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Effect of molecular functionality on the photocatalytic oxidation of gas-phase mixtures

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ABSTRACT

Developing an effective air purifier for indoor air quality (IAQ) purposes requires knowledge of the reaction rate of target compounds in the presence of other compounds that compete favorably with the target compounds for surface sites. To address this issue, the photocatalytic oxidation (PCO) of five C3 organic compounds on a sol-gel derived TiO_2 thin-film catalyst was examined. Photocatalytic degradation of the five compounds was first compared in single component experiments at 50% relative humidity. The photocatalytic oxidation reaction rates proceeded in the following order: 1-propanol > propanal > propanone > propene > propane. The order of reaction rates was partially explained by considering the intermolecular forces of attraction that exist between the gas-phase molecules and the hydrated titania surface, with the lone exception of the ketone. A model that incorporates Henry's law constant and hydroxyl radical reactivity was successful at predicting PCO reactivity. Relative photocatalytic degradation was also studied using multi-component experiments. Multi-component experiments with propanone + propene, propanal + propanone, and ethanol + propanone were conducted. In each case it was observed that compounds with stronger binding energy to the photocatalyst surface displaced compounds with weaker binding energies and inhibited their further reaction until the stronger binding species was oxidized to sufficiently low levels. Further investigation of relative binding energies of compounds of interest for PCO applications should be pursued in the future through combinations of experimental studies and theoretical molecular modeling techniques.

1. Introduction

Photocatalysis is an interesting phenomenon that has been vigorously pursued in both industrial and academic environs over the last several decades [1–8]; it was reported as long ago as 1964 [9]. This is due, in large part, to the potential for mineralizing trace contaminants in both air and water to innocuous products (e.g., CO_2 and H_2O). A plethora of air and water purifiers based on photocatalytic technology have been developed, deployed as prototypes in various environments, and marketed throughout Japan, Europe, and North America. Claims on the performance of these products are rarely realized in practice, since there exists a lack of fundamental understanding of the photocatalytic process, which results in the inability to predict reactor (purifier) performance in a real-world environment.

Our joint interest in photocatalysis arises from the application of this technology to Indoor Air Quality (IAQ) improvement. Developing an effective air purifier for IAQ purposes requires the ability to predict the performance of the device over the range of variability of the appropriate atmospheric variables (e.g., temperature, humidity, species, and concentration) and design variables (e.g., flow rate, light intensity distribution, and catalyst surface area). This means that one needs to measure or estimate rate constants for the photocatalytic oxidation (PCO) of the primary contaminants of interest over the expected range of concentrations and atmospheric conditions for the catalyst of choice and in the range of light intensity of choice. Furthermore, one needs to understand what the effect of mixing all these species into one atmospheric soup has on the individual rates.

Several groups have measured PCO removal rates of single contaminant species [10–12] and mixtures [13–19] that are important to IAQ. Several of these studies showed a correlation between molecular functionality, structure, and/or properties and PCO removal rates. For example, Obee and Hay [14] demonstrated oxidation rates for C4 species in the order: 1-butanol > 2-butanone > 1-butene > *n*-butane and hypothesized that the ranking followed the order of intermolecular forces attracting the gas-phase species to the polar catalyst surface. They further showed that PCO

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rates increased with molecular mass for alkanes. This is consistent with the expected increase in London forces. They hypothesized that the hierarchy of intermolecular forces of attraction between the gas-phase molecules and the polar partially hydroxylated titania surface could be used to both explain the observed rates and predict the PCO rates for species that had not been measured in the laboratory.

Hodgson et al. [19] studied PCO removal rates in a prototype reactor of a 27 compound mixture to simulate an indoor air environment. Their observed oxidation rates of (represented) chemical classes followed the approximate order of alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic and alkane hydrocarbons > halogenated hydrocarbons. Their results are consistent with Obee and Hay [14] and with the results reported in this paper. They attempted to correlate their conversion efficiency with a variety of parameters including: Henry's law constant, octanol-water partition coefficient, vapor pressure, aqueous solubility, and gas-phase reaction rates with hydroxyl radicals; correlation with Henry's law constant was found to be the single most accurate descriptor. They hypothesized that in their observed humidity range (42–65% RH), physisorbed water on the surface would be expected to be on the order of ca. 2 monolayers [20], and that interaction of the gas-phase molecules with the catalyst surface could be related to gas dissolving into aqueous solution. In this humidity range, the photocatalyst surface contains a significant amount of physisorbed water, and only about 3–5% of the water is hydrogen bonded or chemisorbed [19,21].

It is apparent from these studies that PCO rate constants are related to the forces of attraction between gas-phase molecules and the catalyst surface and that there is significant competition for adsorption on the catalyst surface between all the components in the gas phase. The exact nature of the catalyst surface depends on the photocatalyst composition, the crystalline phase, the surface morphology, the extent of chemisorptions, and so on. Physisorption on the surface depends on the concentration of the various species in the gas phase and the nature of the surface. At low concentrations, species may be expected to react independently of each other; however, at higher concentrations, the species that dominate the surface would be expected to dictate reaction rates.

