EVALUATION OF TITANIUM DIOXIDE AS A PHOTOCATALYST FOR REMOVING AIR POLLUTANTS

PIER FINAL PROJECT REPORT

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by binging environmentally safe, affordable, and reliable energy services and products to the marketplace.

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For more information about the PIER Program, please visit the Energy Commission's website at www.energy.ca.gov/pier or contact the Energy Commission at (916) 654-5164.

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Abstract

This project investigated the potential for passive cleaning of outdoor air using nanoparticles of anatase titanium dioxide, which have been shown to photocatalyze the oxidation of atmospheric pollutants such as oxides of nitrogen (NOx) and volatile organic compounds (VOCs). Active indoor air cleaners using this technology are commercially available for eliminating malodorous compounds. Research has been ongoing for more than a decade in Japan, and a major multi-institutional project was recently completed in Europe. Still, the practical feasibility of passive photocatalytic air cleaning remains controversial. Some claim that pollution can be halved with straightforward measures; others are unconvinced.

This project clarified the technology potential by focusing on measured values of catalytic activity—that is, the rate at which air can be cleaned by a given area of photocatalyst (if 1 m^2 of catalytic film or plate can clean 100 m^3 of air per day, it has an activity of 100 m/day). Laboratory data show that a high-quality TiO$_2$ catalyst has an activity of about 200 m/day for NOx, about 60 m/day for typical VOCs, and approximately 0 m/day (not useful) for carbon monoxide.

Prior to widespread deployment of passive photocatalytic air-cleaning technology, large-scale meteorological simulations are needed to validate deployment strategies.

Keywords: Photocatalysis, catalytic activity, NOx, VOC, TiO$_2$, clean air

Executive Summary

Introduction

Photocatalytic air cleaning[1] has the potential for removing nitrogen oxides (NOx) and volatile organic compounds (VOCs) from polluted urban air, and, consequently, for reducing concentrations of toxic and irritating ozone, a key constituent of smog that forms on hot, sunny days. Titanium dioxide (TiO_2) nanoparticles absorb the ultraviolet component of sunlight, acting as a catalyst to form reactive hydroxyl (OH) radicals in the presence of atmospheric moisture. These radicals can oxidize and destroy most pollutant molecules. Research and development on this topic originated largely in Japan and has recently been pursued in Europe; there is little current activity in the United States. Widespread use of titanium dioxide nanoparticles in building materials, and on roads, freeway sound walls, and so forth, is proposed by proponents of the technology, but the efficacy of this approach has been unclear.

Purpose

This project evaluated the efficacy of passive photocatalytic air cleaning technology using titanium dioxide nanoparticles.

Project Objectives

Specific objectives were to:
- Clarify the potential for smog removal with widespread deployment of TiO_2 nanoparticles.
- Outline research and development activities that can enhance the practicability of photocatalytic air cleaning technology.

Project Outcomes

The extensive literature on photocatalysis using TiO_2 was reviewed.

Project researchers at Lawrence Berkeley National Laboratory hosted a daylong workshop on "Passive Photocatalytic Oxidation of Air Pollution," at which participants discussed the technical state of the art in this field.

Efficacy of photocatalytic materials was summarized and tabulated in terms of catalytic activity. Each square meter of high-performance photocatalytic material, exposed to outdoor sunlight, can remove nitrogen oxides from about 200 cubic meters of air per day. The removal rate for volatile organic species is about 60 cubic meters of air per day. These numbers are rough estimates but are based on careful quantitative investigations published in references cited by this report.

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[1] Photocatalytic air cleaning refers to chemical reactions initiated by sunlight—and expedited by a special catalyst—that convert harmful substances in the air into more benign substances.

Conclusions

Photocatalytic reduction of air pollution using titanium dioxide nanoparticles is technically feasible. However, accomplishing this goal in a cost-effective way will be challenging, due to the large volumes of air that must be processed.

Recommendations

Numerical meteorological simulations of smog formation, transport, and destruction are needed to study how to best deploy and use photocatalytic oxidation technology.

