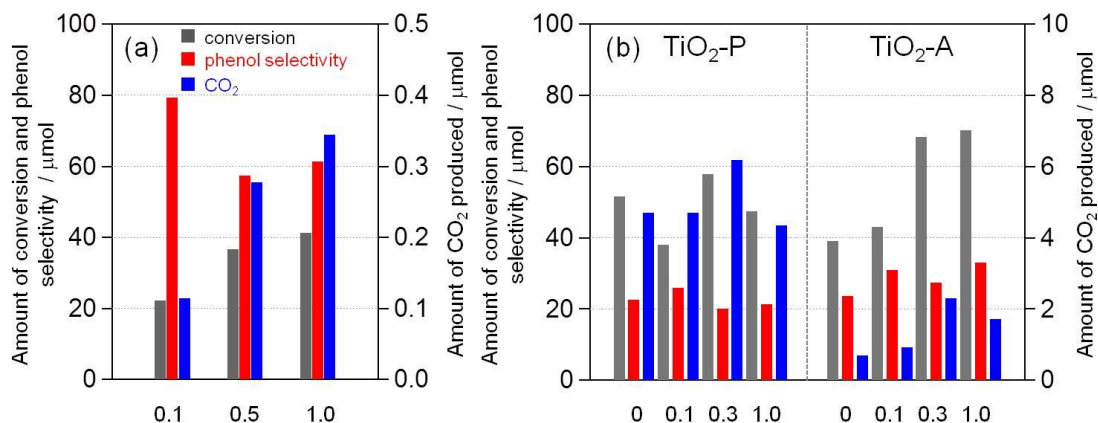


Figure S3. Influence of Pt amount on the amount of conversion, phenol selectivity, and amount of CO<sub>2</sub> on (a) Pt/WO<sub>3</sub>-K and (b) TiO<sub>2</sub> photocatalyst during hydroxylation of benzene (irradiation time 1 h).

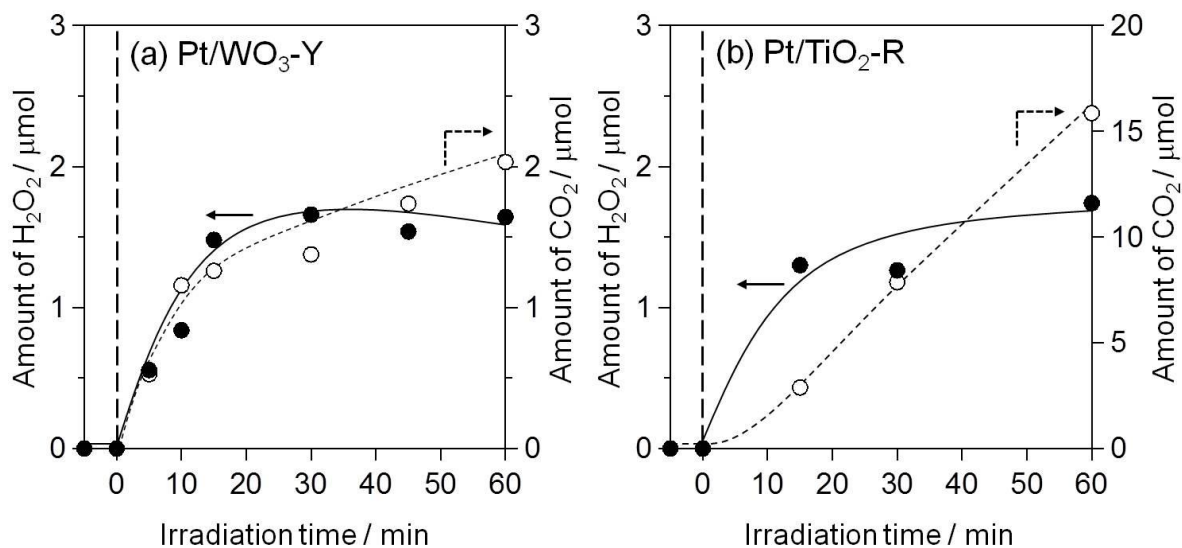


Figure S4. Time course curves of H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> generation over (a) Pt/WO<sub>3</sub>-Y and (b) Pt/TiO<sub>2</sub>-R photocatalysts suspended in AcOH solution under ultraviolet and visible light irradiation ( $300 < \lambda < 500$  nm).

