

# Heterogeneous Photocatalysis for Control of Volatile Organic Compounds in Indoor Air

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## ABSTRACT

Research results concerning the photocatalytic activity and selectivity of benzene are discussed. This compound, which represents one of an important class of volatile organic compounds found in indoor air, was oxidized in an annular photocatalytic reactor featuring a thin film of titanium dioxide and illuminated by a fluorescent black light. The gas phase products, carbon dioxide and carbon monoxide, were quantified with a Fourier transform infrared spectrometer (FTIR). Adsorbed intermediates were extracted from the surface with water. The extract was analyzed via high performance liquid chromatography and some of the adsorbed species were provisionally identified by retention time matching. The adsorption of reactants on the catalyst surface was studied explicitly, particularly with respect to the effect of near-UV radiation on adsorption processes. Maximum and steady-state rates of the surface reactions are reported here as functions of the operating conditions. Deactivation of the catalyst surface is characterized and methods of regeneration of catalyst activity are explored.

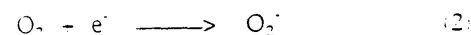
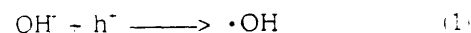
This established research methodology provides the framework for a broader outline of research into enhancement of indoor air quality via photocatalytic oxidation. The results of investigations are discussed that pertain to a variety of classes of compounds representative of indoor air pollutants.

## IMPLICATIONS

Photocatalytic oxidation has the potential to be an effective process for removing and destroying low-level pollutants in air. A photocatalytic reactor traps and chemically oxidizes volatile organic compounds, converting them primarily to carbon dioxide and water. Photocatalytic reactors are also modular and may be scaled to suit a wide variety of indoor air quality applications. They operate at room temperature and with negligible pressure drop, and therefore may be readily integrated into new and existing heating, ventilation, and air conditioning systems.

## INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) is a semiconductor photocatalyst with a band gap energy of 3.2 eV. When this material is irradiated with photons of less than 385 nm, the band gap energy is exceeded and an electron is promoted from the valence band to the conduction band. The resultant electron-hole pair has lifetime in the space-charge region that enables its participation in chemical reactions. The most widely postulated reactions are shown in Equations 1 and 2.



Hydroxyl radicals and super-oxide ions are highly reactive species that will oxidize volatile organic compounds (VOCs) adsorbed on the catalyst surface.<sup>1</sup> They will also kill and decompose adsorbed bioaerosols.<sup>2,3</sup> The process is referred to as heterogeneous photocatalysis or, more specifically, photocatalytic oxidation (PCO).

Several attributes of PCO make it a strong candidate for indoor air quality (IAQ) applications. Pollutants, particularly VOCs, are preferentially adsorbed on the surface and oxidized primarily to carbon dioxide (CO<sub>2</sub>). Thus, rather than simply changing the phase and concentrating the contaminant, the absolute toxicity of the treated air stream is reduced, allowing the photocatalytic reactor to operate as a self-cleaning filter relative to organic material on the catalyst surface. Photocatalytic reactors may be integrated into new and existing heating, ventilation, and air conditioning (HVAC) systems due to their modular design, room temperature operation, and negligible pressure drop. PCO reactors also feature low power consumption, potentially long service life, and low maintenance requirements. These attributes contribute to the potential of PCO technology to be an effective process for removing and destroying low-level pollutants in indoor air. Technical issues that must be confronted before PCO reactors can be used in this application include the formation of products of incomplete oxidation, reaction rate inhibition due to humidity, mass transport issues

associated with high-flow rate systems, catalyst deactivation, and inorganic contamination (dust and soil).

**EXPERIMENTAL METHODS**

The schematic of the experimental apparatus is shown in Figure 1, and has been described in detail in the literature.<sup>4,5</sup> The photocatalytic reactors used during the course of this investigation have an annular geometry. An annular reactor consists of a glass tube coated on the inner surface with a thin film of TiO<sub>2</sub>, photocatalyst. Inside the glass tube is a cylindrical ultraviolet (UV) light source, which also serves as the inner surface of the annulus. The gas flows through the annular region. This design is well adapted to the research environment because the amount of catalyst exposed to UV irradiation is known with some precision.<sup>6</sup>

The application of a thin, uniform TiO<sub>2</sub> coating on the inside of the glass reactor tubes was essential. The Pyrex surface to be coated was first etched with a 5M sodium hydroxide solution at 100 °C. An aqueous suspension containing 5% Degussa P-25 (~75% anatase TiO<sub>2</sub>) was used to introduce the catalyst to the glass support. The coated reactor was then baked for an hour at 120 °C. After poorly adhered catalyst particles were rinsed off with distilled water, the sequence was repeated until a coating smooth and opaque to UV was achieved.