Innovative research and development is needed to improve the catalytic activity of available materials. Important is synthesis and characterization of novel, more effective catalysts, as verified by laboratory testing. Eventually, small- and large-scale field demonstrations can be used to accelerate technology deployment.

Before implementation, additional research should be conducted to ensure that deployment of the photocatalyst does not lead to any adverse environmental consequences—such as the release of harmful compounds into the atmosphere or water (runoff).

Benefits to California

As a result of this work, it is clear that further research and analysis is required for wide-spread implementation and deployment of photocatalytic oxidation technology for cleaning outdoor air in California.

Research and development tasks have been identified that could lead to technology deployment, and consequently less smog, in California air.

1.0 Introduction

Small particles of titanium dioxide (TiO_2) act to catalyze oxidation of adsorbed molecules in the presence of above-bandgap ultraviolet light (UV, wavelengths smaller than 390 nanometers). The particle size is usually in the range of 5 to 50 nm. The absorption of UV light produces electron-hole pairs in the titanium dioxide particles. The particles are naturally n-type semiconductors,[2] containing a considerable number of mobile electrons, so that the additional electrons produced in the photo-absorption process do not greatly perturb thermodynamic equilibrium. However, the photo-produced holes represent stored energy. For example, if they encounter one of the many available electrons, they can combine with it and release an amount of energy equal to semiconducting energy gap, 3.2 electron volts. If instead of recombining with an electron, the hole reaches the particle's surface, it can react with hydroxyl (OH^-) ions from adsorbed surface water and form highly reactive hydroxyl radicals. These radicals form when an OH^- group loses its electron during an encounter with a hole. They are electrically neutral but highly reactive chemically. Airborne pollutant molecules can be adsorbed on the TiO_2 particle surface, at which time they react with adsorbed hydroxyl radicals. Ideally, reaction products remain on the surface until they are fully oxidized. For example, benzene (C_6H_6) ultimately forms six CO_2 molecules and three H_2O molecules.

The process just described represents the essence of catalytic photo-oxidation, but it should be understood that variations on this theme are encountered, and that, in fact, even all the important reactant species and reactions are not known. One variation can occur if an adsorbed pollutant molecule reacts directly with a semiconducting hole, without the need for an intervening OH radical. Another point that should be mentioned is that the destruction of the semiconducting hole entails the transfer of an electron to the particle from its environment. The particle must remain (nearly) electrically neutral or it will repel additional electrons. It is thought that, in most cases, molecular oxygen (O_2) is reduced to form the radical O_2^-, which allows excess electrons to exit the particle (Fujishima et al. 1999).

Research is underway to characterize the photocatalytic rates and reaction pathways for various polluting volatile organic compounds (VOCs, such as benzene, toluene, terpenes, etc.) that act as smog precursors. TiO_2 nanoparticles can also catalyze the breakdown of oxides of nitrogen (NOx) and sulfur (SOx), and these reaction pathways are being studied as well.

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1. Semiconductors are materials that conduct electricity more poorly than metals and more readily than insulators. Usually, the type of conductivity is determined by intentional or unintentional impurities (dopants). If the conduction is due to negatively charged species (electrons) it is termed n-type. If the conduction is due to positively charged species (holes, missing electrons in a nearly filled band) it is termed p-type.

In addition, research is identifying improved photocatalysts. The two industrially useful phases of titanium dioxide are rutile and anatase; generally, anatase particles perform better as photocatalysts, and consequently most R&D focuses on variants of anatase. Anatase nanoparticles are currently commercially available as thin, transparent films that can coat glass, tiles, and other materials. Proponents of TiO_2 deployment on exterior walls, windows, and roofing of buildings, and on road surfaces, sound walls, etc., assert that great air quality benefits will result. However, in the marketplace, it appears that such nanoparticles are often deployed for another reason, namely that the surfaces are self-cleaning or easily cleaned, and air quality benefits are not a decisive factor. This project aims to clarify the importance of the air quality benefits of photocatalytic TiO_2 nanoparticles.

The work plan for this project includes six tasks:

Task 1: Review of TiO_2 Photocatalytic Technologies is an information gathering activity described in Section 2.0, Data Source Summary, with results presented throughout this report.

