



Competitive role of structural properties of titania–silica mixed oxides and a mechanistic study of the photocatalytic degradation of phenol



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ABSTRACT

TiO₂–SiO₂ mixed oxide materials were hydrothermally synthesized and the photocatalytic degradation of phenol under UV-irradiation was evaluated. We also demonstrated that varying the co-solvent, modulates the structural properties of the materials. In particular, the use of non-polar co-solvents such as toluene seemed to increase the crystallinity, surface area, and pore diameter while the crystallite size of titania seemed to change little. A comprehensive characterization using surface and bulk techniques evidenced the role of porosities, crystallinity, and Ti–O–Si linkages of the mixed oxides as significant factors that contribute to the degradation of phenol. The TiO₂–SiO₂ mixed oxide material prepared using only ethanol as the solvent showed 24% degradation of phenol after 120 min of irradiation whereas other mixed oxide materials degraded phenol more efficiently (57% to 100%) in the same duration of time. The higher photocatalytic activities of the mixed oxide materials prepared using non-polar solvents is attributed to a combination of factors that include higher Apparent Surface Coverages of Ti–O–Si heterolinkages, larger pore sizes, and most importantly higher crystallinities of the titania phase. Larger pore sizes enabled better transport of reactant molecules and products to and from the active sites (Ti–O–Si heterolinkages) and the higher crystallinities of the titania phase helped in minimizing the electron–hole recombination in these photocatalysts, and thus resulted in high degradation efficiencies.

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1. Introduction

Persistent pollution of our hydrosphere is one of the major socio-economic challenges in the world today. The existing techniques employed to curb pollution are energy inefficient and are still prone to the formation of secondary toxic intermediates and by-products that may require intricate procedures for remediation. Organics such as phenol and phenolic compounds are major components of a myriad of industrial chemicals and as such have a prevalence in waste water [1]. Ingestion of excess amounts of phenol poses a threat to organ and tissue functions and thus there is an impetus for their complete removal from water sources for human consumption [2–4].

The advanced oxidation process (AOP), however, has emerged as an attractive technology that promises a renewable and energetically sustainable approach through which the complete mineralization of highly toxic organic compounds such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in water can be achieved [5–7]. AOP techniques for

water purification are mainly based on the hydroxyl radical ($\cdot\text{OH}$) formation and their eventual reactivity with the organic molecules. Jaeger and Bard [8] evidenced the presence of $\cdot\text{OH}$ radicals in irradiated aqueous suspensions of titanium dioxide (TiO₂) based composites using spin trapping agents *via* electron spin resonance spectroscopy, and several investigators later credit these highly reactive species as responsible for the degradation of organic molecules [2,7,9].

TiO₂ has been widely used as a photocatalyst for pollutant degradation due to its photochemical stability, low toxicity, and relative affordability [10]. However, because of the notion that limited efficacy of the semiconductor may be related to its low surface area and hydrophobicity, several investigators have opted to incorporate TiO₂ in supports such as silica [11–14], alumina [12], zeolite [15–17], and activated carbon [15,18] etc. to enhance the efficiency, mechanical, and thermal stability. Even though most of the mixed materials show good efficiency, silica is a popular support of choice because it is inert, transparent to UV light, porous, and can facilitate the dispersion of photocatalysts. In numerous literature studies, improved dye adsorption has been attributed to increased hydrophobicity due to the presence of a silica supporting phase. This has prompted the premise that the hydrophobic phase improves adsorption capacities and consequently enhances

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the catalytic activity of TiO₂ based mixed oxides for all organic substrates [11,12]. This may not universally hold truth as demonstrated in this study. Elsewhere, the addition of SiO₂ phase to TiO₂ does not only prevent the phase transformation from anatase to potentially inactive rutile, but it also facilitates in the effective dispersion of the anatase crystallites [19,20] that serve as photoactive centers essential for the cleavage of organic pollutants and their degradation to innocuous intermediates and by-products [21].

Several elaborate methods have been implemented for the preparation of TiO₂-SiO₂ mixed oxides such as flame hydrolysis, and chemical vapor deposition (CVD); however, the sol-gel process provides an avenue through which structural features can be tuned by simply optimizing the synthesis recipe to achieve materials of enhanced properties [11,22–24]. In a recent publication, we successfully explored the effect of various co-solvents on the physicochemical properties of hydrothermally synthesized TiO₂-SiO₂ mixed oxide materials, and revealed that introduction of aromatic co-solvents such as benzene, toluene, and *p*-xylene induces the gelation rate, expands the pore cavities, and results in materials of high surface area due to minimized surface tension of the pore walls [25]. The type of co-solvent used in the synthesis of the material modulates the porosities resulting in varied diffusion properties of reactant and product molecules accessing and leaving the pores, respectively, hence resulting in varying activities at the initial stages of the reaction. This new work extends and conceptualizes the role of textural properties in providing a detailed mechanistic study for the identification of degradation products formed during the photocatalytic degradation of phenol. UV illumination of the semiconductor photocatalyst results in the formation of charge carriers (electrons and holes) that eventually form highly reactive oxidation species (ROS) [26–28] such as ·OH, O₂^{·-}, ·OOH, HOOH, or OH⁻ [29–31]. At a constant light intensity, catalyst amount, temperature, and solution pH, the concentration of all intermediates formed during the degradation process were quantified by using high performance liquid chromatography (HPLC) in this study.

