Abstract: Activation of C(sp2)-H in aromatic molecules such as benzene is one of the challenging reactions. The tungsten trioxide supported Pt nanoparticles (Pt-WO₃) exhibited hydroxylation of benzene in the presence of air and H₂O under visible-light (420 < λ < 540 nm) irradiation. The photocatalytic activities (yields and selectivity of phenol) were studied under several experimental conditions. Furthermore, investigations of mechanistic insight into hydroxylation of benzene have been carried out by analyses with apparent quantum yields (AQY), an H₂¹⁸O isotope-labeling experiment, kinetic isotope effects (KIE), electrochemical measurements and density functional theory (DFT) calculations. It was proposed that dissociation of the O–H bond in H₂O is the rate-determining step. Furthermore, the substitution of the OH derived from H₂O with H abstracted from benzene by photo-formed H₂O₂ indicated a mechanism involving a push-pull process for the hydroxylation of benzene into phenol.

Keywords: Pt-WO₃ photocatalyst; visible light; hydroxylation of benzene; phenol formation; isotope H₂¹⁸O-labeling

1. Introduction

Visible light-driven photocatalysts for environmental conservation, securing energy resources and selective organic synthesis have received considerable attention because they can utilize unlimited solar energy [1–7]. Tungsten trioxide (WO₃) is one of the promising visible-light responsible photocatalyst having a direct band-gap excitation at ca. 2.7 eV. Recently, WO₃ has been proven to be an effective strategy for improving the photocatalytic degradation of volatile organic compounds (VOCs) such as acetaldehyde [8–11], toluene [12], acid [13]; water splitting to form O₂ in the presence of sacrificial agent [1]; as well as selective organic conversion such as oxidation of alcohol [14].

Phenols are important precursors for many chemicals and industrial products such as dyes and polymers, and they are currently produced from benzene by a three step cumene process. The cumene process for phenol formation exhibits low activity (~5% yield of phenol) and emission of large amounts of waste although the reactions require high temperature, high pressure and strong acidic conditions. Therefore, it is a great challenge to develop a one-step synthesis of phenol from benzene by using homogeneous and heterogeneous inorganic catalysts such as palladium membrane, titanium-containing...
mesoporous molecular sieves and vanadium-substituted phosphomolybdate by hydrogen peroxide ($H_2O_2$) [15–17]. Although $H_2O_2$ is often used as environmentally friendly oxidant only to produce $H_2O$ in catalytic hydroxylation of benzene, $O_2$ is more ideal oxidant than $H_2O_2$ due to its abundance in nature.

In a recent study, one-step direct hydroxylation of benzene toward phenol has been extensively studied using homogeneous photocatalysts such as quinolinium ions and $[Ru^{II}(Me_2phen)_3]^{2+}$ ions, [18–21], and heterogeneous semiconductor photocatalyst such as TiO$_2$ [22–27] and WO$_3$ [28,29] have been employed for selective photocatalytic hydroxylation of benzene to phenol under photo-irradiation ultraviolet (UV) light and/or visible-light. Yoshida et al. previously reported that platinum (Pt)-loaded TiO$_2$ (Pt-TiO$_2$) photocatalyst exhibited direct hydroxylation of benzene to form phenol and $H_2$ in the absence of $O_2$ under UV-light irradiation [22]. Also, Tomita et al. reported that the Pt-deposited WO$_3$ (Pt-WO$_3$) photocatalyst exhibited selective hydroxylation of benzene to phenol in the presence of $O_2$ and $H_2O$ under light irradiation of both UV light and visible light ($300 < \lambda < 500$ nm) [28,29]. It was also confirmed that OH derived from $H_2O$ is included in phenol by employing an $H_2^{18}O$ labeling experiment [29]. However, in a previous study, photocatalytic activities and reaction mechanisms for hydroxylation of benzene on the Pt-WO$_3$ have not been demonstrated under only irradiation of visible-light ($\lambda > 420$ nm).

