

## *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**

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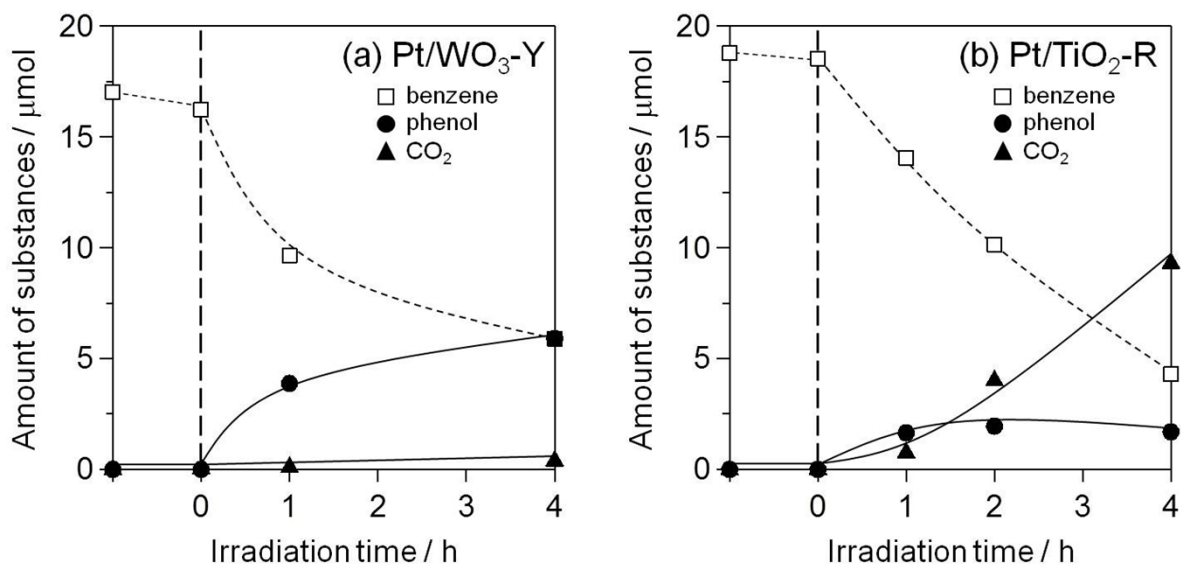


Figure S1. Time course of hydroxylation and oxidation of benzene over (a) Pt/WO<sub>3</sub>-Y and (b) Pt/TiO<sub>2</sub>-R photocatalysts in aerated aqueous solutions of benzene (18.8  $\mu\text{mol}$ ) under ultraviolet and visible light irradiation ( $300 < \lambda < 500 \text{ nm}$ ).