The TiO<sub>2</sub> catalyst can be excited by photons with wavelengths shorter than 385 nm. The photon source in this investigation was an 8-W fluorescent black light (F8T5/BLB) with a spectral maximum of 356 nm. The intensity of the UV radiation on the catalyst surface was determined with a Blak-Ray ultraviolet radiometer (model J-22 1), which is specifically designed to measure the near-UV output from fluorescent black lights.

A Nicolet 8220 Fourier transform infrared spectrometer (FTIR) was plumbed downstream of the reactor, although it could also be fed directly from the injector assembly for feed gas analysis. The FTIR collected spectra with two-wave number resolution and had a multi-pass sample cell with a 9.85 m pathlength.

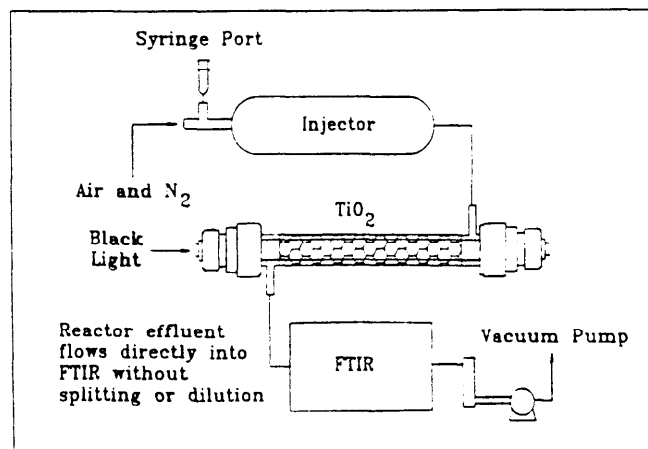


Figure 1. Schematic of the experimental apparatus

The FTIR was calibrated at a standard operating pressure of 67 kPa (500 torr) and experiments were carried out at room temperature. National Institute of Standards and Technology traceable gas standards (Matheson) were used to calibrate the FTIR for dilute mixtures of CO, and carbon monoxide (CO). Standards for benzene and other subject compounds were created by injecting the neat liquid directly into the evacuated analytical chamber. The pressure increase upon injection was measured and then compared with the pressure increase predicted by the ideal gas law to verify complete vaporization and accurate calibration. The FTIR's analytical chamber was then backfilled to appropriate analysis pressure with high-purity nitrogen. Water vapor standards were created by taking spectra of laboratory air of a known temperature and relative humidity flowing through the FTIR. Feed-gas mixtures were created in batch mode by evacuating a 4L sample cylinder, injecting liquid reactants, and backfilling to 160 psig with zero-grade air or high purity nitrogen. Standard operating conditions are listed in Table 1. During the discussion of experimental results, significant deviations from these conditions are explicitly reported. These conditions were chosen to enhance the precision of the experiments, to match the capability of the apparatus, and to provide an accelerated approach to steady state. Concentrations of aromatic hydrocarbons and water vapor that more closely match those found in the indoor environment have been documented elsewhere<sup>7</sup> and will be incorporated into subsequent experiments.

**RESULTS AND DISCUSSION**

**Products and Mass Balances**

Figure 2 shows the composition of the effluent from a photocatalytic reactor on the primary y axis as a function of elapsed time. Instantaneous carbon mass balance and conversion of benzene are plotted on the secondary y axis. The feed contained partial pressures of 58 mtorr benzene and 500 mtorr water vapor. As the standard operating pressure was 500 torr, ppm units are obtained by

Table 1. Typical operating conditions

Parameter	Value
Reactor hydraulic diameter*	4.53 mm
Area coated with catalyst	107 cm <sup>2</sup>
Weight of catalyst film	40 mg
UV Light Intensity	5 ± 1 mW/cm <sup>2</sup>
Volumetric flow rate	265 ml/min
Residence time	4.9 s
Operating pressure	500 torr (67 kPa)
Benzene feed partial pressure	58 mtorr (116 ppm)
Water vapor feed partial pressure	500 mtorr (1,000 ppm)

\*Hydraulic diameter is defined as the inside diameter of the glass tube minus the outside diameter of the lamp or twice the distance between the light source and the catalyst film

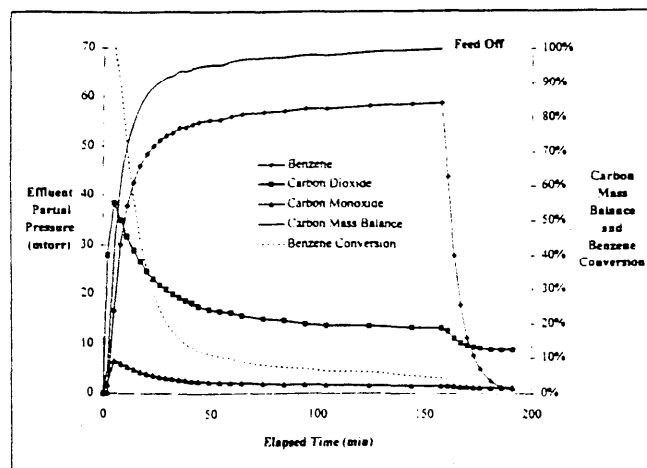


Figure 2. Photocatalysis of benzene showing reactant and product partial pressures, reactant conversion, and carbon mass balance as a function of elapsed time.

