

Photocatalytic conversion of benzene to phenol using modified TiO₂ and polyoxometalates

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Abstract

The application of photocatalytic reactions to organic synthesis has attracted interests in view of the development of environmentally benign synthetic processes. This study investigated the effects of various parameters (electron acceptor, surface modification, and the combination of photocatalysts) on the direct synthesis of phenol from benzene using photocatalytic oxidation processes. The OH radicals generated on UV-illuminated TiO₂ photocatalyst directly hydroxylate benzene to produce phenol, hydroquinone, and catechol. The addition of Fe³⁺, H₂O₂, or Fe³⁺ + H₂O₂ highly enhanced the phenol production yield and selectivity in TiO₂ suspension. Surface modifications of TiO₂ had significant influence on the phenol synthetic reaction. Depositing Pt nanoparticles on TiO₂ (Pt/TiO₂) markedly enhanced the yield and selectivity. Surface fluorination of TiO₂ (F-TiO₂) increased the phenol yield two-fold because of the enhanced production of mobile (free) OH radicals on F-TiO₂. Polyoxometalate (POM) in phenol synthesis played the dual role both as a homogeneous photocatalyst and as a reversible electron acceptor in TiO₂ suspension. POM alone was as efficient as TiO₂ alone in the phenol production. In particular, the addition of POM to the TiO₂ suspension increased the phenol yield from 2.6% to 11% (the highest yield obtained in this study). Reaction mechanisms for each photocatalytic system were discussed in relation to the phenol synthesis.

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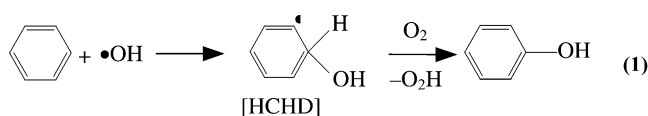
Keywords: Photocatalysis; Phenol synthesis; TiO₂; Polyoxometalate; Environmentally benign reaction

1. Introduction

Phenol is considered one of the most important industrial chemicals due to its wide usage such as a disinfectant, a precursor of phenolic resins, a reagent in chemical analysis, and a preservative for pharmaceutical aid [1]. In order to meet this high demand, phenol is being produced over 5×10^6 t/yr globally [2,3]. The current manufacturing process of phenol starts from benzene and consists of three steps (so-called *cumene process*): benzene alkylation to cumene (isopropylbenzene), cumene oxidation to cumene hydroperoxide, and decomposition of the latter to phenol and acetone. However, this multistage process has a low overall yield (less than 5%), requires high energy [2,3], and accompanies the generation of undesirable by-products such as acetophenone, 2-phenylpropan-2-ol, and α -methylstyrene. The development of alternative synthetic processes of

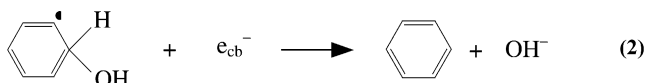
phenol that are more efficient and environmentally benign is highly desirable.

A direct synthesis of phenol from benzene has been tried using various methods: thermal catalysis [2–4], oxidation reaction using H₂O₂ [5,6], Fenton process [7–13], and semiconductor photocatalysis [14]. In Fenton process in which OH radicals are generated from the reaction of Fe²⁺ + H₂O₂, benzene can be directly converted into phenol through the reaction with OH radicals (reaction (1)). The hydroxyl radical adds directly to benzene to produce a hydroxycyclohexadienyl (HCHD) radical, which subsequently undergoes an H-atom abstraction by oxidants (e.g., O₂, Fe³⁺, and Cu²⁺) to yield phenol [9,11,12,15,16]. The OH radical addition to benzene is a diffusion-limited process ($k_{\text{OH}} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [17]:



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It is widely accepted that OH radicals can also be generated on illuminated TiO₂ surfaces. The photogenerated valence band (VB) holes oxidize surface hydroxyl groups into OH radicals. Therefore, TiO₂ photocatalysis has been applied to the hydroxylation of aromatic compounds for synthetic purposes [14,18,19] but the conversion efficiency in photocatalysis was lower than that of Fenton processes. Reported yield (Y_P) and selectivity (S_P) of phenol production from benzene were about 5% and 80–90% in Fenton process [7–13], and ca. 0.5% and 80% in TiO₂ photocatalysis [14], respectively. The efficiency of the photocatalytic phenol synthesis can be enhanced by optimizing various experimental parameters. First of all, the surface modifications of TiO₂ should change the reaction yield and selectivity. Photocatalytic reaction kinetics and mechanisms of surface-modified TiO₂ can be often very different from those of pure TiO₂ [20–24]. The kind of electron acceptors available is also important in determining Y_P and S_P because reductive electron transfers as well as reactions of OH radicals are involved in the overall reaction mechanism [25]. Conduction band (CB) electron transfer to electron acceptors (e.g., O₂) should increase Y_P because of the retarded charge pair recombination but the CB electron transfer to a HCHD radical regenerates benzene with decreasing Y_P (reaction (2)) [11]:



In addition, the OH radicals are so reactive and non-selective that most reactions of organic compounds with these result in oxidative degradation and mineralization. Therefore, minimizing the unwanted pathways such as the oxidative degradation and reductive back reaction (reaction (2)) is important for achieving selective hydroxylation.