In this study, we focus on understanding the photocatalytic activities for hydroxylation of benzene on the Pt-WO$_3$ photocatalyst under irradiation of only visible light ($420 < \lambda < 540$ nm). Furthermore, investigation of mechanistic insight has been carried out by combination with apparent quantum yields (AQY), $H_2^{18}O$ isotope labeling experiment, kinetic isotope effects ($C_6D_6$, $D_2O$), electrochemical measurements and density functional theory (DFT) calculations.

2. Results

2.1. Preparation of Pt-Deposited Tungsten Trioxide (WO$_3$) and Its Characterization

The Pt-WO$_3$ photocatalyst was characterized by X-ray diffraction (XRD), ultraviolet–visible (UV–Vis) spectroscopy, scanning transmittance electron microscope with energy-dispersed X-ray emission spectroscopy (STEM-EDS) and X-ray photoelectron spectroscopy (XPS) measurements. The XRD patterns of WO$_3$ and Pt-WO$_3$ were identified with a monoclinic structure in accordance with standard XRD profile of JCPDS cards No. 43-1035, and no other phase of Pt species was observed (see Figure 1 [I]). The WO$_3$ exhibited absorption spectrum in the visible-light region. Bandgap of the WO$_3$ was estimated to be ca. 2.6 eV from tauc plots $\eta (F(R) \times h\nu)^2$ vs. $h\nu$ (See Figure S1). Furthermore, the Pt-WO$_3$ with different amounts of Pt species exhibited optical absorbance above 450 nm, which is attributable to the scattering effects from the Pt particles [30] or surface resonance [31]. The optical absorbance significantly increased as an increase of the Pt species deposited on the WO$_3$ (See Figure 1 [II]). The scanning transmittance electron microscope with the STEM-EDS image of Pt(0.4)-WO$_3$ confirmed that Pt nano-particles were dispersed on the WO$_3$ surface (See Figure 1 [III]). The XPS analysis indicated that the Pt(0.4)-WO$_3$ photocatalyst was observed to possess two different types of doublet peaks (4f$_{5/2}$ and 4f$_{7/2}$) at 74.8 and 71.6 eV for Pt$^0$ as a major species, at 75.8 and 72.5 eV for Pt$^{2+}$ as a minor species (See Figure 1 [IV]). These results indicated that Pt nano-particle deposition on the WO$_3$ was successfully performed by photo-electrochemical deposition methods.
was saturated at 0.4 atom%. The selectivity of phenol was optimized at 0.1 atom% and then slightly decreased as an increase of Pt-deposition (see Figure 2 [I], Table S1). Reaction time profile for phenol evolution on the Pt(0.2)-WO$_3$ photocatalyst was shown in Figure 2 [II]. The yields of phenol decreased, while the selectivity of phenol improved over 70% (See Table S3). Therefore, a trade-off relation between the yields and selectivity of phenol was observed. The surface coverage of the photocatalyst by condensation of the adsorbent could be considered to prevent over oxidation of benzene leading to form H$_2$O$_2$.

Moreover, when the volume of solvent in the reaction became small, the yields of phenol decreased, while the selectivity of phenol improved over 70% (See Table S3). Therefore, a trade-off relation between the yields and selectivity of phenol was observed. The surface coverage of the photocatalyst by condensation of the adsorbent could be considered to prevent over oxidation of benzene leading to form H$_2$O$_2$.