multiplying partial pressure in mtorr by a factor of 2 (e.g.,  $58 \times 2 = 116$  ppm benzene in the feed). Conducting the experiment involved a catalyst pretreatment period of several hours, during which zero-grade air flowed through the illuminated photocatalytic reactor. During this interval, steadily decreasing evolution of CO, and CO was observed, indicating the oxidation of organic compounds adsorbed on the catalyst surface during its exposure to laboratory air. When the CO<sub>2</sub> and CO signals reached near-zero asymptotic levels, the feed containing benzene, water vapor, and zero air was introduced. The asymptotic values of CO<sub>2</sub> and CO evolution were subtracted from the measurements made during the subsequent experimental run to ensure that only the products of benzene oxidation would be reflected in the data. Because the volume of the photocatalytic reactor was small compared to the volume of the analytical chamber, a continuous stirred-tank reactor model was used to compute the instantaneous composition of the effluent of the reactor, based on the instantaneous composition of the contents of the sample cell. The assumption of perfect mixing is valid because the folded pathlength nature of the FTIR cell samples an average of its entire contents.

Examination of Figure 2 reveals that the primary product observed in the gas phase was CO<sub>2</sub>. CO was also formed; at steady state, approximately 10% of the carbon atoms in the benzene molecule was converted to this product. The OSHA eight-hour exposure limit for CO in the workplace is 35 ppm. The combined concentration of VOCs measured in "sick buildings" is a few ppm.<sup>7</sup> Therefore, under conditions relevant to the use of PCO to enhance IAQ, conversion of 10% of the carbon atoms in VOCs to CO would create a negligible addition to the ambient levels of this compound. In addition, room temperature CO oxidation catalysts can be integrated with the PCO system, if this is warranted by the application.

By the end of the experiment, steady state had been attained, as shown by closure of the instantaneous carbon mass balance. In addition, the product concentrations and benzene conversion were virtually unchanging. It should be noted that although the steady-state conversion of benzene was about 4%, the feed contained a pollutant concentration several orders of magnitude higher than those typical of indoor air. Complete, steady-state conversions of lower concentrations of aromatic hydrocarbons have been observed.<sup>7</sup>

Since the FTIR has sub-ppm sensitivity for most asymmetric molecules, one may conclude that products of incomplete oxidation (other than CO) were not desorbing from the surface into the gas phase. This is significant, since some compounds, particularly nonaromatic, chlorinated organics, form volatile byproducts.<sup>7</sup>

When the influent to the photocatalytic reactor was switched from the benzene/water vapor/air feed back to zero air (as indicated by the "feed off" notation on Figure 2), CO<sub>2</sub> and CO continued to evolve. This evolution resulted from oxidation of surface-bound reactants and adsorbed intermediates, illustrating the function of the PCO reactor as a self-cleaning filter with respect to adsorbed organic compounds. Within several hours, the near-zero asymptotic levels of CO<sub>2</sub> and CO observed prior to the experimental run were once again observed, and closure of the overall carbon mass balance had been achieved.

Identification of polar intermediates adsorbed on the catalyst surface was investigated through water extraction of the catalyst used in experiments that had reached steady state. (Extraction of nonpolar intermediates with a nonpolar solvent is planned.) The extract was subsequently analyzed via high performance liquid chromatography (HPLC). This results of this experiment are summarized in Table 2 and in Figures 3 and 4. The runs lasted 3 hours each, except for the run corresponding to Sample A, which lasted 1.75 hours. The discrepancies from the standard conditions reported above included a feed containing 130 ppm of benzene and 980 ppm of water vapor at a total pressure of 623 torr and a flow rate of 210 ml/min, with the exception of the run corresponding to Sample A, which had a flow rate of 460 ml/min.

The catalyst films were rinsed in about 2 ml of water, which was then diluted threefold in 18 MΩH<sub>2</sub>O. Blanks were created by rinsing unused catalyst films. In addition to benzene, six organic standards of likely partial oxidation products were made in acetonitrile solvent at concentrations of  $300 \pm 50$  ppm. These included phenol (hydroxybenzene), hydroquinone (1,4-benzenediol), catechol (1,2-benzenediol), resorcinol (1,3-benzenediol), benzoquinone (2,5-cyclohexadiene-1,4-dione), oxalic (ethanedioic) acid, and malonic (propanedioic) acid. Chromatograms of these standards are shown in Figure 3. The chromatography was performed using a gradient separation, from 90% water/acetonitrile to 10% water/acetonitrile over 15 minutes at 1.0 ml/min.

Table 2 Results of the water extraction experiments.

