Relationship concerning the nature and concentration of Fe(III) species on the surface of TiO₂ particles and photocatalytic activity of the catalyst

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Abstract

There have been contradictory results concerning the effect of doping TiO₂ with Fe(III) upon its photocatalytic activity. We believe that this is due to the method used in adding the Fe(III) to TiO₂. This paper addresses this issue by using a precise adsorption process for loading stable aqueous suspensions (sols) of TiO₂ doped with Fe(III). In this manner, we control the speciation of Fe(III) on the surface of TiO₂ and subsequently use these loaded sols to produce stable thin-film photocatalysts. Adsorption isotherms for these systems at different pH (2.0 and 2.5) values showed that both pH and the concentration of Fe(II) in solution influence the adsorption density of Fe(III), the stability of the resulting sols, and the speciation (degree of polymerization) of Fe(III) ions on the surface of the TiO₂ nano-particles. UV-Vis spectroscopy on selected systems was the technique employed to confirm these results. The pore structure of the resulting gels (xerogels) prepared from these sols, as well as thermal stability of porous materials prepared by firing the xerogels have been determined by measuring N₂ adsorption as a function of firing temperature. Thermal analysis (TG–DTA) studies on xerogels obtained from some of these systems showed that the presence of Fe(III) species on the TiO₂ retards the conversion of anatase into rutile and therefore increases the thermal stability of the gel microstructure. Lastly, porous films, resulting from the casting of the sols on glass rings and subsequent firing, were used in photocatalytic studies. In the presence of UV light, these supported films were capable of degrading ethanol in the gas phase. While photocatalytic activity for Fe(III) loaded TiO₂ films is less than for TiO₂ films without Fe(III), the speciation of Fe(III) on the surface directly influences the behavior of the intermediate—acetaldehyde—formed in this reaction. Since we have only evaluated the effect of iron speciation on the degradation of ethanol, other target species may be influenced either advantageously or deleteriously depending upon the state of Fe(III) on the surface of TiO₂ photocatalysts.

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1. Introduction

TiO₂ is considered the most common photocatalyst employed in oxidation studies of organics in both the aqueous and gas phase [1–10]. Unfortunately, photocatalytic oxidation rates for many target pollutants have been too slow to be of practical interest. As such, a large amount of research has been performed

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on means to speed up these processes or reduce the volume of photocatalytic reactors by optimizing certain system parameters, e.g. light intensity [11–13], O₂ concentration [14], temperature [15,161, reactor geometry [17,18], etc. Efforts have also been made to improve the photocatalytic activity of the TiO₂ itself. In this respect, numerous studies have focused on the relationship between chemical, crystallographic and morphologic properties of the TiO₂ and its photocatalytic activity [19,20]. In addition, other efforts have been made to improve upon photocatalytic activity by adding dopants to TiO₂. This latter research can be divided into two categories: one is associated with shifting the absorption band gap edge to the red in order to enhance activity in visible portion of the spectra. Some researchers have pursued doping TiO₂ with transition metals as a way to shift the absorption edge to larger wavelengths. For example, Anpo [21] claimed to have successfully shifted the absorption edge of TiO₂ to the red by doping TiO₂ with Cr(III) ions. The second category of research has been to increase the photocatalytic activity of TiO₂ in the near UV. In one aspect of this category, Fu and Anderson have studied the influence of surface acidity and pore structure of the photocatalyst on binary mixtures of oxides (e.g. TiO₂-ZrO₂, TiO₂-SiO₂) [22].

In a second aspect of improving photocatalytic activity, the recombination of holes and electrons in activated TiO₂ (nanoseconds) has also been a subject of intense interest [23,24]. It is generally agreed that a lower rate of recombination will translate into an increase in photoefficiency. The most common method proposed to lower charge recombination rates has been to dope TiO₂ with transition metals [24–27]. Metal ion dopants may act as electron or hole traps and, consequently, alter electron-hole pair recombination rates. Indeed, special efforts have been dedicated to doping TiO₂ with Fe(III) [24,26,28]. This interest is based on the idea that Fe(III) ions act as shallow charge traps in the TiO₂ lattice [29–31]. However, the role of Fe(III) dopants in TiO₂ is controversial. Some authors suggest the Fe(III) behaves as an electron/hole recombination center [23,32]. Other authors have postulated that the role of the dopant ion is to favor electron-hole separation, which enhances photoactivity [24,29,33,34]. To put this controversy into a more realistic and practical catalytic perspective, Ranjit and Viswanathan [24] have indicated that Fe(III)-doped TiO₂ improves photocatalytic activity up to a certain doping level (1.8 wt.% of Fe(III)). In contrast, Litter and Navio [26] showed that photocatalytic oxidation of compounds such as toluene and benzaldehyde were degraded more slowly on Fe(III)-doped TiO₂ than pure TiO₂. As a result of this controversy, some authors have concluded that the doping technique seems to be one of the most important factors for controlling the reactivity of Fe(III)-doped titania [26,27].