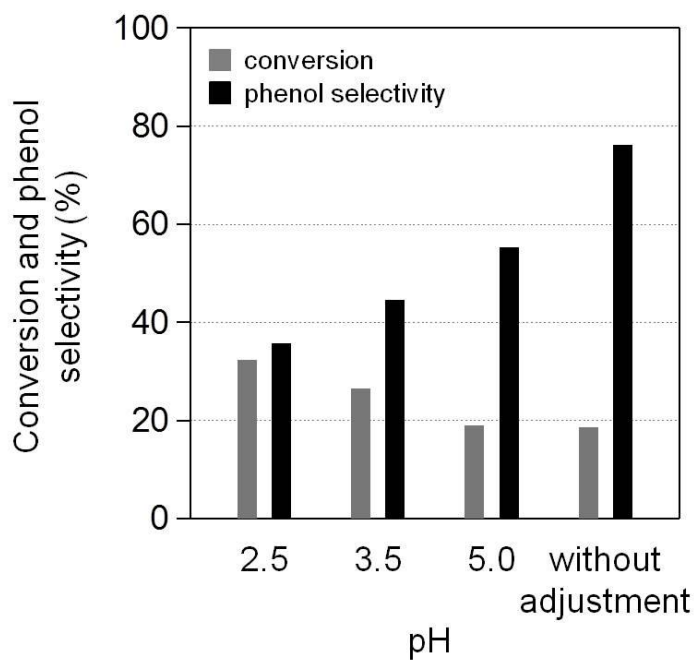


Figure S5. Dependence of photocatalytic hydroxylation of benzene on pH for use of Pt/WO<sub>3</sub>-K photocatalyst.

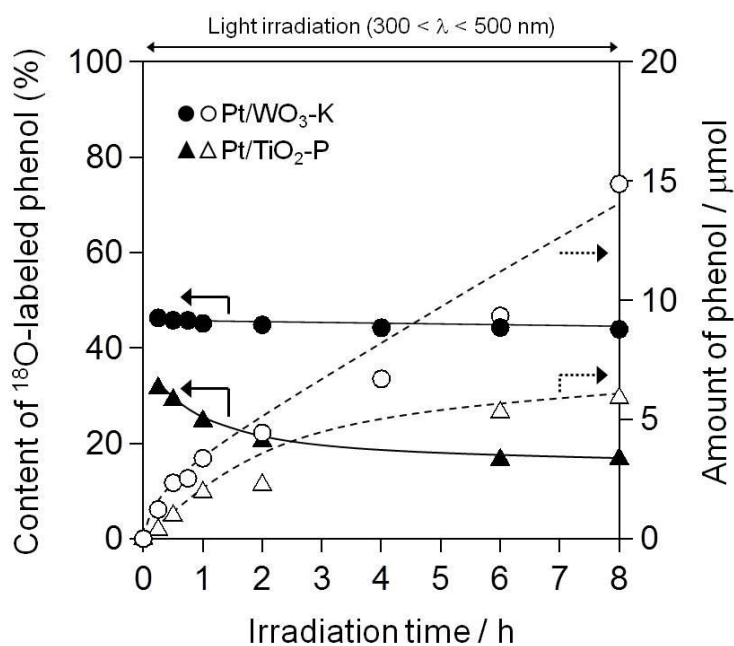


Figure S6. Time course of photocatalyzed phenol production from benzene on Pt/WO<sub>3</sub>-K and Pt/TiO<sub>2</sub>-P samples. Reactions were conducted in H<sub>2</sub><sup>16</sup>O-H<sub>2</sub><sup>18</sup>O mixed solvent containing benzene and normal molecular <sup>16</sup>O<sub>2</sub>.