Sample ID	TiO <sub>2</sub> tint	Water Wash tint	Comments	Tentative Peak ID
A	dark yellow	very light yellow	Run on fresh catalyst	Malonic Acid
B	dark yellow	very light yellow	Run on catalyst regenerated with zero air and light for 20 hours	Phenol; Malonic Acid Hydroquinone/ Benzoquinone
C	dark yellow	very light yellow	Run on fresh catalyst	Phenol Malonic Acid
D	dark yellow	very light yellow	Run on fresh catalyst	Phenol Hydroquinone/ Benzoquinone
E	white	clear	Run on fresh catalyst then zero air and light for 21 hours	None
Blank 1	white	clear	Zero air and light for 1 hour	None
Blank 2	white	clear	Zero air and light for 1 hour	None

The column (250 x 4.6 mm) was packed with 5 mm C4 Kromasil stationary phase and held at 30 °C. Data were collected at 5 Hz from a UV-Vis detector set at 254 nm. The standard injections were 10 mL and the sample injections were 50 mL, due to the difference in concentration between the standards and the samples. The provisional identifications of adsorbed intermediates shown in Table 2 and on Figure 4 were made on the basis of retention time matching.

Determining retention times for the organic standards was complicated by the reactivity (which resulted in low standard purity) and structural similarity between the organic standards. Hydroquinone, benzoquinone, catechol, malonic, oxalic acid, and benzene standards all had some degradation products in addition to the parent compounds. The parent

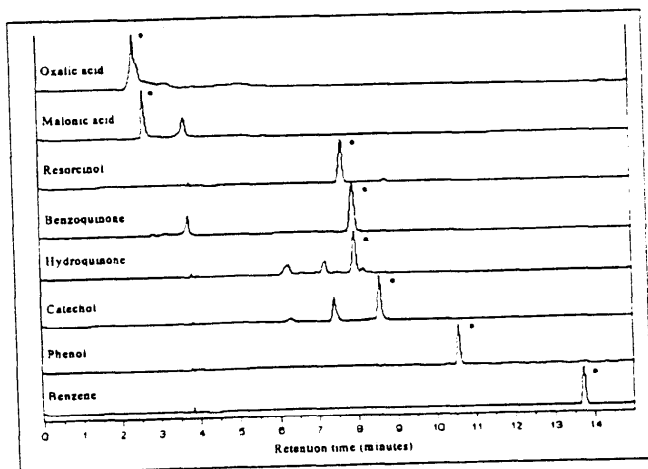


Figure 3. HPLC chromatograph showing the elution times of standards of benzene and seven possible partial oxidation products

peaks for hydroquinone and benzoquinone eluted simultaneously, making it impossible to differentiate these two species without a spectral analysis. Phenol was stable and eluted as a single peak.

The provisional identification of phenol, malonic acid, and hydroquinone and/or benzoquinone as surface-bound intermediates provides a starting point for a detailed investigation of the mechanism of the PCO of benzene in air. Examination of Figure 4 reveals that the chromatogram of the extract of the film that was exposed to clean air and Light after the benzene reaction (Sample E) was identical to the chromatogram of the blanks. Further, the ex-

tract and the catalyst film for this sample were not discolored. This supports the contention that the adsorbed intermediates eventually are oxidized to CO<sub>2</sub> and CO. Thus, the PCO reactor acts as a self-cleaning filter with respect to adsorbed organics.

### Adsorption

A heterogeneous catalytic reaction proceeds along the following pathway:<sup>8</sup> (1) bulk mass transport of the reactants from the gas-phase to the surface of the catalyst particle; (2) mass transport of the reactants within the catalyst particle; (3) adsorption of the reactants onto the catalyst surface; and

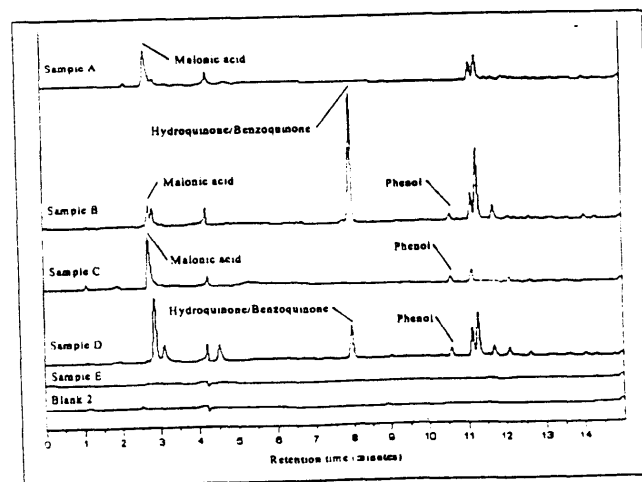


Figure 4. HPLC chromatograph showing the elution times of adsorbed intermediates from the benzene reaction extracted with water from the surface of the TiO<sub>2</sub> catalyst.