### 2.2. Photocatalytic Hydroxylation of Benzene on the Pt-WO$_3$ under Visible-Light Irradiation

The photocatalytic hydroxylation of benzene in the presence of air and H$_2$O was performed on the WO$_3$ photocatalyst under visible-light irradiation. It was confirmed that the hydroxylation reaction does not take place under photo-irradiation without a photocatalyst nor with a photocatalyst without irradiation, i.e., both photocatalyst and irradiation are required in combination for hydroxylation reaction to occur. The WO$_3$ exhibited very low activity for phenol formation under visible-light irradiation (See Table S1). After the photocatalytic reaction, the color of suspension was slightly bluish, suggesting that the WO$_3$ was partially reduced and the ability for oxygen reductive reaction (ORR) was retarded. On the other hand, Pt-WO$_3$ exhibited significant improvement of photocatalytic activities for the formation of hydroxylated products such as phenol and catechol. The yields of phenols significantly improved as an increase of loading amounts of Pt species up to 0.2 atom%, and the activity was saturated at 0.4 atom%. The selectivity of phenol was optimized at 0.1 atom% and then slightly decreased as an increase of Pt-deposition (see Figure 2 [I], Table S1). Reaction time profile for phenol evolution on the Pt(0.2)-WO$_3$ photocatalyst was shown in Figure 2 [II]. The photocatalytic activity increased as an increase of reaction time: producing 29 μmol of phenol with 47 % selectivity after photocatalytic reaction for 20 h, and 40 μmol phenol with 64% selectivity for 70 h. (See distribution of side products shown in Table S2). After the reaction for 70 h, the amount of photo-formed H$_2$O$_2$ was only 0.15 μmol, which are much less than hydroxylated products assuming two electron reduction of O$_2$ to form H$_2$O$_2$. It can be considered that the H$_2$O$_2$ may be self-decomposed on the photocatalyst and/or participate in the reaction for the hydroxylation of benzene. The role of H$_2$O$_2$ will be discussed later. Moreover, when the volume of solvent in the reaction became small, the yields of phenol decreased, while the selectivity of phenol improved over 70% (See Table S3). Therefore, a trade-off relation between the yields and selectivity of phenol was observed. The surface coverage of the photocatalyst by condensation of the adsorbent could be considered to prevent over oxidation of benzene leading...
to high selectivity of phenol, of which the similar phenomena was previously reported on the TiO$_2$ photocatalyst [25].

![Graph showing Dependencies](image)

**Figure 2.** Dependence of loading amounts of Pt deposited on the WO$_3$ [I]; and reaction time profile on the Pt(0.2)-WO$_3$ [II] for hydroxylation of benzene to form phenol (yields: a, c; and selectivity: b and d) under visible-light irradiation.

Apparent quantum yields (AQY) on the Pt(0.2)-WO$_3$ were measured. Assuming one photon producing one phenol, the AQY for phenol formation reached over 2% by excitation at 400 nm as shown in Figure 3. The AQY profile was found to be very similar with the absorption spectrum of WO$_3$, suggesting that phenol formation is strongly correlated with the light absorbance of WO$_3$, not with Pt scattering [30] and/or resonance absorbance [31].

![Graph showing Wavelength dependence](image)

**Figure 3.** Dependence of wavelength photo-irradiated on apparent quantum yields, AQY (a) for hydroxylation of benzene to phenol, and UV–Vis absorbance of WO$_3$ (b) and Pt(0.2)-WO$_3$ (c).

### 2.3. Role of H$_2$O on the Photocatalytic Reactions

In order to understand role of H$_2$O, the H$_2^{18}$O-labeling experiments for photocatalytic hydroxylation of benzene were performed by liquid chromatography–mass spectrometry (LC-MS), and results are shown in Table 1 and Figure S2. It is noted that the atomic exchanges between O$_2$ and H$_2$O, and between O$_2$ and phenol are very slow even under photo-irradiation [23,32]. Therefore, H$_2^{18}$O was used for tracing O species incorporated in phenol. When the photocatalytic reactions were carried out in the presence of H$_2^{18}$O (100%), the photo-formed phenol was only observed at the mass number of 93 (m/z), which is attributed to the phenolic anion (C$_6$H$_5^{18}$O$^-$). Furthermore, when the photocatalytic reactions by employing H$_2^{16}$O (90%)/H$_2^{18}$O (10%) were carried out, the peaks at 93 (m/z) for the C$_6$H$_5^{16}$O$^-$ as well as 95 (m/z) for C$_6$H$_5^{18}$O$^-$ were observed. The peak intensities indicated that the ratio of $^{18}$O to $^{16}$O involved in the photo-formed phenol was 9.9% under visible-light
exhibited same activity for hydroxylation of benzene, it was concluded that hydroxyl groups in phenol is almost derived from H$_2$O under both irradiation of visible-light and UV-light.