Task 2: Review of Methods and Metrics Used to Measure Removal of Airborne Pollutants, has its results presented in Section 3.3, Data Comparison Summary.

Task 3: Analysis of the Efficacy of TiO_2 Photocatalytic Air Pollutant Removal. Results of Task 3 are presented in Section 3.4, Summary of Large-Scale Efficacy: Extrapolating to Neighborhoods and Cities.

Task 4: Liaison with Coating Industry, has its results summarized in Section 3.2, Summary of Large-Scale Coating Production.

Task 5: This task consisted of a workshop, with results summarized in Section 3.1, Workshop Summary.

Task 6: Technology Transfer Activities, the main result of which is this final report, features discussion of various research, development, and implementation issues related to the successful deployment of TiO_2 as a large-scale area-wide pollution removal catalyst, as presented in Section. 3.5, Issues for Future Program Planning for Research, Development, and Demonstration.

2.0   Data Source Summary

A summary of photocatalytic literature up to 2001 was presented by Blake (2001). This bibliography and its predecessors covered the removal of hazardous substances from both water and air. During the year 2000, Blake identified about 600 patents and found about 500 additional references were found in the form of journal and conference papers, and laboratory reports. The treatment of roughly 1000 distinct compounds had already been examined by 2001. A good early review paper was presented by Hoffman et al. (1995).

A literature search of archival publications for the last ten years (1998–2007), based on the keywords "photocatalysis" and "TiO$_2$" yielded 3,167 citations, which formed a primary information source for the current project. While some publications were randomly selected for reading, the large number of papers required that additional criteria be used. High priority was given to about a dozen review papers, and to papers that were widely cited by other authors. Several monographs were useful as well (Fujishima et al. 1999; De Lasa et al. 2005; Kaneko et al. 2002). Only a few patents were examined, mainly those that were cited in the primary literature. Information on commercial products and large-scale testing was poorly represented in the scientific literature. For this reason, Internet searches for recent reports, manufacturers' literature, and news reports were performed.

A daylong Workshop on Passive Photocatalytic Oxidation of Air Pollution was held at Lawrence Berkeley National Laboratory (LBNL) on June 29, 2007. At this workshop, recent applied photocatalytic research and development in Europe, Japan, and Texas was reviewed. Also, speakers from Berkeley Laboratory and the California Air Resources Board addressed the numerical simulation of smog formation, and the health impacts of smog, respectively. Since the technology of active photocatalytic air cleaners is more advanced than the passive techniques, this technology was reviewed as well. Discussions at the workshop helped clarify which concepts are either well established or disproved and which concepts remain controversial.

3.0 Results

3.1. Workshop Summary

A major effort during this project was directed toward the organization of the workshop on "Passive Photocatalytic Oxidation of Air Pollution," held June 29, 2007, at LBNL (see Appendix A, B, and C). In addition to the project team at LBNL (Heat Island Group, Akbari, Berdahl, Levinson), additional Berkeley Laboratory speakers were Hugo Destaillats of the Indoor Air Group on active air cleaners and Shaheen Tonse of the Atmospheric Sciences Group on computer simulations of pollutant formation and transport. Lori Miyasato of the California Air Resources Board spoke on the health benefits of reducing air pollution in California.

A highlight of the meeting was Professor Pierre Pichat's report on recent photocatalytic oxidation research and development in Europe. Dr. Pichat's advice during workshop discussions was also very helpful since he is an expert in photocatalysis (more than 100 publications) and he takes a balanced view, presenting both advantages and disadvantages of the technology. Professor Robert L. Yuan described ongoing experimental photocatalysis work at Lamar University in Beaumont, Texas. In the absence of a representative from Japan, Paul Berdahl summarized the extensive Japanese literature. He also led an informal discussion designed to elicit opinions from the workshop attendees about future directions for related research and development.