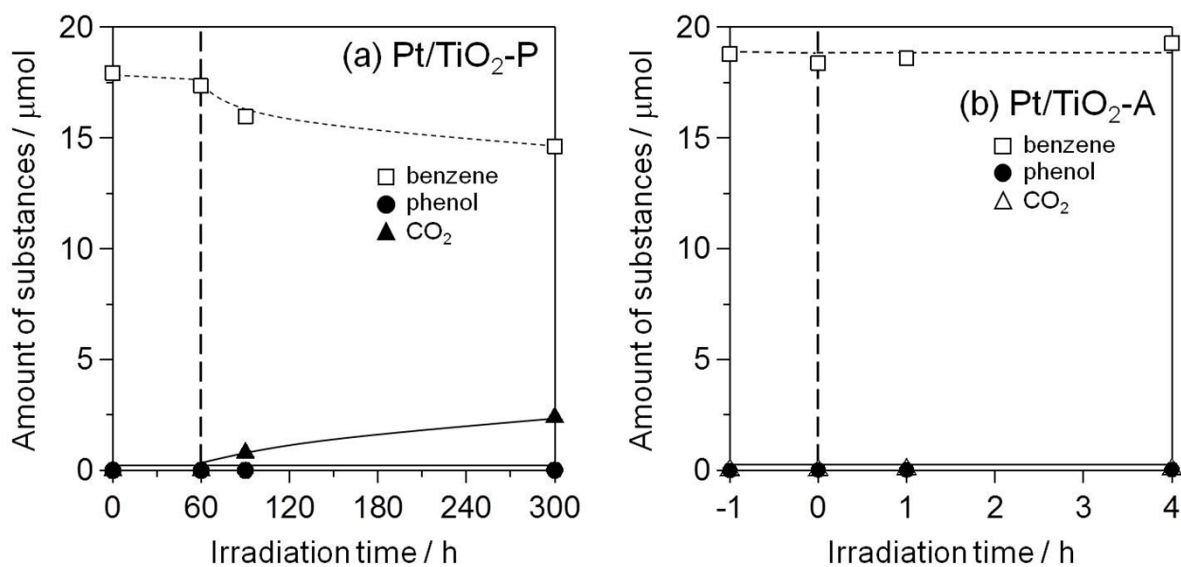


Figure S2. Time course of photocatalytic oxidation of benzene over (a) Pt/TiO<sub>2</sub>-P and (b) Pt/TiO<sub>2</sub>-A photocatalysts in aerated aqueous solutions of benzene (18.8  $\mu\text{mol}$ ) under visible light irradiation ( $400 < \lambda < 500 \text{ nm}$ ).

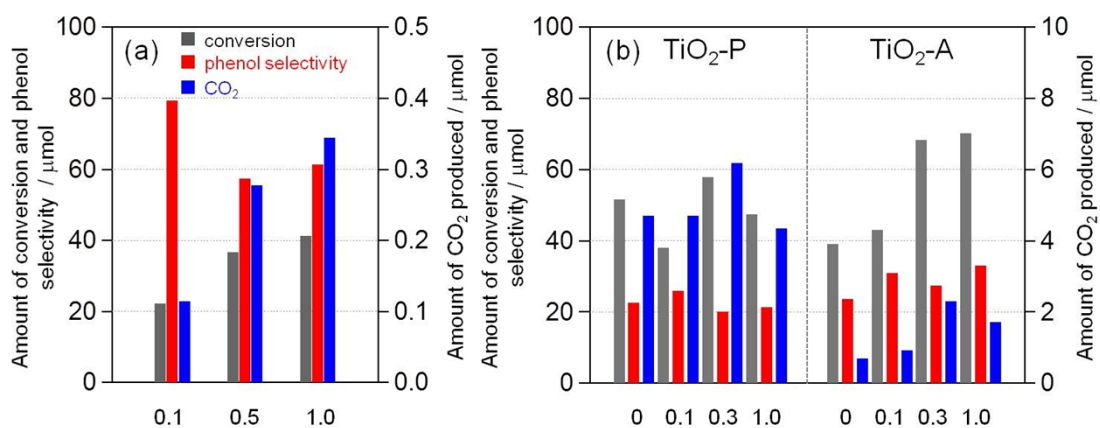


Figure S3. Influence of Pt amount on the amount of conversion, phenol selectivity, and amount of CO<sub>2</sub> on (a) Pt/WO<sub>3</sub>-K and (b) TiO<sub>2</sub> photocatalyst during hydroxylation of benzene (irradiation time 1 h).