These results suggest that the dissociation of O–H bond in the H$_2$O plays an important role in the rate determining step for the hydroxylation of benzene.

Table 1. H$_2^{18}$O isotope labeling test for photocatalytic hydroxylation of benzene on the Pt(0.2)-WO$_3$.

| Entry | Products/µmol | $^{18}$O/^{16}$O$ Ratios in Phenol/% |
|-------|---------------|-------------------------------------|
| 1     | PH 22.0 RE 1.4 BQ 0.01 CA 4.3 HQ 0.1 PL 3.4 PG 1.9 | 9.9 |
| 2     | PH 18.0 RE 0.4 BQ 0.03 CA 5.9 HQ 1.3 PL 5.5 PG 1.7 | 9.1 |

$^{1}$ H$_2^{18}$O (90%)/H$_2^{16}$O (10%) (5 mL), benzene: 300 µmol, visible-light irradiation (entry 1) and UV-light irradiation (entry 2) for 20 h. Abbreviation: phenol (PH), resolcinol (RE), p-benzoquinone (BQ), catechol (CA), hydroquinone (HQ), phloroglucinol (PL), pyrogallol (PG).

The rate determining step for hydroxylation of benzene was investigated by the kinetic isotope effect (KIE) using D$_2$O and C$_6$D$_6$ (See Figure 4). The reaction rate constants for formation of phenol from normal benzene (C$_6$H$_6$) in the presence of H$_2$O and D$_2$O were roughly estimated to be $3.75 \times 10^{-6}$ and $1.42 \times 10^{-6}$ s$^{-1}$ for (a) and (b), respectively. The kinetic isotope effect ($k_{H2O}/k_{D2O}$) was estimated to be ca. 2.7 (see Figure 4 [I]). On the other hand, the reaction rate constants for formation of phenol from C$_6$H$_6$ and C$_6$D$_6$ in the presence of H$_2$O were roughly estimated to be $3.75 \times 10^{-6}$ and $3.77 \times 10^{-6}$ s$^{-1}$ for (c) and (d), respectively. That is, the KIE of $k_{C6H6}/k_{C6D6}$ was estimated to be 1.0 (see Figure 4 [II]). These results suggest that the dissociation of O–H bond in the H$_2$O plays an important role in the rate determining step for the hydroxylation of benzene.

Figure 4. Kinetic isotope effects (KIE) on photocatalytic hydroxylation of benzene in the presence of air and H$_2$O on Pt(0.2)-WO$_3$ (20 mg) under visible light irradiation. Hydroxylation of C$_6$H$_6$ in the presence of H$_2$O (a) and D$_2$O (b) [I]; and that of C$_6$H$_6$ (c) and C$_6$D$_6$ (d) in the presence of H$_2$O [II].

2.4. Role of O$_2$ on the Photocatalytic Reactions

When the half reaction for the photocatalytic hydroxylation of benzene was performed on the Pt-WO$_3$ in the presence of Ag$^+$ ions as electron scavenger instead of O$_2$ under visible-light irradiation, no products could be detected under visible-light irradiation (Table 2). This result indicated that both H$_2$O and O$_2$ (air) in combination are essential for hydroxylation of benzene under visible-light irradiation.
Table 2. Effects of Ag\(^{+}\) ions added on the photocatalytic hydroxylation of benzene on the Pt(0.2)-WO\(_3\) photocatalyst under photo-irradiation.

| Reaction Condition | Products/µmol | Selectivity of PH/\% |
|-------------------|---------------|----------------------|
|                   | PH RE p-BQ CA HQ PL PG |                      |
| Visible light/air | 29.0 1.2 0.2 18.3 0.3 19.0 2.4 | 41.0 |
| Visible light/N\(_2\) (1) | 0 0 0 0 0 0 0 | - |
| UV light/N\(_2\) (1) | 1.1 0.5 0.5 0.6 0.2 6.8 0.06 | 11.7 |

(1) presence of Ag\(^{+}\) (50 µmol) under N\(_2\) purge.