Some highlights of the workshop presentations and discussions were:

1. Airborne exposures to ozone at levels higher than 80 parts per billion (ppb) and particulate matter in excess of 12 micrograms per cubic meter are associated with impaired lung function and premature deaths. Both of these components of smog are the result of emission of nitrogen oxides and VOCs that can potentially be reduced by the passive photocatalytic oxidation technology under consideration.

2. The photochemistry of ozone formation from nitrogen oxides and VOCs is complex. In the absence of VOCs, the concentration of ozone will generally remain below 50 ppb. In the presence of VOCs, values of 50 to 150 ppb can be produced. Decreases in NOx concentrations can lead to *either* decreases or increases in ozone, depending on other conditions such as VOC concentration, temperature, availability of sunlight, etc.

3. The experience in Europe has shown that large-scale photocatalytic oxidation experiments can be expensive and must be carefully designed to obtain reliable information. For example areas of hundreds to thousands of square meters must be covered with catalysts, and air quality monitoring should be performed for a variety of conditions of wind, humidity, temperature, and sunlight. Numerical modeling is seen as an important tool to supplement large-scale experimentation.

4. The choice of the best catalyst from a number of candidates can, of course, depend on the cost. However, cost aside, the performance can also depend on what chemical reactions (i.e., which pollutants) are considered most important.

5. Most VOCs can be readily oxidized by photocatalytic oxidation. However, some partially oxidized intermediates are undesirable compounds like aldehydes. Full oxidation to CO_2 and H_2O (and mineral acids like H_2SO_4 and HCl) is desired.

6. A concern was expressed that the use of titanium dioxide catalyst nanoparticles in roadway pavements could result undesired dispersion of these particles in the environment.

7. The efficacy (including durability) of passive photocatalytic oxidation needs to be established in California before large-scale projects are undertaken.

The workshop brochure is attached as Appendix A. The workshop agenda and attendee list are included as Appendices B and C. The workshop presentations have been posted online at http://coolcolors.lbl.gov/pco-workshop/index.html.

3.2. Summary of Large-Scale Coating Production

The purpose of this section is to briefly summarize the engineering status of commercial large-scale techniques for the manufacture of photocatalytic coatings.

Adding anatase (TiO_2) nanoparticles to many materials is fairly straightforward for the manufacturers. For a low-cost material like cement, the amount of nanoparticles is usually limited to 1% to 5%, to limit the added cost (Strini 2005). It is desired that the

support material be porous to allow the pollutant vapor access to the nanoparticles and the product gases to escape. Also, it is desirable for the support material not to be a strong UV absorber, to permit the UV photons to reach the TiO_2 particles.

The photocatalytic process creates highly reactive OH radicals on the surface of the nanoparticles. It is these radicals that generally initiate the desired oxidation reactions. However, most polymeric materials used for paint-type coatings are readily damaged by the OH radicals, and therefore cannot be used. Fluorinated polymers such as polytetrafluoroethylene (PTFE) and certain siloxane compounds (polymers containing Si-O groups; Allen 2005) are more resistant to damage.

The photocatalytic oxidation of NO leads to the production of nitric acid (HNO_3). Most cement formulations are alkaline, which leads to the neutralization of the nitric acid, and the slow erosion of the substrate. For other product formulations, calcium carbonate can be a desirable addition to promote porosity and neutralize acid (Allen 2005).

Roofing granules in the United States are used to cover asphalt shingles. These granules usually contain pigments (colorants) in a porous coating that is based on potassium or sodium silicate and clay. No doubt these coatings can be engineered to incorporate nanoparticles of anatase TiO_2. One patent (Jacobs 2005) describes how to disperse such particles in order to inhibit biological growth on roofing.

Photocatalytic coatings for glass are commercially available, and coatings for steel are in development (Evans 2007). The coatings for glass are marketed as self-cleaning and hydrophilic, but should assist with oxidation of air pollutants as well. For both glass and steel coatings, an intermediate coating of silica is used to block diffusion of substrate elements that can inactivate the TiO_2 particles. In the case of glass, sodium is identified as the undesirable species, whereas for steel, iron and chromium are undesirable impurities. The TiO_2 nanoparticles are so small that they cannot scatter light if they are uniformly distributed. Hence the coatings on glass can be transparent.