(4) surface chemical reaction. Any one of these steps can limit the rate of the overall process. Evidence will be presented that step 1, bulk transport due to convection and diffusion, occurs at a high rate relative to surface reaction in the annular reactor, and is not rate limiting. Because the  $\text{TiO}_2$  catalyst is configured in a thin film, and reactive sites are limited by light penetration depth, intraparticle transport (step 2) is also not an important process. Thus, steps 3 and 4 must be understood in order to properly apply the PCO process to IAQ, and they are the focus of the remainder of this section.

The process of adsorption was studied explicitly. Of particular interest was the manner in which near-UV irradiation of the catalyst, which transfers energy to the catalyst surface, influences adsorption. A series of experiments was run in which a mixture containing 58 mtorr of benzene and 500 mtorr of water vapor was fed into a photocatalytic reactor. The amount of benzene adsorbed was calculated by monitoring the effluent benzene partial pressure from the photocatalytic reactor and comparing these observations to the inlet benzene partial pressure. Reacted benzene molecules were determined from product concentrations and accounted for in the adsorbed inventory calculation. When the effluent concentration of benzene reached steady state, it was assumed that the benzene molecules on the catalyst surface had reached equilibrium with the benzene molecules in the gas phase. Table 3 outlines the cases investigated.

Table 3. Mass transport/adsorption experiments

Case	Light	Catalyst	Air/ $\text{N}_2$	Water Vapor
i	No	No	Air	500 mtorr
ii	Yes	No	Air	500 mtorr
iii	No	Yes	Air	500 mtorr
iv	Yes	Yes	$\text{N}_2$	500 mtorr
v	Yes	Yes	$\text{N}_2$	Dry
vi	Yes	Yes	Air	500 mtorr

Table 4. VOCs amenable to treatment via PCO.

Class of Compound	Chemicals Tested
Aromatics	Benzene, Toluene
Nitrogen-containing Ring Compounds	Pyridine, Picoline, Nicotine
Aldehydes	Acetaldehyde, Formaldehyde
Ketones	Acetone
Alcohols	Methanol, Ethanol, Propanol
Alkanes	Ethylene, Propene, Tetramethyl Ethylene
Terpenes	$\alpha$ -Pinene
Sulfur-containing Organics	Methyl Thiophene
Chlorinated Ethylenes	Dichloroethylene, Trichloroethylene, Tetrachloroethylene
Acetyl Chlorides	Dichloroacetyl Chloride, Trichloroacetyl Chloride

Figure 5 shows that the interaction between the UV light and the catalyst surface may be important in the adsorption process. Case i shows that small quantities of benzene adsorbed on the Pyrex substrate in the dark, while case ii reveals that slightly more benzene adsorbed when the uncoated substrate was irradiated. The presence of a film of  $\text{TiO}_2$  approximately doubled the affinity of benzene for the surface in the dark (case iii). When the catalyst surface was illuminated in cases iv, v, and vi, a large increase in the adsorbed inventory of benzene was observed. Cases iv and v employed  $\text{N}_2$  as a diluent, in order to decouple the photocatalytic reaction from the photoadsorption. This decoupling was accomplished because oxidation rates are much lower when benzene is mixed with  $\text{N}_2$  relative to air, although some oxidation did occur from residual adsorbed oxidative species or lattice oxygen. Comparison of these cases with case vi, in which the solvent was air, reveal that co-adsorption of oxygen does not interfere with the adsorption of benzene. Co-adsorption of water vapor does affect benzene adsorption. This is shown by comparing cases iv and v. The feed for case iv included a water vapor feed partial pressure of 500 mtorr, while the feed for case v was dry, and benzene exhibited a greater affinity for the catalyst surface in the dry feed. This confirms that water vapor can interfere with the adsorption of aromatics on the catalyst surface.

### Reaction Rates and Catalyst Deactivation

Figure 6 illustrates the maximum and steady-state reaction rates of benzene oxidation as a function of feed benzene partial pressure. The rate of benzene oxidation is calculated from the partial pressures of the products ( $\text{CO}$ , and  $\text{CO}_2$ ) observed in the reactor effluent, thus reflecting oxidation rather than adsorption. The units of reaction rate are  $\mu\text{mol}/\text{m}^2/\text{s}$ . The area term " $\text{m}^2$ " refers to the geometric area of the glass substrate that is covered with a  $\text{TiO}_2$  film. This selection of