The study reported here is concerned with the PCO removal rates of C3 species separately and in a mixture using a recirculating reactor. Utilization of a recirculating reactor has several advantages over reactors that employ a single-pass approach where the contaminant feed stream only passes through the reactor once. First, an entire kinetic data set can be obtained with a single experiment (generally lasting only a few hours or less) using the recirculating design. Conversely, a single-pass approach requires numerous readjustments of the flow rate to catalyst ratio, followed by measurement of degradation, to yield a sufficient number of data points required for a kinetic analysis. Therefore, the time required for single-pass kinetic studies is significantly larger than with a recirculating design. A second major advantage of using a recirculating design is that multiple compounds can be introduced into the system to directly study the co-adsorption interference effects of different chemical classes, as was done in this study.

2. Experimental

2.1. Catalyst preparation

Stable sols of titanium dioxide (TiO_2) nanoparticles were prepared according to the method of Xu and Anderson [22]. In this method, titanium tetra-isopropoxide $Ti\{OCH(CH_3)_2\}_4$ (Aldrich, Milwaukee, WI) was subjected to an acidic hydrolysis by addition to an aqueous solution of nitric acid. The volumetric mixing ratio was 1 HNO_3:136.4 H_2O:11.4 $Ti\{OCH(CH_3)_2\}_4$. The resulting TiO_2 precipitate was peptized at room temperature for 3 days resulting in a stable sol. This acidic sol was then dialyzed for 3 days using a dialysis membrane (Spectra/Por® 3 membrane, 3500 MW cutoff, Spectrum, Laguna Hills, CA) to a final pH of 3.5. Three layers of active catalyst material were deposited onto borosilicate glass cylinders or "rings" (5 mm o.d. × 3 mm i.d. × 10 mm long) that were pre-cleaned prior to coating. The coatings were applied by dipping the rings in the sol and then withdrawing at a rate of 30 cm/min. After applying each layer, the rings were dried in air at 120 °C for 1 h. The coated rings were then fired in air in a furnace at 350 °C for 3 h using a ramp rate of 1 °C/min.

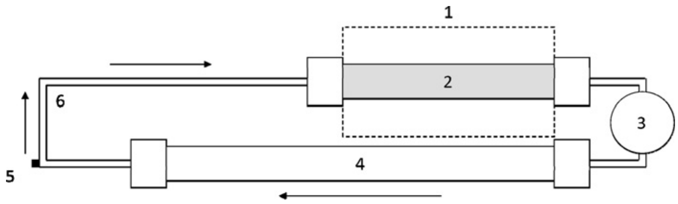

Fig. 1. Recirculating reactor design. 1 – temperature-controlled chamber with two UV light sources; 2 – illuminated glass tube randomly packed with 30 catalyst-coated glass rings; 3 – recirculating pump; 4 – non-illuminated empty glass tube (not packed with catalyst-coated glass rings); 5 – sampling port (septum); 6 – stainless steel tubing.

The mass of catalyst used in this study was measured by digesting a subsample of catalyst-coated rings in hot acid, followed by determination of titanium by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The previously reported digestion procedure [7,23–25] involved adding ∼4 g of ammonium sulfate [$(NH_4)_2SO_4$] to 10 mL of hot concentrated sulfuric acid (H_2SO_4). After the $(NH_4)_2SO_4$ completely dissolved in the H_2SO_4, five catalyst-coated glass rings were added to the solution. The sample was then covered and carefully boiled for 1 h. The acidic solution containing the digested catalyst was diluted to 25 mL with ultra-high purity water; 3 mL of the concentrated solution was then further diluted to 100 mL using ultra-high purity water. Visual inspection of the digested rings suggests that the digestion process completely removed all of the catalyst coating. The sample was analyzed for titanium by ICP-AES using a Varian Liberty Series II Sequential ICP (Varian, Inc., Palo Alto, CA). The total mass of catalyst deposited on each ring was determined to be 0.23 mg TiO_2.

2.2. Reactor apparatus

The photocatalytic oxidation experiments employed a recycling loop as shown in Fig. 1. The recycling loop consisted of a temperature-controlled chamber containing two 4 W fluorescent UV light sources (F4T5BL, EIKO Brand, Bulb Direct Co., Pittsford, NY), a 29 mL glass tube (1.5 cm i.d. × 16.5 cm long) that held 30 catalyst-coated glass rings packed randomly in the center, a non-illuminated 53 mL empty glass tube (1.5 cm i.d. × 30.5 cm long) to add additional volume to the loop, a sampling port (septum), stainless steel tubing, and a recirculating diaphragm pump with chemically inert components (Model UNMP-30 modified with PTFE-coated diaphragm and Kalrez valves and seals, KNF Neuberger, Inc, Trenton, NJ). The total mass of catalyst was 6.9×10^{-3} g and the void volume of the reaction loop was 100 mL. By suitable adjustment of a cooling air stream, the reactor air temperature (measured by placing a J-type thermocouple in a glass insert located at the center of the packed bed) was maintained at a temperature of 30 °C. The two fluorescent light bulbs were spaced at opposite sides (at a radius of 2.5 cm from the centerline) of the glass tube containing the catalyst-coated glass rings. These bulbs produced a strong peak cen-