The ultimate objective of this study was to investigate the relationship between the nature and concentration of Fe(III) species on the surface of TiO₂ particles and its photoactivity. However, to reach this goal, we had to first control the density and the chemical nature of the Fe(III) species on the surface of TiO₂. It is well accepted that adsorption from an aqueous solution of ions (adsorbates) by metal oxide particles (adsorbents) produces evenly distributed monolayers of adsorbates on the surface of the particle [35]. For a given adsorbate/adsorbent system, the density and nature of the ions on the surface normally depends on the concentration of the ion in the solution and on the pH of the suspension [35]. In this paper, we have employed this methodology in order to prepare Fe(III)-doped TiO₂ sols having different Fe(III) adsorption densities with differing surface speciation of adsorbed Fe(III). From the results of these adsorption studies, we have chosen three representative systems as photocatalysts. These systems are investigated in terms of: the nature of the Fe(III) on the TiO₂ surface by UV-Vis absorption spectroscopy, the thermal properties and pore structure of resulting xerogels by TG-DTA and N₂ adsorption respectively, and by studying their photocatalytic behavior using thin-films of these sols coated on glass supports employing ethanol as a probe molecule.

2. Experimental

2.1. Materials

2.1.1. TiO₂ sols

Stable sols of TiO₂ nano-particles were prepared following the method of Anderson and co-workers [22,36,37]. In this method, titanium tetra-isopropoxide (Ti(OC₃H₇)₄ (Aldrich Milwaukee, WI) was subjected to an acidic hydrolysis at a volumetric mixing ratio of 1HNO₃:1.4H₂O:1.4Ti(OC₃H₇)₄ and subsequent
condensation of the hydrolysis products. The resulting white TiO2 precipitate was peptized in acid conditions at room temperature, resulting in a stable suspension (sol) [38]. The sol was then dialyzed against Milli-Q water until the pH of the solution outside of the dialysis membrane tubing (Spectra Por, molecular cut-off = 3500 MW) approached 3. The final product was a TiO2 sol (19.3 g/l) having particles in the neighborhood of 5 nm. This sol is stable for years.

2.1.2. Fe(III)-doped TiO2

Aliquots of the TiO2 sol were titrated with different quantities of a 0.1 M Fe(NO3)3 aqueous solution (Fe(NO3)3·9H2O: Fisher Scientific, 98.9% purity). Titrations were done at constant temperature (25 °C), constant pH (2.0 and 2.5) and constant volume ([TiO2 sol]initial = 19.3 g/l). Titration samples were left to equilibrate for 10 h and then corrected for pH if needed. The adsorption of Fe(III) by the TiO2 particles was calculated from the difference between that of the added Fe(III) and that measured in the supernatant after equilibration. To separate suspended particles from their solution, samples were centrifuged using Centricon® Plus-20, Millipore filters. The Fe(III) concentration in the supernatant was measured by inductively coupled plasma emission spectroscopy using a Perkin-Elmer Plasma 1000/2000 spectrometer.

2.1.3. Photocatalysts

In this study, the photocatalyst consisted of thin-films of TiO2 and Fe-doped TiO2 deposited on glass cylinders, or rings (cylinders of 4 mm o.d. × 3 mm i.d. × 12 mm length) [38]. The thin-films were cast on rings by dip-coating. In this process, a string of rings was soaked in the sol for 1 min and then withdrawn at a speed of 4 mm/s. After drying the coated rings at room temperature, they were subsequently heated at 100°C for 1 h. This process was repeated three times. After depositing the third layer, the rings were removed from the string and fired at 300 °C for 1 h at a heating rate of 2°C/min. The coating of the catalyst on the glass rings appeared to be uniform as observed under an optical microscope.

To determine the mass of catalyst employed in this study, an ammonium sulfate (Fisher Scientific, Pittsburgh, PA) [(NH4)2SO4] solution was added to 10 ml of hot concentrated H2SO4. After the (NH4)2SO4 completely dissolved in the H2SO4, five catalyst-coated glass rings were added to the solution. The samples were covered and carefully heated for 1 h at ca. 80°C. The resulting solution was filtered and diluted to 50 ml with ca. 1M NaOH to obtain a slightly acidic clear solution. Elemental analysis of Ti was subsequently performed using inductively coupled plasma. This analysis was repeated three times. The average total mass of catalyst deposited on each ring was determined to be 0.05 ± 0.001 mg TiO2.

2.1.4. Fe(III)-doped TiO2 xerogels

Selected Fe-doped TiO2 sols, differing in adsorption density and pH of preparation, became brown transparent sheets (xerogels) when they were left to dry at room temperature. These self-standing wafers of xerogels were used as surrogates of the thin-film materials in order to characterize some of their properties, such as thermal behavior and pore structure.

2.2. Materials characterization

2.2.1. Thermal analysis

The physical chemical transformations that the Fe(III)-doped TiO2 materials may suffer on heating were studied by TG–DTA. These studies were performed on ground xerogels of these materials, between room temperature and 800°C, using a Netzsch STA 409 simultaneous thermal analysis system. Samples were heated at a rate of 3 °C/min under a dynamic dry air atmosphere of 20 ml/min.

2.2.2. Pore size distribution and surface area

The pore structure and specific surface area of Fe(III)-doped TiO2 xerogels were determined by N2 adsorption/desorption isotherm analysis (BET method). The measurements were performed using a Micromeritics ASAP 2000 analyser. Pore size distribution was calculated in two ways: one analysis was based on the Kelvin equation using the BJH method and the other was performed by density functional theory (DFT) using a model for cylindrical pores [42].

2.2.3. Fe(III) speciation using UV-Vis spectroscopy

The absorption spectra of Fe(III)-doped TiO2 sols, were recorded on a HP8452A diode array UV-Vis spectrophotometer. TiO2 sols, having the