3.3. Summary of Data Comparison

3.3.1. Removal Rates for Oxides of Nitrogen (NO_x)

Emission of nitrogen oxides is the result of high-temperature combustion. Concentrations near congested roadways and in tunnels can exceed 1–2 parts per million (ppm) of NOx, mostly in the form of NO. At locations away from immediate sources, the NOx is present mostly in the form of NO_2. Annual average values in the Los Angeles area in 2001 were in the range of 0.018 to 0.042 ppm of NO_2 (Wallerstein et al. 2003).

NO_x oxidation rates have been investigated by a number of authors. Ibusuki (2002) used 200 cm^2 porous plates of a fluorocarbon polymer (PTFE, polytetrafluoroethylene), an alkoxysilane polymer, and cement, all impregnated with TiO_2 nanoparticles (crystallite size 7 nm, specific area 320 $m^2 g^{-1}$). With a flow rate of 1.5 l min^{-1} of air (80% humidity) containing 1 ppm of NO, a 70%–90% removal rate of NO_x was demonstrated (see Figure

1). This experiment also demonstrates that differing methods of supporting the titanium dioxide particles leads to differing removal efficacies; thus optimizing material design is important in applications. Using an 85 % conversion rate and a 12-hour day, one finds that about 60 mg m^{-2} d^{-1} of NO$_x$ is removed. This cited conversion rate is roughly proportional to the NO feed gas concentration. Reaction rates can also depend on temperature, humidity, UV flux (which was 0.5 mW cm^{-2}, from fluorescent "black" lamps) and the presence of additional reactants, so caution is necessary in extrapolations based on the data. (Above 0.1 mW cm^{-2} in this experiment, the reaction rate was insensitive to the UV flux.) The normalization area used here is 1 square meter of the catalyst-containing plate, not the much-larger surface area of the catalyst particles.
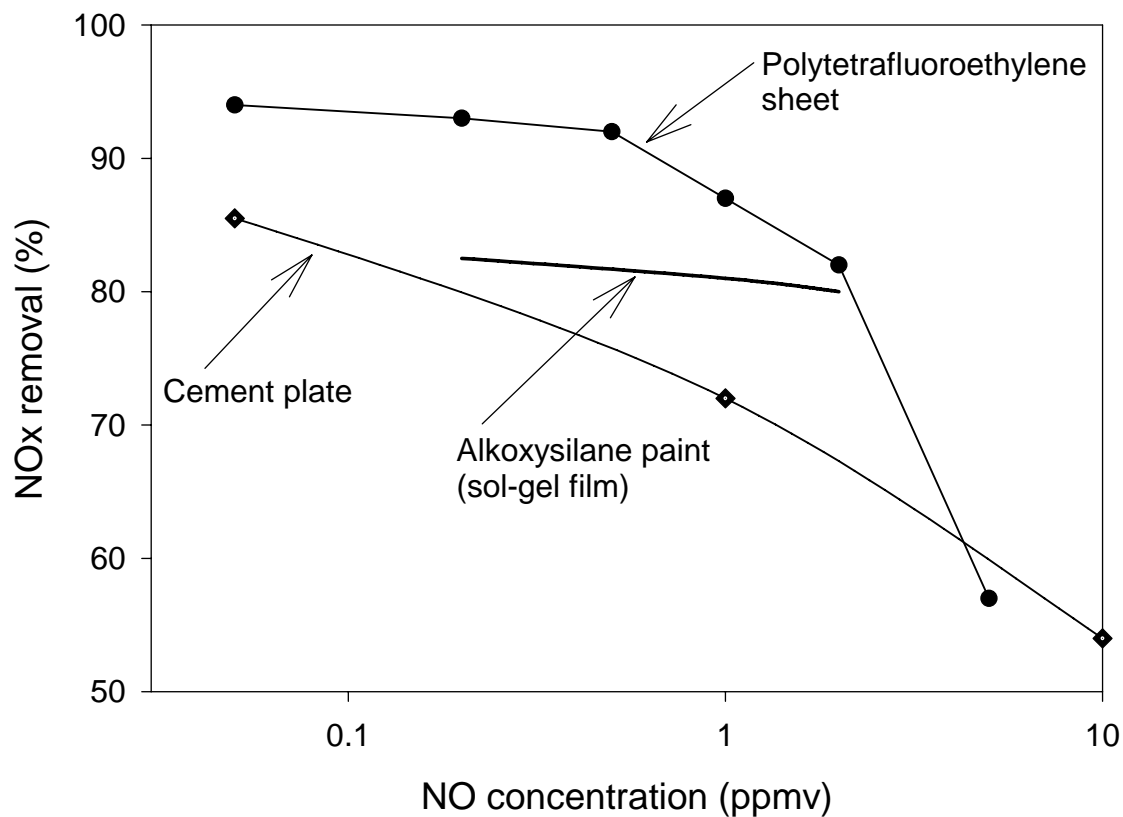
Figure 1. Fraction of NOx removed (%) for several samples containing TiO$_2$ nanoparticles, as a function of NO feed gas concentration (After Ibusuki 2002). The fraction removed is nearly independent of NO concentration, but declines above 1 ppm.