The flat band potential of WO\(_3\) was obtained from capacitance versus voltage measurements. The WO\(_3\) powder was deposited on fluorine-doped tin oxide (FTO) coated glass. Mott–Schottky plots indicated that the flatband potential (=conduction band) of the WO\(_3\)/FTO was estimated to be +0.40 V vs. reversible hydrogen electrode (RHE) (Figure S3). LSV measurements of WO\(_3\) and Pt-WO\(_3\) were carried out in O\(_2\)-saturated 0.1 M Na\(_2\)SO\(_4\) aq. The cathodic current was obtained at the potential more cathodic than the conduction band (+0.40 V vs. RHE) of WO\(_3\) (See Figure S4). This cathodic current would be attributed to the reduction of WO\(_3\). Furthermore, the cathodic current significantly increased by deposition of Pt on WO\(_3\). A deposition of Pt species as a co-catalyst caused an improvement of the ORR. It is noted that multi-electron reduction of O\(_2\) to H\(_2\)O\(_2\), thermodynamically occurred at \(E^0(O_2/H_2O_2) = +0.68\) V [33]. An increase of cathodic current is attributed to the effective electron transfer to O\(_2\) via Pt species to form H\(_2\)O\(_2\) [34].

It was confirmed that the hydroxylation of benzene in the presence of H\(_2\)O\(_2\) did not take place under photoirradiation without a photocatalyst nor with photocatalyst without irradiation. However, both photocatalyst and visible-light irradiation are required for the hydroxylation of benzene (See Table S4). In order to understand the role of H\(_2\)O\(_2\), the hydroxylation of benzene (300 µmol) in the presence of H\(_2\)O\(_2\) (150 µmol) and H\(_2\)\(^{16}\)O (90%)/H\(_2\)\(^{18}\)O (10%) was conducted on the Pt-WO\(_3\) under visible-light irradiation. As a result, the ratio of \(^{18}\)O to \(^{16}\)O was determined to be 8.3%, suggesting that major contribution of OH groups in phenol came from H\(_2\)O even in the presence of H\(_2\)O\(_2\).

2.5. Reaction Mechanisms for Photocatalytic Hydroxylation of Benzene to Phenol

In order to evaluate the oxidation power of photo-induced holes, photocatalytic half reactions on the Pt(0.2)-WO\(_3\) photocatalyst were carried out. It was observed that addition of Ag\(^{+}\) ions instead of O\(_2\) showed no products under visible-light irradiation, while the phenolic compounds were detected under UV-light irradiation (See Table 2). These results suggest that water oxidation by UV-light irradiation induced strong oxidation power possibly to form free OH radicals, which would attack benzene directly [29], but by visible-light irradiation would not form OH radicals. In fact, we employed the tertiary butyl alcohol (TBA) as scavengers of OH radicals. As a result, the TBA added in the photocatalytic system on the Pt-WO\(_3\) under visible-light irradiation did not influence to the yields of phenol (Table 3). However, the amounts of catechol (CA) and phloroglucinol (PL) decreased by the addition of TBA (See Table 3). The di- and tri- OH groups involved in phenolic compounds may be partially derived from O\(_2\). Research is under way using an \(^{18}\)O labeling test.

