

Photocatalytic Oxidation of Gas-Phase Compounds in Confined Areas: Investigation of Multiple Component Systems

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Abstract

Photocatalytic oxidation (or photocatalysis) can be used to convert undesirable compounds present in gas or liquid samples into carbon dioxide and water. Photocatalyst materials are “self-generating”, making the process especially attractive in moderate and long-term applications where consumable materials are to be avoided (e.g., Space Shuttle cabins and in the International Space Station). Photocatalytic studies have traditionally been performed in the presence of a single test compound—a single component system. However, real world application of the technology will most certainly occur in the presence of multiple reactive compounds. In this study, single component photocatalysis experiments were performed on a set of three-carbon compounds that contain different functionality (propane, propene, acetone and propanal). The relative time required for degradation of the compounds was directly dependent upon the predicted affinity for the catalyst surface. In multi-component experiments, compounds with lower affinity for the catalyst surface did not degrade until the higher affinity compounds were reduced to insignificant levels.

Background

The presence of toxic vapors from a variety of sources represents a significant burden to indoor air environments. Chemicals such as tetrachloroethylene (used extensively in dry cleaning establishments), formaldehyde (used in the manufacture of carpeting, furniture, and particleboard), and the vapors from liquid organic solvents (used frequently in the printing industry and in analytical laboratories) are often present at elevated levels in enclosed environments, especially those with limited ventilation. Gas-phase photocatalytic oxidation (or photocatalysis) over UV-illuminated semiconductors constitutes a very promising technique for the destruction of organic and inorganic contaminants (Peral and Ollis 1992, Raupp and Junio 1993, Sauer and Ollis 1994, Obee and Brown 1995, Fu et al. 1996a, Alberici and Jardim 1997, Zorn 1999 and 2000), especially in situations where consumable materials are undesirable. Unlike traditional catalytic processes that occur at high temperatures (e.g., >300°C), photocatalysis occurs readily even at near-ambient temperatures. Unlike filtration, which merely transfers contaminants to a different phase (e.g. via adsorption onto activated carbon) and requires the replacement and disposal of depleted treatment units, photocatalytic treatment systems are “self-generating”. Photocatalytic processes chemically oxidize (or convert) organic compounds into carbon dioxide and water—complete oxidation refers to a reaction in which all

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of the carbon in the target compound is converted to carbon dioxide. Since the photocatalytic material is not consumed during the oxidation process, photocatalysis is applicable to long-term situations where the supply of consumable materials becomes a major concern (i.e., space-related applications).

While precise reaction mechanisms can vary for different compounds, photocatalytic oxidation generally requires the following conditions: 1) sufficient illumination of a semiconductor photocatalyst with light of energy greater than the semiconductor's band-gap (often, this requires UV light); 2) a high surface area of photocatalyst material (greater than 100 – 150 m²/g); and 3) the presence of an oxidizing agent, usually O₂ (Fu et al. 1996b). The most common material employed in photocatalysis is titanium dioxide (TiO₂) due mainly to its corrosion resistance and low cost. TiO₂ becomes active as a catalyst upon illumination with near-UV radiation of 385 nm or less. Although TiO₂ can be used in particulate form, the use of thin films of TiO₂ supported on borosilicate glass greatly reduces non-illuminated areas in the catalyst bed; consequently, optimal reactor efficiency can be achieved (Sirisuk et al. 1999). Thin-film photocatalytic reactors have been previously reported for oxidation of a variety of gas phase compounds (Peral and Ollis 1992, Raupp and Junio 1993, Sauer and Ollis 1994, Obee and Brown 1995, Fu et al. 1996a, Alberici and Jardim 1997, Sirisuk et al. 1999, Zorn 1999 and 2000).

Photocatalysis has potential for use in a number of NASA applications. The most obvious application is for the removal of unwanted gas phase compounds from moderate and long-term confined areas, as in Space Shuttle cabins and in the International Space Station. NASA crewmembers aboard spacecraft are continuously exposed to pollutants in the respirable air. These pollutants can originate from hardware off gassing, crew and microbial metabolism, use of utility chemicals, leakage from fluid systems and payload experiments, and from electrical overheating (James et al. 1994). Several recent publications have reported the presence of the following organic chemicals in spacecraft atmospheres: alkanes, formaldehyde, acetaldehyde, acrolein, methanol, ethanol, isopropanol, acetone, isoprene, benzene, furan, dichloromethane, 1,2-dichloroethane, tetrachloroethylene, Halon 1301, and Freon 113 (James et al. 1994, James 1997). Although these publications suggested that levels were generally within acceptable limits, the presence of some of these compounds at elevated concentrations can lead to negative health effects. A NASA online publication reports that crewmembers “can experience disturbances in cardiac rhythms, eye and respiratory irritation, headache and disorientation, and be at higher risk for developing chronic disease (e.g. cancer)” in the presence of excessive pollution in spacecraft air (James and Mukhamedieva 2001). Photocatalysis has the potential to significantly reduce the gas phase concentration of most, if not all, of these pollutants without requiring the replacement and disposal of depleted treatment units (as with adsorbent technologies).