Ibusuki (2002) also describes outdoor experiments with TiO$_2$-loaded PTFE panels under conditions with ambient NO$_x$ concentrations in the range of 0.5 to 1.5 ppm. Ibusuki summarizes the conversion rate as roughly 3 mmol (NO$_x$) m^{-2} d^{-1}. Since the NO$_x$ is largely NO with a molecular weight of 30, this quantity translates to about 90 mg m^{-2} d^{-1}.

J. C. Yu (2002) evaluated a number of TiO_2-loaded samples for air cleaning potential. Feed gas with 1 ppm NOx was employed, with 0.9 mW cm^{-2} UV flux. A concrete paving block (NOXER paving block, Mitsubishi Materials Corporation, Tokyo, Japan) was found to eliminate 54 mg m^{-2} d^{-1} of NOx. A number of other materials that were evaluated had negligible catalytic activity for NOx removal. However, the three best materials removed 300 ± 50 mg m^{-2} d^{-1}. The testing by Yu (2002) was performed primarily at a low relative humidity of 25%. Supplementary tests showed that the reaction rates at 75% humidity were slowed to 2/3 of the rate at 25%.

P. Pichat (2007a) reported experiments by the Greek National Scientific Research Centre with 250 ppb concentrations of NO at 50% relative humidity, with 0.68 mW UV-A flux, using a 1-mm-thick cement-based photocatalytic coating. The reaction rate was 0.29 μg m^{-2} s^{-1}. Thus, for a 12-hour day, this rate is 12.5 mg m^{-2} d^{-1}. This rate extrapolates to 50 mg m^{-2} d^{-1} at 1 ppm of NOx.

Summarizing the rates cited here, and approximately adjusting the rates to standard conditions of 50% relative humidity and 1 ppm of NOx, we find removal values of 50, 72, 90, and 240 mg m^{-2} d^{-1}. Thus different researchers find similar reaction rates for NOx. It should be noted that these rates require a UV flux of at least 0.1 mW cm^{-2}. Here, the higher rates presumably were achieved by utilizing more, or more active, TiO_2 anatase nanoparticles.

3.3.2. Removal Rates for Volatile Organic Compounds (VOCs)

Strini et al. (2005) report a recent and careful evaluation of oxidation rates for benzene and three alkylbenzenes: toluene, ethylbenzene, and *o*-xylene. This work showed that the reaction rates were proportional to the UV-A photon flux in the range of 0.7 to 1.3 mW cm^{-2}. This behavior is different from the NOx rates, which were independent of UV flux in this range. Also, the reaction rates were shown to be proportional to reactant concentration in the range of 0.5 to 5 μmol m^{-3}. Tables 1 and 2 display the oxidation rates for cement samples with 1% TiO_2, and a simple film of TiO_2 particles, with a mass density of 1 mg cm^{-2}. In both cases, the TiO_2 particles were the commercial (Degussa) catalyst P-25 and the UV-A flux was 1.3 mW cm^{-2}.