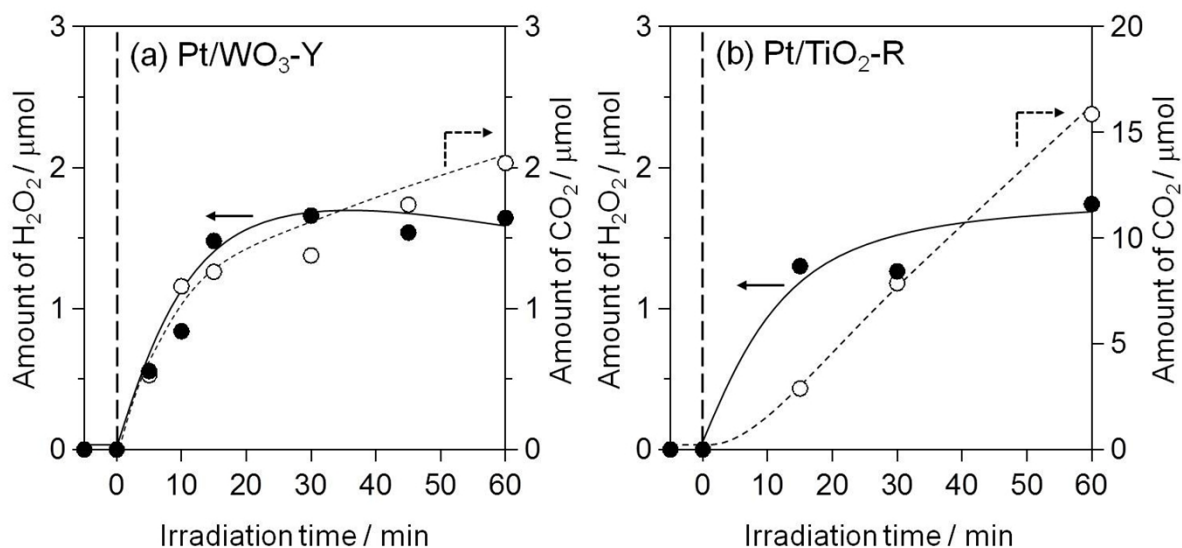


Figure S4. Time course curves of H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub> generation over (a) Pt/WO<sub>3</sub>-Y and (b) Pt/TiO<sub>2</sub>-R photocatalysts suspended in AcOH solution under ultraviolet and visible light irradiation ( $300 < \lambda < 500 \text{ nm}$ ).

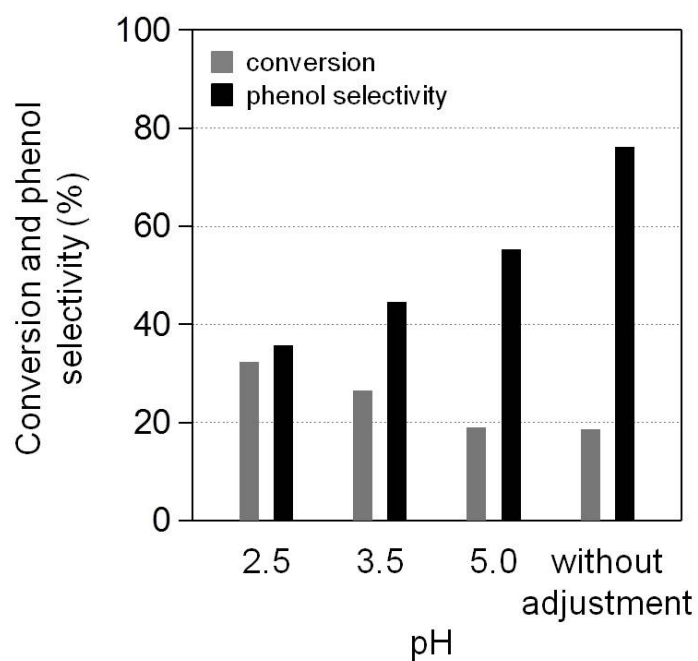


Figure S5. Dependence of photocatalytic hydroxylation of benzene on pH for use of Pt/WO<sub>3</sub>-K photocatalyst.

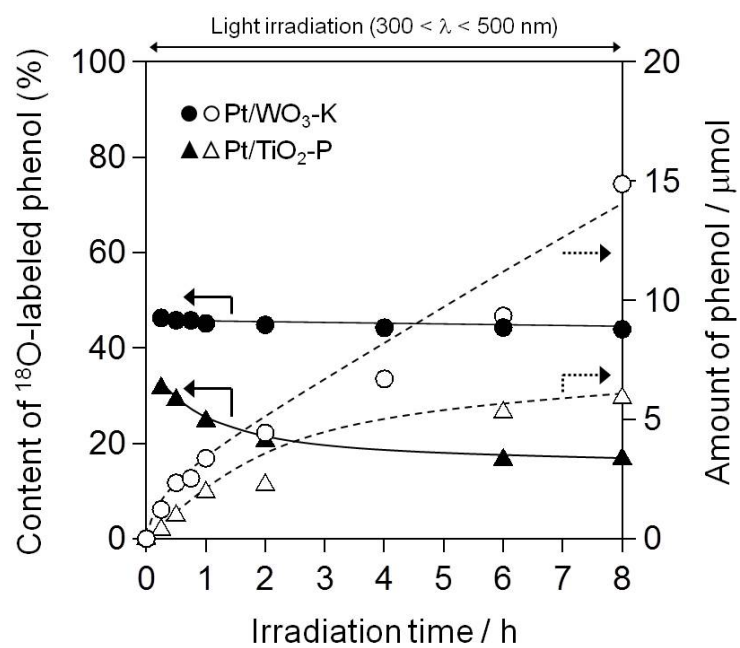


Figure S6. Time course of photocatalyzed phenol production from benzene on Pt/WO<sub>3</sub>-K and Pt/TiO<sub>2</sub>-P samples. Reactions were conducted in H<sub>2</sub><sup>16</sup>O-H<sub>2</sub><sup>18</sup>O mixed solvent containing benzene and normal molecular <sup>16</sup>O<sub>2</sub>.