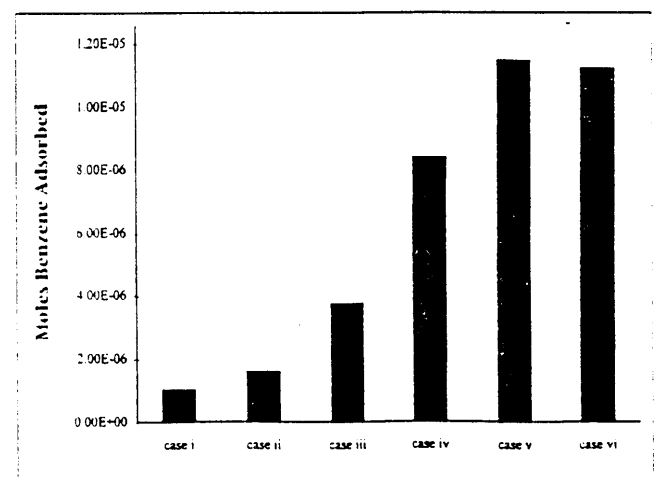


Figure 5. Amount of benzene adsorbed as a function of presence or absence of catalyst and near-UV Irradiation: cases elucidated in Table 3

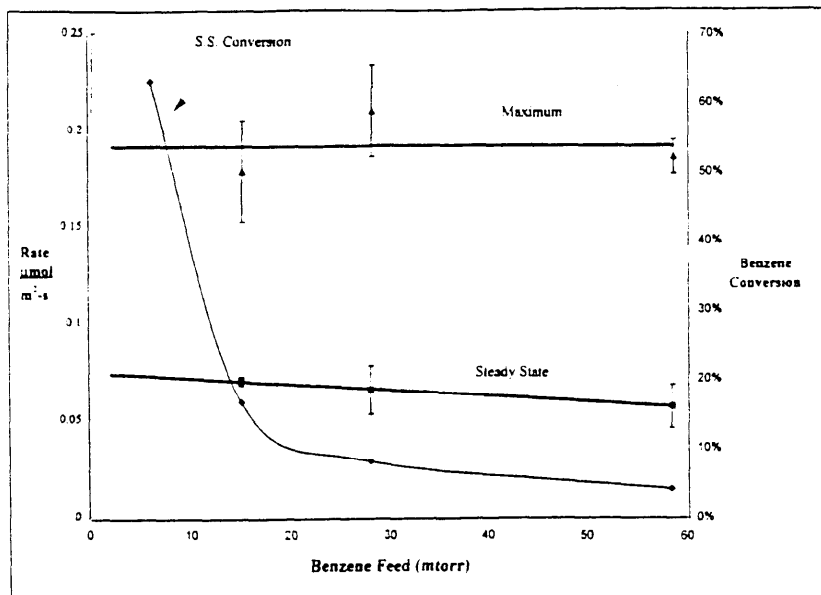


Figure 6. Maximum and steady-state reaction rates for the photocatalytic oxidation of benzene as a function of influent benzene partial pressure

units yields a highly repeatable measurement. Its advantages, disadvantages, and convertibility to other units have been discussed in the literature. Examination of Figure 6 reveals that the maximum and steady-state reaction rates are not strongly dependent on the gas-phase concentration of benzene. This is indicative of a process in which the rate of adsorption is faster than the rate of surface reaction. Thus, surface reaction is the rate-limiting step in this concentration range. As the concentration of the pollutant decreases, the number of molecules adsorbing on the surface at a given flow rate also decreases, and the difference between the rate of adsorption and the rate of surface reaction grows smaller. Extrapolation of the steady-state conversion curve indicates that a feed containing 5 ppm or less of benzene would undergo complete conversion at steady state in a photocatalytic reactor operating under these conditions. This concentration is considerably higher than that typical for indoor air pollutants.<sup>10</sup>

Figure 6 can be interpreted in light of a conceptual model; benzene adsorbs on the surface and undergoes oxidation during which CO<sub>2</sub> and CO are formed. These products desorb and are detected in the gas phase. Also formed are a suite of adsorbed intermediates that remain on the surface and react more slowly than the benzene in the feed, also forming CO<sub>2</sub> and CO as final products. The steady-state rate is a composite of the reaction rates of benzene and the suite of intermediates. This accounts for the fact that the steady-state reaction rate is

lower than the maximum rate, which occurs early in the run. Whenever the penultimate intermediate reacts to form gaseous products, an active site becomes available and another gas-phase benzene molecule adsorbs in its place. This model is also consistent with the findings in the water extraction experiments reported earlier. Figure 7 further supports this concept, showing elapsed time to maximum rate as a function of benzene-feed concentration. It illustrates that at a given flow rate, the higher the partial pressure of the reactant, the faster all active sites were occupied and maximum rate was achieved. In these experiments, a lag time was observed during which no benzene appeared in the effluent. During this interval, all available catalytic sites were being occupied by adsorbing reactants, and no benzene exited the reactor. This lag time amounted to about five minutes, with a benzene feed partial pressure of 58

mtorr and a volumetric flow rate of 265 ml/min (see Figure 2). At lower reactant partial pressures and/or lower flow rates, the lag time would be longer. This behavior endows a photocatalytic reactor with the ability to handle surges in pollutant concentration, a situation typical of indoor environments. As reported above, for a feed containing less than or equal to 5 ppm of benzene flowing at this flow rate, it appears that 100% steady-state conversion would be achieved.