The catalytic activity in the last column of Tables 1 and 2 gives a rough measure of the number of cubic meters of air that can be purified per hour, by a surface of 1 m^2. Tables 1 and 2 show that the catalytic activity depends on how the catalyst is deployed and on the particular organic compound that is being oxidized. Here we can see that benzene oxidizes more slowly than three of its derivatives.

Generally, for conversion rates, one finds the ordering: alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic and alkane hydrocarbons > halogenated aliphatic hydrocarbons (Hodgson et al. 2007). Hodgson et al. also observed that compounds that dissolve easily in water tend to have higher reaction rates, and that compounds that react rapidly with OH radicals in the gas phase also tend to have higher reaction rates. The relationship with water solubility is likely related to the fact that one

or two monolayers of water are usually present on oxide surfaces if the relative humidity is more than about 10%.

Table 1. Oxidation rates for four important volatile organic compounds by a cement sample containing P-25 catalyst. The catalytic activity (last column) is the ratio of the two prior columns.

1% TiO$_2$ in cement sample	Concentration ppbv	Concentration μmol m^{-3}	Oxidation rate μmol m^{-2} h^{-1}	Catalytic activity m h^{-1}
Benzene	85	3.54	0.16	0.05
Toluene	63	2.60	0.76	0.3
Ethylbenzene	34	1.43	1.24	0.9
o-Xylene	28	1.16	1.29	1.1

Table 2. Oxidation rates for four important VOCs by a P-25 film (with no cement). The catalytic activity (last column) is the ratio of the two prior columns.

TiO$_2$ film of P-25 1 mg cm^{-2}	Concentration ppbv	Concentration μmol m^{-3}	Oxidation rate μmol m^{-2} h^{-1}	Catalytic activity m h^{-1}
Benzene	24	1.01	2.73	2.7
Toluene	13	0.52	2.68	5.1
Ethylbenzene	11	0.47	2.34	5.0
o-Xylene	10	0.42	2.11	5.1

In general, the photocatalytic oxidation processes can be complex. For example, in comparison tests of several different catalysts, it was found that the ranking of the catalysts differed when oxidation of NOx or the de-colorizing of rhodamine B dye was used (Pichat 2007b). Neither ranking correlated with catalyst surface area, either. Other important factors can be the chemistry of the specific molecules participating in the reactions, the absorption of UV light, competition of different molecules for reaction sites, and the lifetime of the photo-generated holes.

Standard tests for ranking catalytic materials for various applications are desired. In view of the complexity just mentioned above, and in view of the fact that testing can be complex and expensive, adequate industrial standards are still under development. Work has begun in Japan, and there is recent activity in Europe as well (Fujishima 2006).

3.3.3. Removal Rates for Carbon Monoxide: Negligible

TiO$_2$ is not very active for the photo-oxidation of CO to CO$_2$. Ibusuki (2002) notes that zinc and cerium oxides are more effective. In the photo-oxidation of benzene some CO is produced. This CO can be oxidized only if a small amount of platinum is added to the TiO$_2$. Yu (2002) tested a 10 ppm CO air stream and found no measurable decrease in CO concentration in a TiO$_2$ photoreactor.

3.4. Summary of Large-Scale Efficacy: Extrapolating to Neighborhoods and Cities

The large-scale efficacy of smog reductions by widespread deployment of TiO_2 photocatalytic materials is still an unsolved problem. Very optimistic statements have been made, yet skeptics are unconvinced. In 2007, *Time* magazine quoted Enrico Borgarello, head of R&D for of Italcementi, a global cement producer headquartered in Italy: "When light shines on TX [cement additive containing TiO_2 developed by Italcementi], the material becomes active and neutralizes surrounding pollutants like nitrous oxide and sulfur dioxide." The *Time* article continues: "According to tests conducted by Italcementi, which spent more than a decade and $10 million developing the product, TX can reduce local air pollutants from 20% to 70%, depending on sunlight levels and wind. (It also adds as much as 20% to the cost of the cement.) Cover 15% of the exposed surfaces of a city like Milan, Borgarello estimates, and you could cut pollution in half. And as a bonus, TX helps buildings stay whiter than white by resisting the pollutants that scar and stain cement over time."