Table 3. Effects of tertiary butyl alcohol (TBA) added on the photocatalytic hydroxylation of benzene on the Pt(0.2)-WO\(_3\) photocatalyst under visible light irradiation for 20 h under air.

| TBA Added/µmol | Products/µmol | Selectivity of PH/\% |
|---------------|---------------|----------------------|
|               | PH RE BQ CA HQ PL PG |                      |
| 0             | 29.0 1.2 0.19 18.3 0.34 19 2.4 | 41.0 |
| 50            | 29.2 1.39 0.25 13.3 0.27 7.9 5.0 | 51.0 |
As mentioned above, $\text{H}_2\text{O}_2$ was confirmed to form as intermediate species by multi-electron reduction of $\text{O}_2$ during photocatalytic hydroxylation of benzene. The reaction mechanisms were investigated by DFT calculations. Figure 5 [Ia] showed the optimized structures of the reactant, transitional state (TS) and product by the interactions of benzene, $\text{H}_2\text{O}$ with $\text{H}_2\text{O}_2$. The O–H bond length in $\text{H}_2\text{O}$, O–O in $\text{H}_2\text{O}_2$ and C–H in benzene were observed to increase through the reaction path. It was found that $\text{H}_2\text{O}_2$ could assist C-H bond dissociation from benzene. Subsequently, OH species derived from $\text{H}_2\text{O}$ was incorporated within phenol in the final product. Moreover, the reaction path in the presence of the Pt co-catalyst was investigated (See Figure 5 [Ib]). Strong interaction of $\text{H}_2\text{O}_2$ with Pt$_3$ was observed to dissociate the O–O bond to form O species, and subsequently, the C–H bond in benzene was dissociated by an assist of the O species and/or Pt$_3$. The energy changes for overall reactions were indicated in Figure 5 [II]. The hydroxylation of benzene proceeded on much lower potential energy surface with the Pt$_3$ co-catalyst than that without Pt$_3$ co-catalyst. Thus, we have demonstrated the possible reaction path for hydroxylation of benzene to form phenol including OH groups derived from $\text{H}_2\text{O}$.

![Figure 5. Optimized structures at the reactant, TS and product between benzene, $\text{H}_2\text{O}$ and $\text{H}_2\text{O}_2$ system in the absence [Ia] and presence [Ib] of Pt$_3$ as co-catalyst for the hydroxylation of benzene to form phenol; and energy potentials for intrinsic reaction coordinates (IRC) [II]. The stabilization energy at each state was calculated by the difference from the energy of isolated system. The bond distance (Å) of O–H in $\text{H}_2\text{O}$ (blue), O–O in $\text{H}_2\text{O}_2$ (green) and C–H in benzene (red) were indicated.](image-url)
The reaction mechanism for the direct hydroxylation of benzene to phenol on the Pt-WO₃ was proposed (See Figure 6). This reaction is initiated by visible-light irradiation of the WO₃. The photo-induced holes and electrons are generated in the VB and CB of the WO₃, respectively. It was assumed that the photo-induced holes can oxidize H₂O to form O₂ [1], as well as activated (H₂O)* intermediate species of which the O–H bond length would be increased. On the other hand, the electrons effectively transfer from CB to O₂ via Pt species to form peroxide species such as H₂O₂, which would be further activated on the catalyst surface. The activated (H₂O)* species would attack the π electrons of the aromatic benzene ring, assisting the activated (H₂O₂)* to dissociate the C–H bond in benzene. It was, thus, proposed that the hydroxylation of benzene occurs by a mechanism involving a push-pull process, which promotes the formation of phenol.

![Figure 6. Reaction mechanisms for the hydroxylation of benzene into phenol in the presence of O₂ and H₂O on the Pt-WO₃ under visible light irradiation. (*) indicates formation of activated H₂O and H₂O₂ intermediates by photo-excitation.](image)

### 3. Materials and Methods

#### 3.1. Materials

Tungsten trioxide (WO₃, 99.9%) from Kojundo Chemical Laboratory (Osaka, Japan), H₂PtCl₆·6H₂O (99.9%) from Wako Pure Chemical Industries (Osaka, Japan); and water-¹⁸O (97 atom% ¹⁸O) and titanium (IV) oxysulfate solution (99.99%) from Sigma-Aldrich (St. Louis, MO, USA) were purchased. All chemicals were used without further purification.