Titania-silica materials have been widely studied for a variety of catalytic reactions involving selective oxidation, cumene dealkylation, 2-propanol dehydration, 1,2-dichloroethane decomposition, phenol amination etc. [32]. Thus, the unique chemical and physical properties exhibited by titania-silica provide a basis for the fundamental understanding of structure-activity relationship in mixed oxide systems. TiO₂ supported on silica has been extensively investigated for the degradation of a variety of dyes [11,12,33–35], non-aromatics [36–38], pesticides [39,40], and benzyl compounds [14,41,42] in aqueous phase reactions. Although TiO₂-SiO₂ photocatalysts have been also employed for photocatalytic degradation of phenol [13,14,30,31,43–46], existing literature have only examined the effects of the particle size of titania and its loading, and lack several key factors that includes: (i) a systematic and thorough characterization of the surface properties of the TiO₂-SiO₂ materials, (ii) comprehensive and detailed investigation of textural properties of the TiO₂-SiO₂ materials to understand the role of porosities, (iii) effect of Ti-O-Si heterolinkages towards the degradation of phenol, (iv) detailed identification and quantitative analysis of the reaction intermediates and photodegradation products, and (v) elucidation of the reactive oxidative species that are responsible for the degradation process.

In addition, some earlier reports reported kinetics and product identification of phenol degradation by TiO₂ and metal doped TiO₂ [47–49], but such studies pertaining to the mechanistic pathways using titania-silica photocatalysts are still missing in the literature, and is the motivation for this work. We thus provide new knowledge implicating Ti-O-Si hetero linkages, pore sizes of the materials, and crystallinity as factors that optimally contribute to

the overall photocatalytic efficiencies in TiO₂-SiO₂ mixed oxide materials.

2 Experimental

2.1 Materials and preparation

Commercially available tetraethylorthosilicate (TEOS, Acros 98%), titanium isopropoxide (Ti(ⁱOPr)₄, Acros 98+%), anhydrous ethanol (EtOH, Pharmco-AAPER, ACS/USP grade, 200 proof), conc. nitric acid (HNO₃), pentane, hexane, nonane, benzene, toluene, *p*-xylene (all ACS grade) were used as received to prepare the TiO₂-SiO₂ mixed oxides. Phenol (Acros, 99+% ACS grade), hydroquinone (Sigma, >99%), maleic acid (Alfa Aesar), acetic acid (Fisher), fumaric acid (Acros), pyrogallol (Alfa Aesar, 99% ACS Grade), catechol, and methanol (Acros, 99.9% HPLC grade) were purchased and used for the HPLC studies without further purification. triethanolamine (TEA, Acros, ACS grade), sodium hydroxide (Acros), terephthalic acid (TPA, Acros, 98%), and sodium bisulfite (Acros) were used as received. Nano pure water (resistivity >18 Ω cm) was used to prepare the solution mixtures. Benzoquinone (TCI America, 98%) was purified by sublimation to obtain bright yellow crystals and subsequently used in the product identification analyses.

2.1.1. Synthesis of TiO₂-SiO₂ mixed oxides (HTS-01 to HTS-06)

A series of TiO₂-SiO₂ mixed oxide sols were prepared by simultaneous hydrolysis and condensation of TEOS and (Ti(ⁱOPr)₄) and varying the co-solvents. In a typical synthesis to obtain titania-silica mixed oxides with the molar ratio of Ti:Si=1:1, 1.65 mL of TEOS was added slowly into a solution containing 9 mL of co-solvent dissolved in 9 mL of EtOH under vigorous stirring in a Teflon liner. The hydrolysis process was initiated by the introduction of 1 mL of H₂O and the process was catalyzed by the addition of 100 μL of conc. HNO₃. (Ti(ⁱOPr)₄) was added drop wise to ensure homogenous distribution and the suspension left to stir until gelation. The resultant gels were subjected to hydrothermal treatment in a Thermolyne autoclave reactor furnace and heated to a temperature of 120 °C for 14 h. The gelatinous precipitate attained was filtered, washed, and oven dried at ~80 °C for 9 h. These powders were then ground and calcined in static air at 500 °C for 6 h at a heating rate of 3 °C min⁻¹.

2.1.2. Synthesis of pure TiO₂ (HTS-07)

The sample HTS-07 (containing only TiO₂) was prepared as a control by adding the titania precursor (Ti(ⁱOPr)₄) into a mixture of 9 mL of EtOH and 9 mL of toluene, and 100 μL of conc. HNO₃ under stirring at 300 rpm followed by the drop wise addition of 1 mL of water with rapid stirring till gel formation. It was then subjected to hydrothermal treatment in an autoclave at 120 °C for 14 h. The gelatinous precipitate attained was filtered, washed, oven dried at ~80 °C for 9 h, then ground and calcined by heating in air at 500 °C for 6 h at heating rate of 3 °C min⁻¹. The product obtained was a white powder.

2.2 Characterization

Powder X-ray diffraction patterns were recorded at ambient conditions using a Rigaku Ultima IV instrument with Cu Kα radiation (λ = 1.5408 Å), operated at an accelerating voltage of 40 kV, and emission current of 44 mA. The scanned range was between 2θ = 20° and 80° with a step size of 0.02° and the scan speed was 1° min⁻¹. The crystallite sizes of the titania phase in the mixed oxide materials were determined by applying the Debye-Scherrer equation to the peaks at 2θ = 48.3°, 62.9°, and 75.4°. The diffraction patterns were analyzed using PDXL software provided by Rigaku. Raman spectra

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