This study investigated the hydroxylation reactions of benzene in several photocatalytic systems using TiO₂ as a heterogeneous photocatalyst and polyoxometalate (POM) as a homogeneous photocatalyst. Effects of various electron acceptors such as O₂, Fe³⁺, H₂O₂, Ag⁺, N₂O, and POM were tested to find out optimal conditions for the phenol synthesis. Surface-modified TiO₂ (platinization, fluorination, and silica loading) was also used to investigate how the surface properties affect the hydroxylation reaction.

2. Experimental

2.1. Materials and reagents

TiO₂ (Degussa P25, anatase:rutile = 8:2), HNa₂PW₁₂O₄₀ (Sigma), H₄SiW₁₂O₄₀ (Fluka), and H₃PMo₁₂O₄₀ (Fluka) were used as heterogeneous and homogeneous photocatalysts. Benzene (Aldrich), phenol (Junsei), hydroquinone (Aldrich), catechol (Aldrich), CH₃CN (Aldrich), FeCl₃·6H₂O (Kanto), AgNO₃ (Aldrich), and H₂O₂ (30%, Aldrich) were

used as received. For the preparation of surface-modified TiO₂ photocatalysts (i.e., metal-deposited TiO₂, surface fluorinated TiO₂, and silica-loaded TiO₂), the following reagents were used: HF (J.T. Baker), NaF (Aldrich), H₂Pt^{IV}Cl₆·xH₂O (Aldrich), Pd^{II}Cl₂ (Aldrich), CH₃OH (Mallinckrodt), and (CH₃CH₂O)₄Si [TEOS: tetraethylorthosilicate] (Aldrich). Gases (O₂ and N₂O) used were of >99% purity: O₂ was obtained from BOC Gases and N₂O from Dongbang Inc. Water used was ultrapure (≥18 MΩ cm) and prepared by a Barnstead purification system.

2.2. Surface Modifications of TiO₂

Metallization of TiO₂ surface (Pt/TiO₂ and Pd/TiO₂) was carried out using a photodeposition method [20]. An aqueous suspension of TiO₂ (0.5 g/L) with 0.1 mM chloroplatinic acid (H₂PtCl₆) or palladium chloride (PdCl₂) and 1 M methanol (electron donor) was irradiated with a 200 W mercury lamp, and then the metal-loaded TiO₂ particles were filtered, washed and dried. A typical Pt and Pd loading on TiO₂ was estimated to be ca. 3 and 2 wt.%, respectively, by comparing the initially added aqueous Pt (or Pd) concentration and the remaining aqueous Pt (or Pd) concentration after photodeposition that were determined by inductively coupled plasma-atomic emission spectroscopy. The TEM image of Pt/TiO₂ exhibited Pt particles with a size range of 1–4 nm dispersed on TiO₂ particles (20–30 nm diameter). Surface fluorinated TiO₂ (F-TiO₂) was obtained by adding 10 mM NaF to the TiO₂ suspension (1 g/L) at pH 3.4–3.7 [21,22]. Rutile TiO₂ was prepared from selectively etching out the anatase phase of P25 TiO₂ by HF solution (10 wt.%) to obtain rutile particles with comparable particle size to P25 [23]. The fluoride contaminants adsorbed on the rutile surface were removed by washing with alkaline (1N NaOH) solution. Silica-loaded TiO₂ (SiO₂/TiO₂) was prepared by mixing 0.5 g of TiO₂ with 0.1 mL TEOS, drying at room temperature and subsequent heating at 700 °C for 1 h.

2.3. Photochemical synthesis and product analysis

Photocatalytic benzene conversion reactions were carried out in aqueous TiO₂ suspension containing benzene (20 mM) and acetonitrile as a co-solvent (typically 4 vol.%). Plain or surface-modified TiO₂ powder (25 mg) was suspended in 24 mL distilled water, and an aliquot of acetonitrile (1 mL) containing benzene (50 μL) was added to the suspension and mixed well. When necessary, electron donors, acceptors or other reagents were added to the suspension. A 450 W Xe arc lamp (Oriel) was used as a light source. Light passed through a 10 cm IR water filter and a cutoff filter (λ > 300 nm), and then the filtered light was focused onto the reactor. Sample aliquots were withdrawn by a 1 mL syringe intermittently during illumination and filtered through a 0.45 μm PTFE filter (Millipore) to remove TiO₂ particles. Benzene, phenol, and other aromatic

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