#### 3.2. Photoelectrochemical Deposition of Pt Species as Co-Catalyst on the WO₃

Photoelectrochemical deposition of Pt species was conducted on the WO₃ surface. WO₃ powder (1.0 g) was suspended in distilled water (25 mL) involving desired amounts of H₂PtCl₆ (4.32 × 10⁻⁶ ~ 2.16 × 10⁻⁵ mol), and the suspension was photo-irradiated by a light-emitting diode (LED) lamp (420 < λ < 540 nm) for 1 h under stirring in order to disperse photo-adsorbed Pt species. Subsequently, methanol (5 mL) as reductant was added into the suspension, and then it was continuously photo-irradiated for 4 h. The solid products were separated by centrifuge (LC-200, TOMY, 4500 rpm), followed by washing with distilled water and acetonitrile, and drying under vacuum condition at ambient temperature over night. The photocatalyst was referred to be as Pt(x)-WO₃(x: atom%). The photocatalyst was kept in the ambient temperature, and the photocatalytic reactions were carried out without further treatment of photocatalyst.
3.3. Characterizations

The X-ray diffraction (XRD) patterns were obtained with a RIGAKU RINT2000 using Cu Kα radiation (λ = 1.5417 Å) (RIGAKU, Tokyo, Japan). The oxidative states of Pt species were analyzed by an X-ray photoelectron spectroscopy (XPS), KRATOS, AXIS Ultra, using Al Kα radiation (E = 1486.8 eV) (Shimadzu, Kyoto, Japan). The UV–Vis spectroscopic measurements were carried out on diffuse reflectance with a UV–Vis scanning spectrophotometer (UV-3100PC, Shimadzu, Kyoto, Japan). The elemental distribution images were taken with scanning transmittance electron microscope with energy-dispersed X-ray emission spectroscopy (STEM-EDS; JEOL JSM-2100, Tokyo, Japan).

3.4. Photocatalytic Reactions

Photocatalyst (20 mg) was suspended in distilled water (2, 5 or 10 mL) in a pyrex reaction tube (volume: 20 mL) under air capped with precision seal septum. If specific description was not given, the distilled water (10 mL) was introduced. And subsequently, 26.8 μL of benzene (300 μmol) was dropped into the suspension by a syringe under vigorous stirring. The reaction cell was photo-irradiated by a blue LED (visible light: 420 < λ < 540 nm) or black light (UV light: 300 < λ < 400 nm) at 298 K. The light energy intensities were shown in Figure S5. After the reaction, the catalysts were immediately separated from the suspension by filtration through a 0.20 μm membrane filter (Dismic-25JP, Advantec, Tokyo, Japan). The solution was, then, analyzed by High Performance Liquid Chromatography (HPLC, Shimadzu LC10ATVP, Kyoto, Japan, UV–Vis detector, column: Chemcopak, mobile phase: a mixture of acetonitrile and 1.0% formic acid aqueous solution), and several products were identified (see Figure S6). The gas phase (CO2) was analyzed by Gas Chromatography–thermal conductivity detector (GC-TCD, Shimadzu GC-8A, Kyoto, Japan; column: porapak Q). Titanium sulfate (100 μL) was added to 1 mL of the reaction solution, and amounts of H2O2 formed in solution were analyzed by colorimetry from the value of absorbance at 410 nm in the UV–Vis absorption spectrum.

For the tracer experiment, H218O was used as the oxygen isotope source. The photocatalytic hydroxylation of benzene or phenol was carried out over Pt-WO3 photocatalyst in the presence of H218O (10%)/H216O (90%) as solvent and air under visible-light irradiation for 20 h. The photocatalytic hydroxylation of benzene was performed in the presence of H216O2 (100 μmol) and H218O (10%)/H216O (90%) under visible-light irradiation for 2 h. Phenol in aqueous solutions were extracted by toluene, and the molar ratios of Ph-18OH and Ph-16OH were identified by LC-MS (Shimadzu LCMS-2020 spectrometer, Kyoto, Japan).