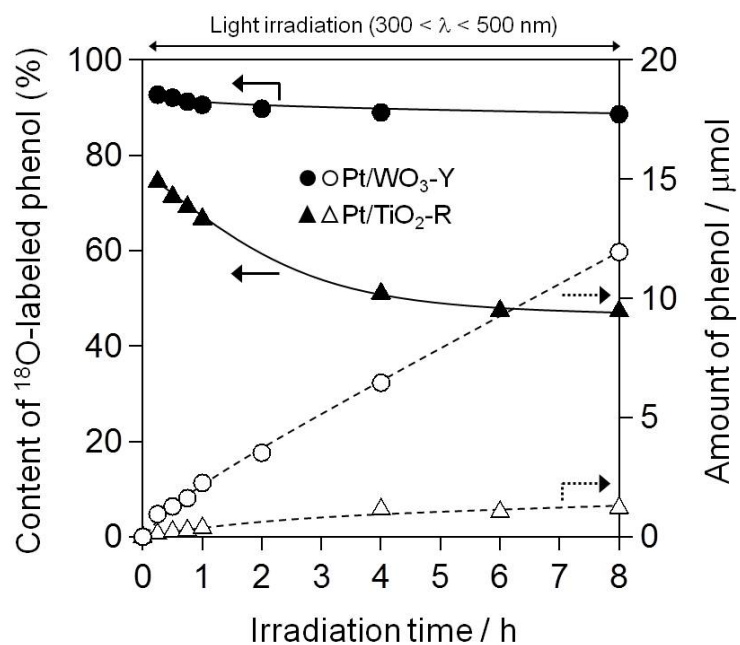


Figure S7. Time course of photocatalyzed phenol production from benzene on Pt/WO<sub>3</sub>-Y and Pt/TiO<sub>2</sub>-R samples. Reactions were conducted in <sup>18</sup>O-enriched water (98% H<sub>2</sub><sup>18</sup>O) containing benzene and normal molecular <sup>16</sup>O<sub>2</sub>.

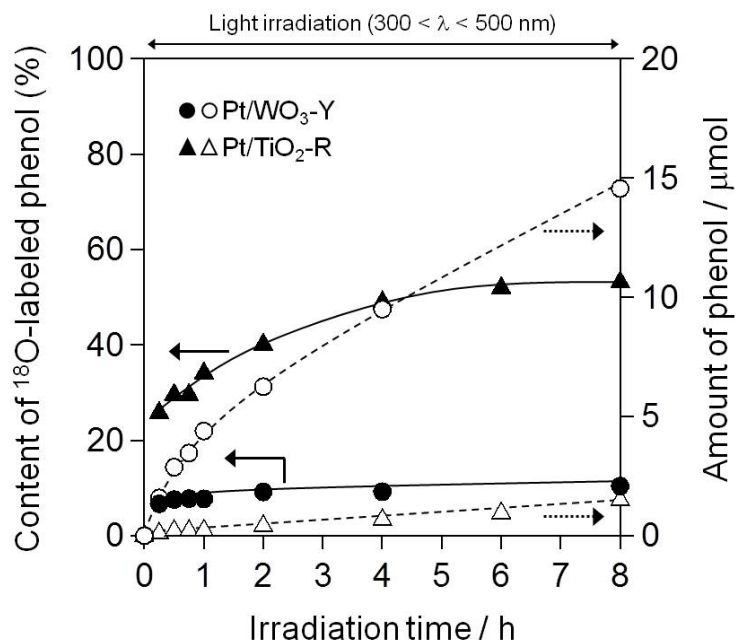


Figure S8. Time course of photocatalyzed phenol production from benzene on Pt/ $\text{WO}_3$ -Y and Pt/ $\text{TiO}_2$ -R samples. Reactions were conducted in normal water ( $\text{H}_2^{16}\text{O}$ ) containing benzene and molecular  $^{18}\text{O}_2$ .