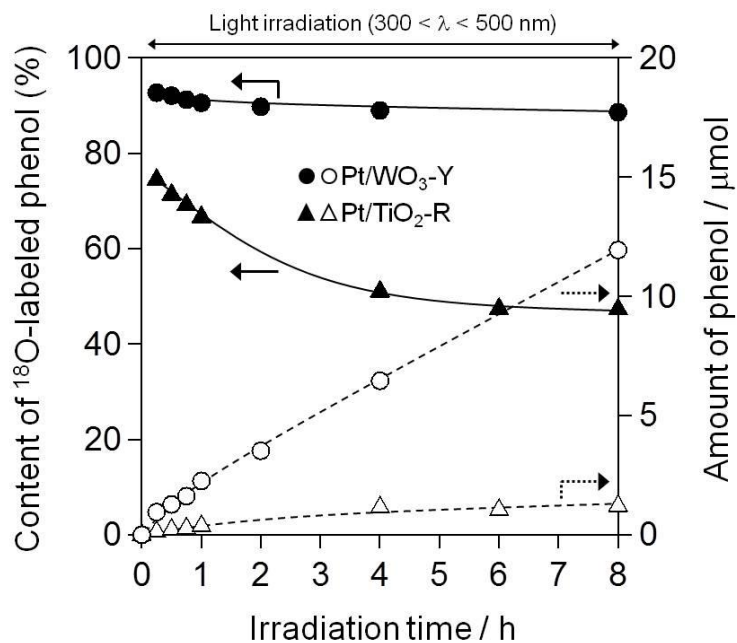


Figure S7. Time course of photocatalyzed phenol production from benzene on Pt/WO<sub>3</sub>-Y and Pt/TiO<sub>2</sub>-R samples. Reactions were conducted in <sup>18</sup>O-enriched water (98% H<sub>2</sub><sup>18</sup>O) containing benzene and normal molecular <sup>16</sup>O<sub>2</sub>.

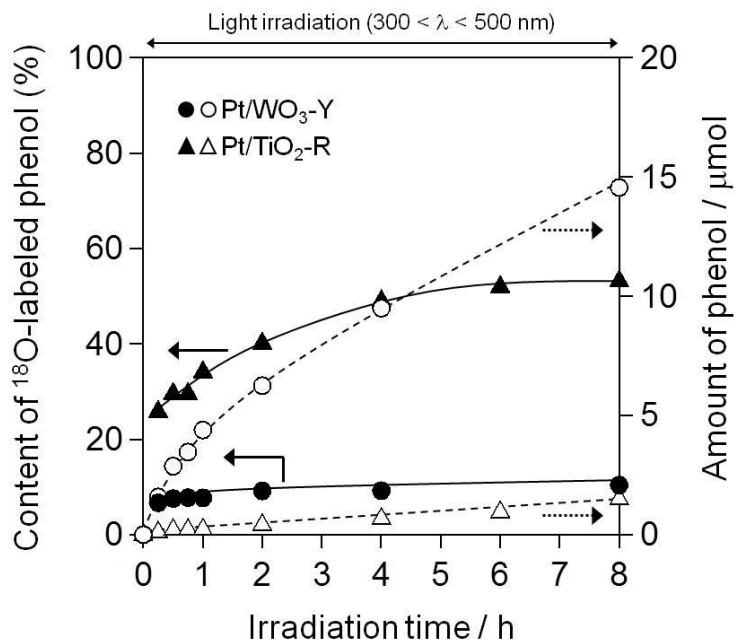


Figure S8. Time course of photocatalyzed phenol production from benzene on Pt/WO<sub>3</sub>-Y and Pt/TiO<sub>2</sub>-R samples. Reactions were conducted in normal water (H<sub>2</sub><sup>16</sup>O) containing benzene and molecular <sup>18</sup>O<sub>2</sub>.

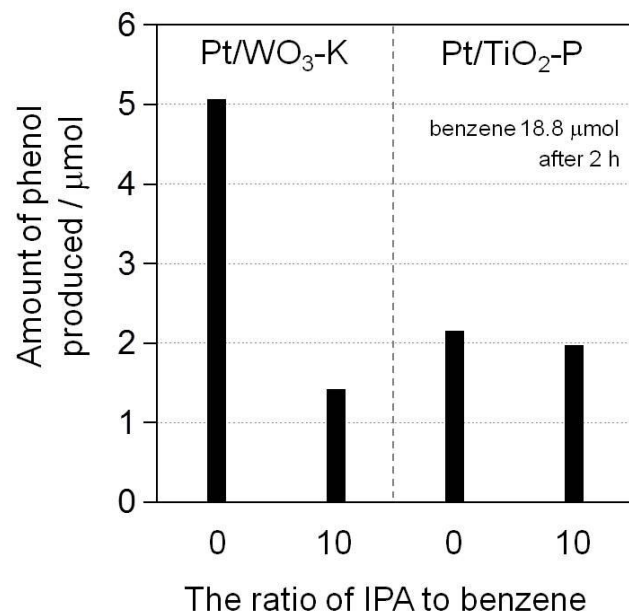


Figure S9. Amount of phenol produced from hydroxylation of benzene in the presence of IPA over Pt/WO<sub>3</sub>-K and Pt/TiO<sub>2</sub>-P photocatalysts.