A series of experiments was run to measure the maximum and steady-state reaction rates during repeated use of a catalyst film. In each individual experiment, a steady state was achieved according to the standard operating conditions listed

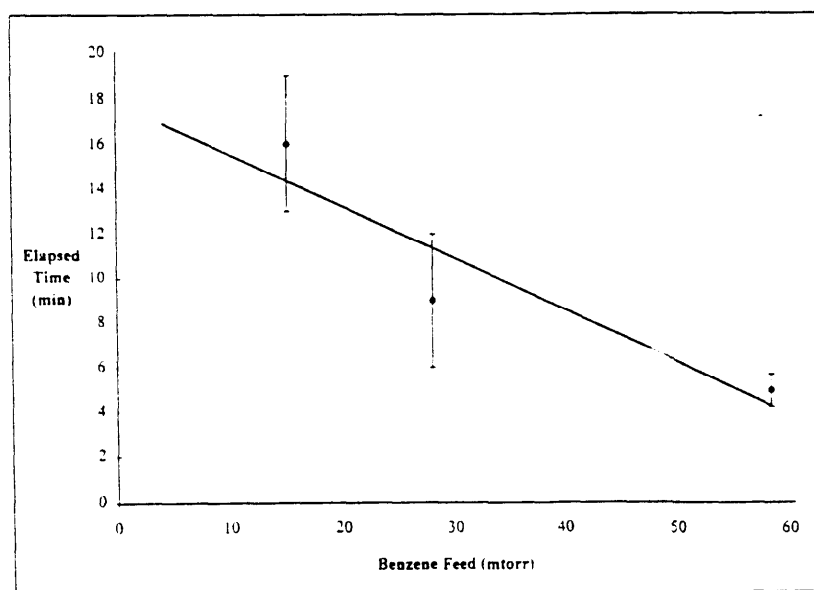


Figure 7. Time to maximum rate of the photocatalytic oxidation of benzene as a function of influent benzene partial pressure.

in Table 1. The feed was then switched to zero grade air in the presence of UV light. During this interval, adsorbed intermediates were oxidized from the surface. Figure 8 shows that the activity of the catalyst was entirely recovered, and maximum and steady-state reaction rates were repeatable within experimental error. These experiments support the contention that photocatalytic reactors can act as self-cleaning filters with respect to organics. Once again, the relative rates of adsorption and surface reaction afford PCO reactors the capacity to effectively control short-term surges in pollutant concentrations. In a separate experiment, photocatalytic activity was also restored by washing the catalyst surface with water in a manner similar to the water extraction experiment described above. This regenerative process works very quickly, but it may not be a practical option if the intermediates in the extract render it a hazardous waste stream.

### Other VOCs

Most of the VOCs found in indoor air can be trapped and destroyed in a PCO reactor in single-component and multi-component mixtures. Table 3 lists classes or compounds, as well as specific chemicals, that have shown photocatalytic activity in our laboratory. Information on other studies is available in a bibliography that contains more than 600 photocatalysis citations.<sup>9</sup> The possibility of forming gas-phase intermediates must be carefully investigated relative to each compound. In some cases, it may be necessary to integrate a PCO reactor with a co-catalyst bed, a scrubber, or a granular-activated carbon bed, as a safeguard against the release of undesirable byproducts.

The control of organic molecules containing heteroatoms, such as nitrogen, sulfur, or chlorine, provides a unique challenge for a PCO reactor. Nitrogen-containing

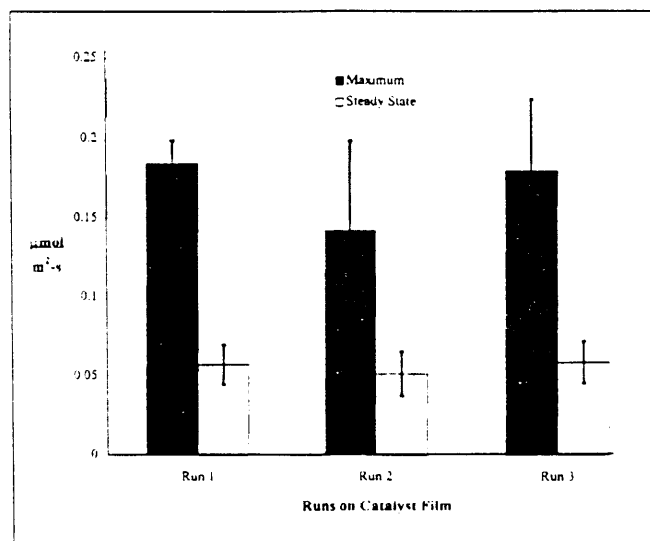


Figure 8. Maximum and steady-state reaction rates of the photocatalytic oxidation of benzene as a function of consecutive runs on the same catalyst film. In between runs, the catalyst film was regenerated by exposure to clean air and near-UV irradiation.

ring compounds are one of the most common classes of indoor air contaminants (e.g., nicotine found in environmental tobacco smoke!). During the PCO of pyridine, CO, and a small amount of CO were formed. So nitrogen-containing products were observed in the gas phase. This does not preclude the formation of N<sub>2</sub>, which is not detectable via FTIR. The concern arises, therefore, that nitrogen-containing intermediates may build up on the catalyst surface and lead to irreversible deactivation.