3.5. Electrochemical Measurements

Flatband potentials of the photoelectrodes were measured by a Potentiogalvanostat (PGSTAT204, Autolab). The electrolysis cell was constructed with three electrodes, the WO3 photoelectrode as working electrode, the platinum wire as auxiliary, and Ag/AgCl as the reference electrode. The WO3 photoelectrodes were prepared as follows: the WO3 (20 mg) was suspended in ethanol (0.2 mL) by a super-sonification to form a paste. The paste was then spread onto the FTO (active space 1.0 cm2, Aldrich) by spin coating (2200 rpm, 30 s) for 3 times, followed by heat-treatment at 773 K for 1 h in air. Prior to measurements, 0.10 M Na2SO4 aqueous solution was vigorously bubbled by N2 gas for 20 min in order to remove O2.

Linear sweep voltammetry (LSV) was conducted at the rate of 10 mV s−1. The photocatalyst (20 mg) was added into ethanol (0.2 mL) followed by a super-sonification for 5 min to disperse. The paste was casted by spin-coating (2200 rpm, 30 s) on the conductive transparent glass (FTO, 10 Ω/□, Sigma Aldrich, St. Louis, MO, USA) 3 times, followed by heat-treatment at 373 K overnight. Prior to LSV measurements, 0.10 M Na2SO4aq. was vigorously bubbled by O2 for 20 min.
3.6. Density Functional Theory (DFT) Calculation

Gaussian 09 program [35] and the hybrid B3LYP functional [36] were used. For Pt atoms, the Los Alamos effective core potentials [37] were employed along with the corresponding valence double basis sets [38]. For other atoms, a 6-311G(d,p) basis set was used. After the transition state (TS) was characterized, the intrinsic reaction coordinate (IRC) analysis [39] was carried out for both directions, reactant and product sides. The IRC analyses were followed by normal optimization runs, and the reactant and product were optimized as local minima.

4. Conclusions

In this study, we provided an understanding of photocatalytic activities for the hydroxylation of benzene under irradiation of only visible-light (420 < λ < 540 nm). It was demonstrated that hydroxylation of benzene on the Pt-WO3 photocatalyst in the presence of air and H2O produced several products such as phenol, catechol and phloroglucinol etc., and the selectivity of phenol improved over 70%.

One of novelties in our findings was to confirm the reaction mechanisms for photocatalytic hydroxylation of benzene into phenol by experimental and theoretical studies. An investigation of the mechanistic insights has been carried out by the combination with apparent quantum yields (AQY), an H218O isotope-labeling experiment, kinetic isotope effects (C6D6, D2O), electrochemical measurements, and DFT calculations. It was proposed that the substitution of the OH derived from H2O with H abstracted from benzene by photo-formed H2O2 indicated a mechanism involving a push-pull process for the hydroxylation of benzene into phenol. Our results showed new perspectives for the enhancement of yields and selectivity of phenol, as well as deeper understanding of the reaction mechanisms for the hydroxylation of benzene into phenol on the Pt-WO3 photocatalyst.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/5/557/s1: Figure S1: Tauc plots of WO3, Figure S2: H218O isotope labeling experiments, Figure S3: Mott–Schottky plots of WO3, Figure S4: LSV measurements of WO3 and Pt-WO3, Figure S5: Photo-intensities emitted from light-emitting diode (LED) and UV lamp, Figure S6: Molecular structures of products, Table S1: Photocatalytic activities depending on the amounts of Pt-deposition, Table S2: Time profiles in the photocatalytic reaction, Table S3: Effects of volumes in the reaction on the photocatalytic activity, Table S4: Role of H2O2 for the photocatalytic reactions.

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