Photocatalysis can also be used to remove unwanted compounds in other specialized space applications. For example, the Wisconsin Center for Space Automation and Robotics (WCSAR) in Madison, WI currently conducts plant research in microgravity environments; several of their devices have flown on Space Shuttle flights. This research requires plant growth chambers that are completely enclosed and well controlled; however, the use of a tightly closed system enables the build up of ethylene gas. Ethylene (C₂H₄) is a growth hormone that is produced by plants but which can adversely affect plant development at increased concentrations. WCSAR has developed an ethylene reduction technology, based on photocatalyst materials, for use in their

plant growth chambers (Tibbitts et al. 1999). The prototype unit has been shown to be successful at degrading ethylene to below measurable levels even under conditions of up to 86% relative humidity.

The vast majority of previous photocatalytic studies have been focused on single component systems (i.e., only one compound was degraded in each experiment). Real-world application of photocatalysis will rarely occur under such simple conditions. Unfortunately, very few publications to date have described the photocatalytic oxidation process in the presence of multiple reactive components. It is the problem of multi-component systems that is a main focus of this research.

Experimental Methods

Catalyst preparation. Stable sols of titanium dioxide (TiO_2) nanoparticles were prepared following the original method of Xu and Anderson (1991). In this method titanium tetraisopropoxide ($\text{Ti}(\text{OPr}^i)_4$) (Aldrich, Milwaukee, WI) was subjected to an acidic hydrolysis by addition to an aqueous solution of nitric acid at a volumetric mixing ratio of 1 HNO_3 :136.4 H_2O :11.4 $\text{Ti}(\text{OPr}^i)_4$. The resulting white TiO_2 precipitate was peptized at room temperature for 3 days resulting in a stable suspension (sol). This acidic sol was then dialyzed for three days (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. x 3 mm i.d. x 10 mm long) that were precleaned prior to coating. The coatings were applied by dipping the rings in the sol and then withdrawing at a rate of 31 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.

Reactor apparatus. The catalytic and photocatalytic oxidation experiments employed a recycling loop as shown in Figure 1. The recycling loop consisted of a 29 mL (1.5 cm i.d. x 16.5 cm long) glass tube that held 30 catalyst-coated glass rings packed randomly in the center, a 53 mL (1.5 cm i.d. x 30.5 cm long) empty glass tube, a sampling port (septum), stainless steel tubing, and a recirculating gas pump with chemically inert components. 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. For the photocatalytic experiments, two 4W fluorescent light bulbs (F4T5BL, EIKO Brand, Bulb Direct Co., Pittsford, NY) 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 produce a strong peak centered at ca. 365-370 nm. At the beginning of an experiment, the UV lights were energized, the pump was started, the reactor temperature was allowed to reach the set temperature of 30°C, and the loop was flushed with ultra zero air (<0.1 ppm total hydrocarbons, <5 ppm water vapor, AGA Specialty Gas, Cleveland, OH) that was preconditioned to 50% relative humidity. Test compounds were then introduced into the reaction system through the sampling port using either pure liquids or gas mixtures. Gas samples (50 μL) were withdrawn from the recycling loop at regular intervals by inserting a gastight syringe through the sampling port.