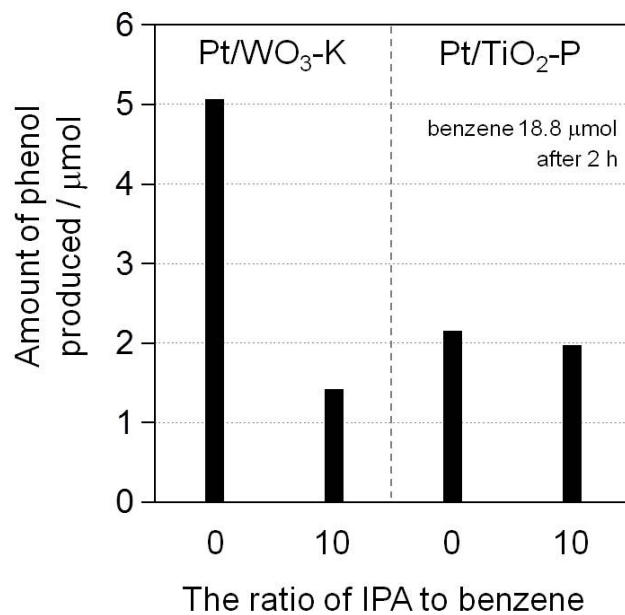


Figure S9. Amount of phenol produced from hydroxylation of benzene in the presence of IPA over Pt/ $\text{WO}_3$ -K and Pt/ $\text{TiO}_2$ -P photocatalysts.

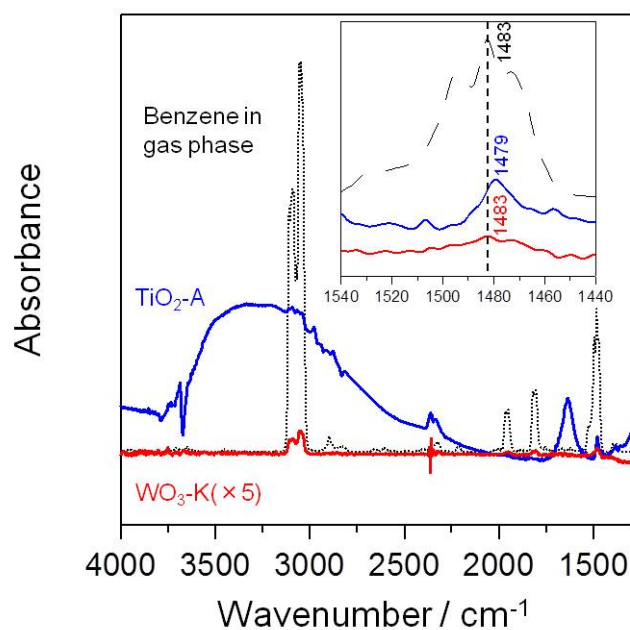


Figure S10. FT-IR subtraction spectra of benzene on photocatalysts.

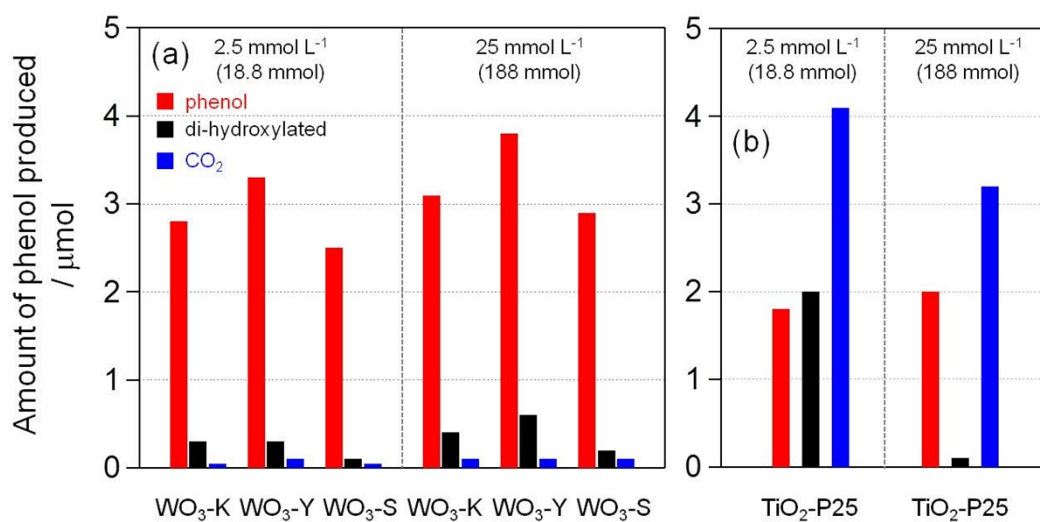


Figure S11. Influence of initial concentration of benzene on the amount of phenol, di-hydroxylated benzene and  $\text{CO}_2$  on (a)  $\text{Pt}/\text{WO}_3$  and (b)  $\text{TiO}_2$  photocatalysts during hydroxylation of benzene (Pt: 0.1 wt.%).