Figure 9 illustrates the results of an experiment designed to investigate this possibility. A feed mixture containing a pyridine partial pressure of 70 mtorr and a water vapor partial pressure of 800 mtorr flowed through a photocatalytic reactor coated with 96 mg of TiO<sub>2</sub>. All other experimental conditions were similar to those specified in Table 1. When a steady state was achieved, the feed mixture was switched to zero-grade air, with the light still on, and a self-cleaning cycle proceeded overnight or until the near-zero asymptotic levels of CO, and CO were attained. This process was repeated six times using the same reactor. During the entire experiment, the catalyst was exposed to the pyridine feed for more than 16 hours, and about 0.5 μmols of pyridine were adsorbed and destroyed. Examination of Figure 9 reveals that although some catalyst activity was lost between the first and second runs, both the adsorptive capacity (as measured by the lag time before pyridine appears in the effluent) and the oxidative capacity (as measured by CO<sub>2</sub> evolution) remained approximately constant during the remaining runs. XPS examination of the catalyst surface revealed the presence of some nitrogen atoms on the surface. Identification of surface-bound intermediates also proceeded through liquid extraction of the catalyst and analysis of the extract via HPLC. One may conclude from this experiment that during the reaction of pyridine via PCO, the self-cleaning function of the photocatalytic reactor is preserved and nitrogen-containing, surface-bound intermediates do not lead to immediate and irreversible deactivation of the catalyst.

### CONCLUSIONS

The only gas-phase products formed during the photocatalytic oxidation of benzene are CO, and a small amount of CO. Intermediates phenol, benzoquinone and/or hydroquinone, and malonic acid have been provisionally identified on the catalyst surface. Closure of instantaneous and overall mass balances has been achieved. Adsorption of benzene on the surface of TiO<sub>2</sub> appears to be promoted by the presence of UV light. The adsorption of water vapor interferes with the adsorption of benzene, but oxygen adsorption has no effect. The surface reaction is the rate-limiting step under the conditions investigated; adsorption of benzene occurs more rapidly than surface reaction, affording a photocatalytic reactor the capacity to control transient surges in pollutant concentration. During the photocatalytic oxidation of pyridine, no nitrogen-containing products were

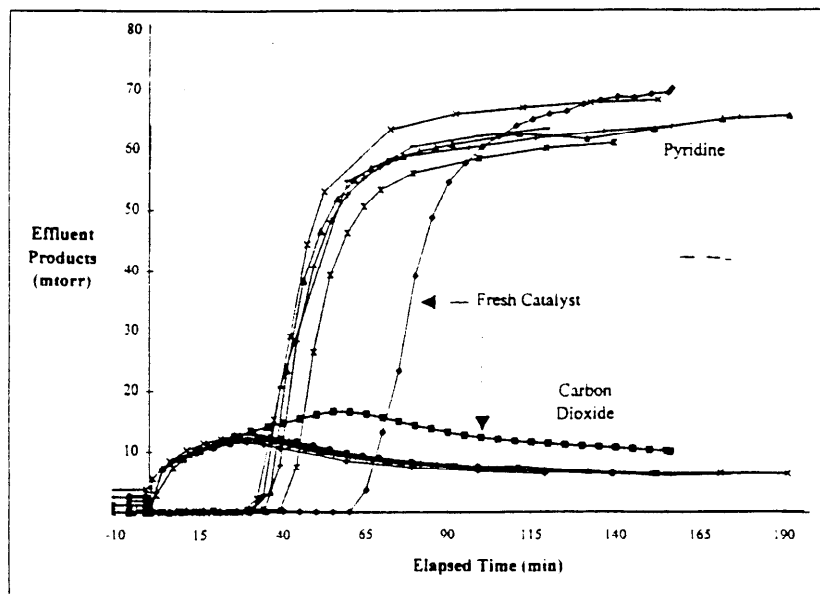


Figure 9. Effluent product and reactant partial pressures as a function of elapsed time for the photocatalytic oxidation of pyridine for consecutive runs on the same catalyst film. In between runs, the catalyst film was regenerated by exposure to clean air and near-UV irradiation.

observed in the gas phase, but buildup of surface-bound nitrogen-containing species did not lead to deactivation during repeated runs. Finally, it has been established that a photocatalytic reactor can function as a self-cleaning filter with respect to adsorbed organic compounds in the IAQ application. This ability, combined with operational attributes that will allow integration of these reactor devices into new and existing air handling systems, could make the photocatalytic reactor an important tool in the effort to improve the quality of the indoor environment.

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