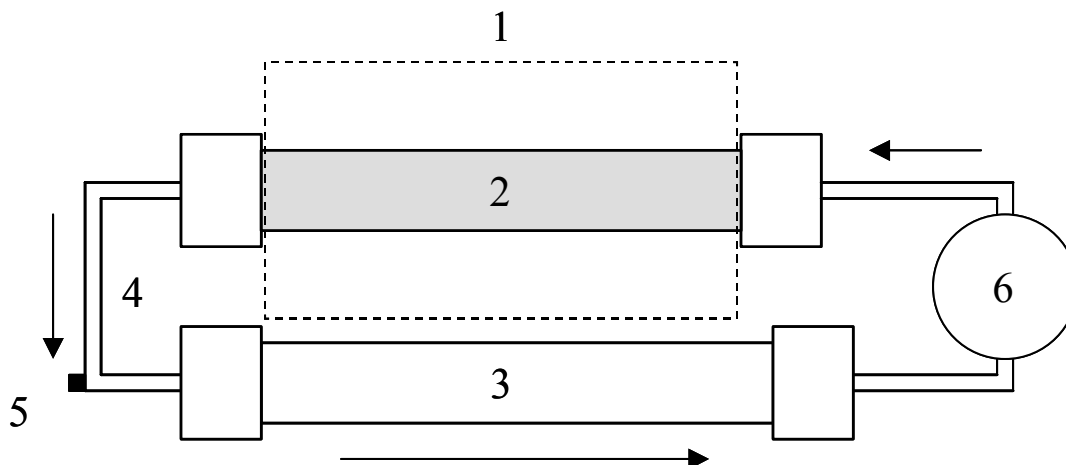


Figure 1. Recirculating reactor design. 1-temperature controlled chamber with two UV light sources; 2-illuminated glass tube randomly packed with 30 catalyst-coated glass rings; 3-nonilluminated empty glass tube (not packed with catalyst-coated glass rings); 4-stainless steel tubing; 5-sampling port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

Gas chromatography. The reactor contents were analyzed using a Hewlett-Packard 5890 Series II gas chromatograph with a mass selective detector, GC/MS. Helium was used as the carrier gas. A 50 μL injection was performed using a gas-tight syringe. The GC column was an HP-5 capillary column (25 m long x 0.2 mm i.d. x 0.33 μm film thickness) that was maintained at 35°C for 3 min.

Results and Discussion

Photocatalysis experiments were performed on a set of three-carbon compounds that contain different functionality (likely leading to different affinity for the catalyst surface). The following four compounds having similar molecular weight but varying polarity were identified: propane (C_3H_8 , a saturated hydrocarbon), propene (C_3H_6 , an unsaturated hydrocarbon), propanal ($\text{C}_3\text{H}_6\text{O}$, an aldehyde), and acetone ($\text{C}_3\text{H}_6\text{O}$, a ketone, *aka* propanone). Initially, each compound was tested in the absence of the others (i.e., single component systems). Figure 2 shows the data sets derived from these experiments. As mentioned, all experiments were conducted at a relative humidity of 50% and at a reaction temperature of 30°C.

As shown, the four compounds all required different amounts of time for complete degradation. All four began at approximately equivalent concentrations (ca. 600 ppmv); however, propane required 400 minutes to degrade, propene required 140 minutes, acetone required 60 minutes, and propanal required 30 minutes. The different reaction times agree well with the predicted affinity of the compounds for the catalyst surface. These results suggest that the presence of these four compounds in a single test environment would result in a competitive disadvantage for the slower reacting compounds (i.e., propane and propene) and a competitive advantage for the faster reacting compounds (i.e., acetone and propanal).