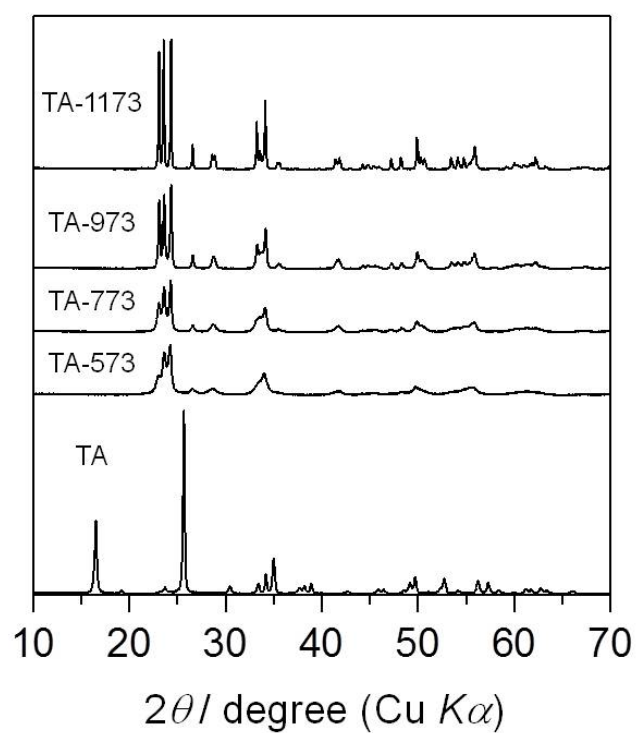


Figure S12. XRD pattern of  $\text{WO}_3$  samples obtained from tungstic acid ( $\text{H}_2\text{WO}_4$ , TA) as the W precursor.

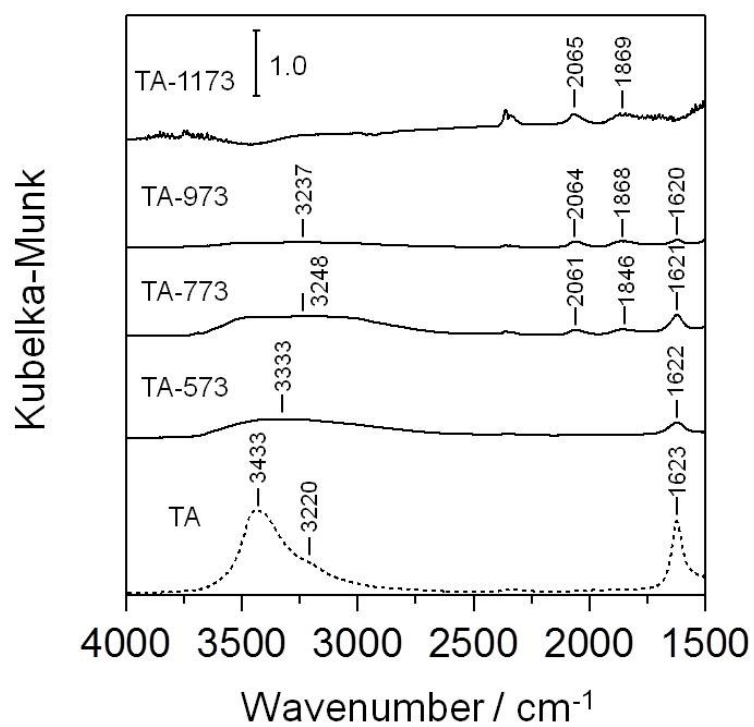




Figure S13. IR spectra of WO<sub>3</sub> samples obtained from tungstic acid (H<sub>2</sub>WO<sub>4</sub>, TA) as the W precursor.

Table S1. Direct hydroxylation of benzene to phenol on WO<sub>3</sub>-TA (prepared by calcination of tungstic acid powder) in normal water (H<sub>2</sub><sup>16</sup>O) containing benzene and molecular <sup>18</sup>O<sub>2</sub>.

Entry	Calcination temperature / K	Content of labeled phenol (%) (Amount of phenol produced / μmol)	
		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 μmol, Amount of solvent : 1.0 mL

Light source : 300 W Xe lamp (300 < λ < 500 nm)