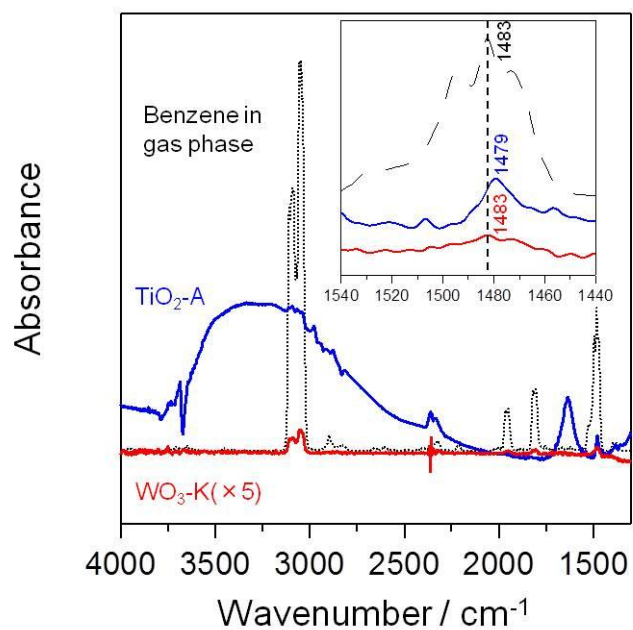


Figure S10. FT-IR subtraction spectra of benzene on photocatalysts.

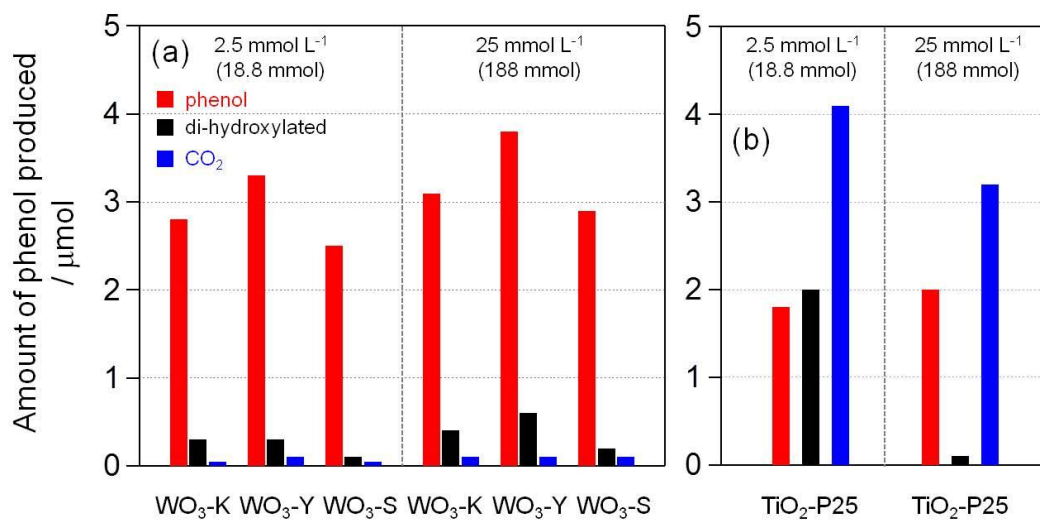


Figure S11. Influence of initial concentration of benzene on the amount of phenol, di-hydroxylated benzene and CO<sub>2</sub> on (a) Pt/WO<sub>3</sub> and (b) TiO<sub>2</sub> photocatalysts during hydroxylation of benzene (Pt: 0.1 wt.%).