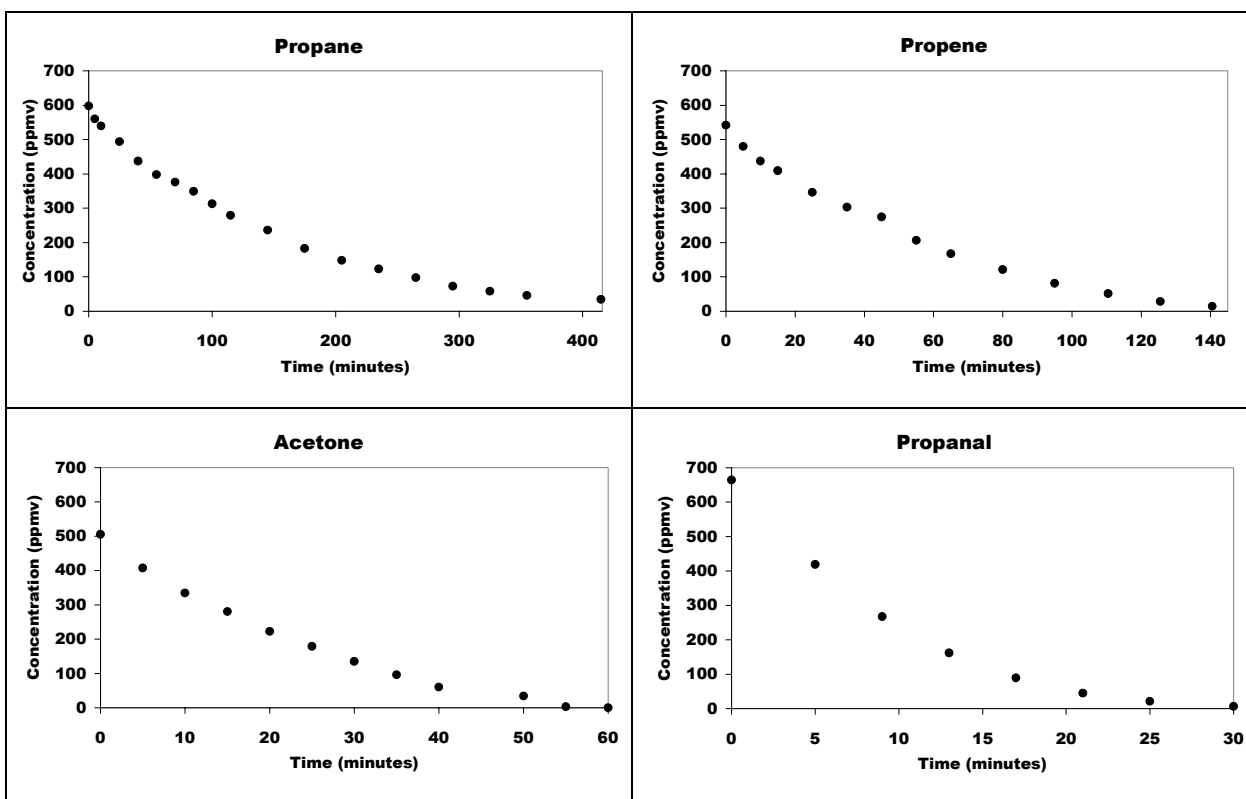


Figure 2. Photocatalytic oxidation of propane (a saturated hydrocarbon), propene (an unsaturated hydrocarbon), acetone (*aka* propanone, a ketone), and propanal (an aldehyde) at 50% relative humidity and 30°C.

Subsequent photocatalysis experiments were conducted in the presence of more than one test compound to qualitatively illustrate the effect of competitive adsorption on the photocatalytic degradation of each. These experiments were also conducted at a relative humidity of 50% and at a reaction temperature of 30°C. In one such experiment, two compounds (propene and acetone) were both introduced into the recirculating reaction system, and the concentrations were monitored over time. The results of this experiment are shown in Figure 3. In contrast to the reaction behavior shown in Figure 2, where propene began to break down immediately, propene degradation was significantly delayed in this two-component system where the presence of acetone significantly inhibited the degradation of propene. Evidence of this effect is shown by the drastic difference in degradation rate of propene before and after about 30 minutes. Before 30 minutes, acetone is present in the reactor at significant levels. Since acetone is more polar than propene, acetone out-competes propene for surface sites on the catalyst surface, thereby limiting its degradation. After 30 minutes, acetone is reduced to insignificant levels, allowing propene to react at a rate comparable to that in the experiment with propene alone (see Figure 2).

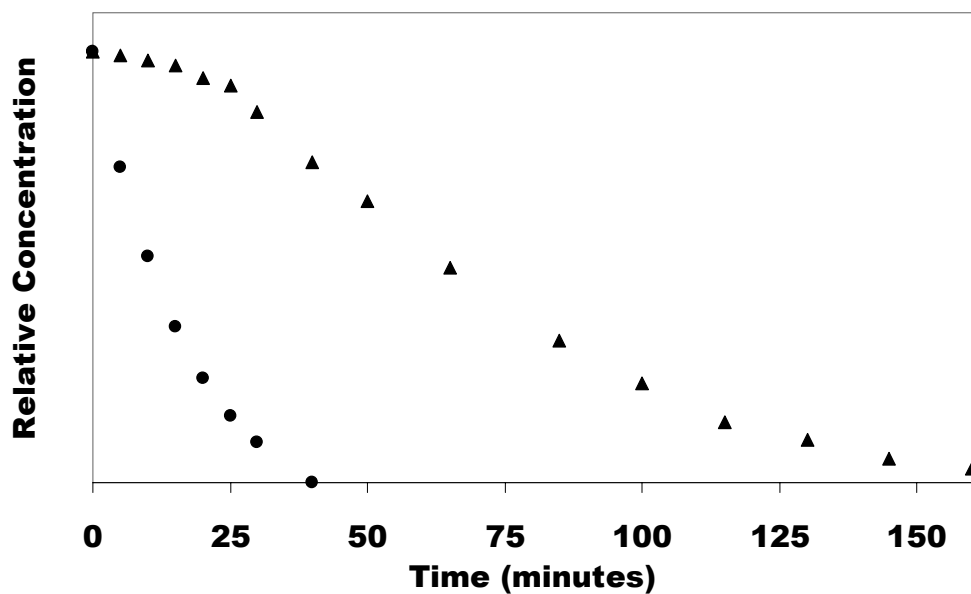


Figure 3. Simultaneous photocatalytic oxidation of acetone (circles) and propene (triangles). The presence of acetone during the first 30 minutes of the experiment inhibits the degradation of propene. After 30 minutes, acetone is reduced to insignificant levels, allowing propene access to the polar catalyst surface, resulting in faster degradation. Compare this behavior to that shown in Figure 2 where propene degradation begins immediately.

In another similar experiment, ethylene (an unsaturated two-carbon compound of importance in the plant growth chamber studies mentioned in the introduction) and acetone were simultaneously introduced into the recirculating reaction system, and the concentrations were monitored over time. The results of this experiment are shown in Figure 4. Ethylene degradation was significantly delayed in this two-component system. As shown, acetone, the more polar of the two compounds, began to degrade immediately. However, the photocatalytic oxidation of ethylene (the less polar of the two compounds) did not begin to occur until acetone was completely reacted. Similar to propene in the previous example, ethylene molecules in this example do not compete favorably with the more polar acetone molecules for adsorptive sites on the catalyst surface. Since adsorption of the compound onto the surface of the catalyst is required for the reaction to occur, ethylene does not adsorb (and subsequently react) until the acetone concentration is reduced to insignificant levels. Once this occurs, ethylene can adsorb on the catalyst surface and undergo degradation.

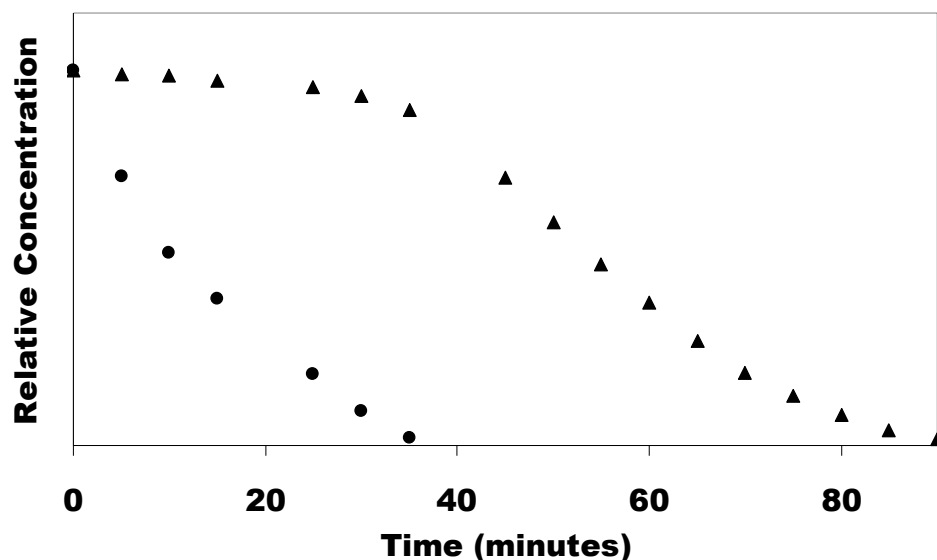


Figure 4. Simultaneous photocatalytic oxidation of acetone (circles) and ethylene (triangles). The presence of acetone during the first 30 minutes of the experiment inhibits the degradation of ethylene. After 30 minutes, acetone is reduced to insignificant levels, allowing ethylene access to the polar catalyst surface, resulting in faster degradation.

Findings of this nature can have significant implications for applying photocatalysis in real-world situations. For instance, the degradation of ethylene in WCSAR's plant growth chambers would be inhibited due to the presence of additional gases that have higher affinity for the catalyst surface than ethylene. The experiment depicted in Figure 4 suggests that the degradation of ethylene would be impaired in the presence of these other compounds. These findings also have major implications for use of photocatalysis to eliminate pollutants from confined spaces for other NASA applications (like the Space Shuttle and the International Space Station) as well as for the general use of photocatalysis in non-NASA applications. These results suggest that the ability to degrade any target analyte will be directly dependent on the presence of other compounds of similar or greater affinity for the catalyst surface. Research that attempts to better understand these competitive processes will be important for successful application of photocatalysis under real world conditions.

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