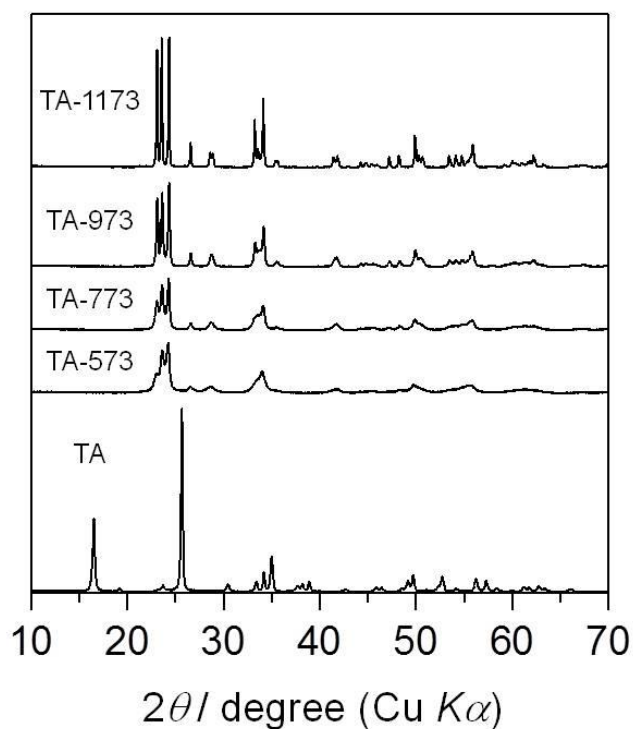


Figure S12. XRD pattern of WO<sub>3</sub> samples obtained from tungstic acid (H<sub>2</sub>WO<sub>4</sub>, TA) as the W precursor.



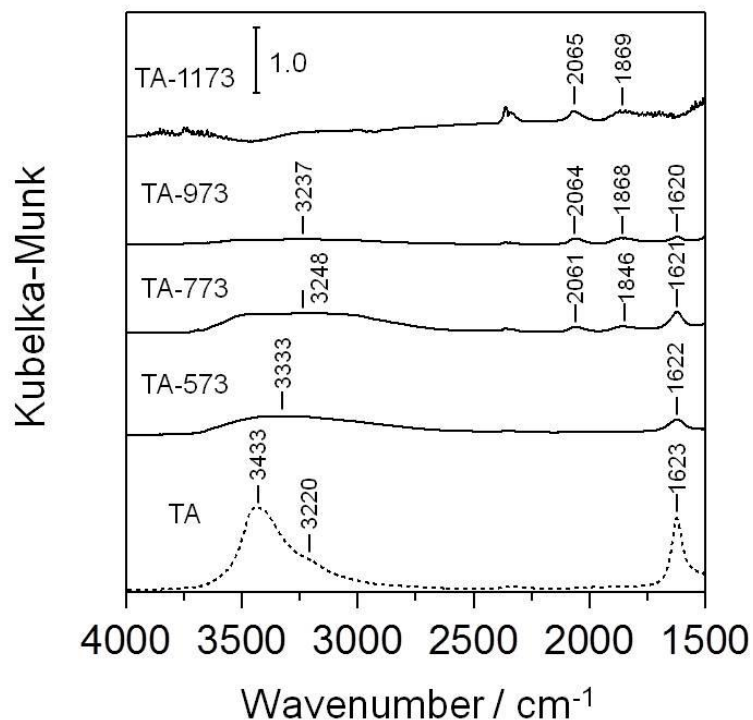


Figure S13. IR spectra of  $\text{WO}_3$  samples obtained from tungstic acid ( $\text{H}_2\text{WO}_4$ , TA) as the W precursor.

Table S1. Direct hydroxylation of benzene to phenol on  $\text{WO}_3$ -TA (prepared by calcination of tungstic acid powder) in normal water ( $\text{H}_2^{16}\text{O}$ ) containing benzene and molecular  $^{18}\text{O}_2$ .

Entry	Calcination temperature / K	Content of labeled phenol (%) (Amount of phenol produced / $\mu\text{mol}$ )	
		1 h	8 h
1	573	95.1 (0.6)	95.2 (2.5)
2	773	94.4 (1.2)	92.0 (3.8)
3	973	96.3 (1.3)	93.3 (4.9)
4	1173	94.9 (0.9)	94.0 (2.2)

Initial concentration of benzene : 500  $\mu\text{mol}$ , Amount of solvent : 1.0 mL

Light source : 300 W Xe lamp ( $300 < \lambda < 500$  nm)