While it is clear that photo-oxidation of air pollutants is an important and useful technology, it is not at all clear that it is ready for widespread deployment. The sense of the experts at the project's workshop was that Borgarello's optimistic marketing vision must be received with skepticism unless and until a quantitative model of pollution formation, destruction, and transport can simulate the benefits to be achieved. A highly detailed model is not needed. However, the model must simulate ozone formation from NOx and VOCs and must account for the fact that decreases in NOx can sometimes cause *increases* in ozone.

As one step toward understanding of the large-scale efficacy of photocatalyst deployment, the concept of "catalytic activity" is quite useful. The catalytic activity of a material surface is the rate at which the pollutant is destroyed, divided by the pollutant concentration. The largest rate cited above for NOx was 240 mg m^{-2} d^{-1}. The mass concentration of NOx at 1 ppmv is about 1.2 mg m^{-3}. The ratio of these two quantities, the catalytic activity, is 200 m d^{-1}. A comparable number for the oxidation of some VOCs, taken from Table 2, is about 12 x 5 m h^{-1} = 60 m d^{-1}. (Of course, for some VOC/catalyst combinations, this number will be lower or higher.) If we now suppose deployment of coated surfaces, buildings, roads, sound walls, etc., with a total surface area equal to the land area, we can expect that in a day's time the coating has the potential to remove the content of NOx of a 200-m-thick atmospheric layer and VOCs of a 60-m layer. Whether or not these potential removal rates are achievable will depend upon the details of hydrodynamic transport and mixing, and molecular diffusion. Whether or not these removal rates are large enough depends on the total volume of air that must be cleaned, the time available, and the fraction of pollutant that must be removed.

Because reaction rates are proportional to concentration, it is apparent that more pollutants can be removed when concentrations are high. This behavior will be helpful when planning to mitigate critical pollution events. From a similar perspective, it will be

effective to locate photocatalytic oxidizing surfaces near pollutant sources, where the concentration is high, such as along congested roads. It may also be helpful to locate the catalytic surfaces upwind of ozone nonattainment areas.

3.5. Issues for Future Program Planning for Research, Development, and Demonstration

Over the long term, implementation of passive photocatalytic cleaning of outdoor air will require both small and large demonstration projects. It will also require market development and implementation activities in collaborations that include state agencies, industrial companies, and research organizations. Additionally, over both the short and long term, various technical issues should be addressed.

3.5.1. Meteorological Modeling Supported by Laboratory Experiments and Observational Data

First, meteorological modeling incorporating smog creation, transport, and destruction is needed to identify which implementation strategies will be most effective in addressing the health problems created by smog. Reductions in peak ozone levels are needed. However, it is also important to examine the generation of various partially oxidized species to ensure that the net effects of the photo-oxidation are beneficial; for example to ensure that carbon monoxide generation is at acceptable levels. Furthermore, the meteorological modeling will need to be supported with laboratory experiments and observational data to ensure the reliability of the modeling.

3.5.2. Enhancing Catalytic Activity by Innovation

The catalytic activity of present-day TiO_2 anatase nanoparticle materials is sufficient to remove some NOx and VOCs from the air. However, higher-performance materials are highly desirable. Innovation to enhance catalytic activity without greatly increasing cost is needed. Both improvements in the individual particles (e.g., by doping) and improvements in support substrates for the particles will be useful.

3.5.3. Proving Catalyst Durability

Large-scale implementation projects will not go forward until the chosen catalyst materials have proven durability. Catalyst fouling by reaction products must be shown to be within acceptable ranges. If catalyst regeneration requires liquid water, California's dry summers may prove a liability. The design of systems that can use dew as a moisture source may be helpful.

3.5.4. Avoiding Unintended Environmental Consequences

Before implementation, additional research should be conducted to ensure that deployment of the photocatalyst does not lead to any adverse environmental consequences—such as the release of harmful compounds into the atmosphere or water (runoff).

3.5.5. *Examining Alternative Photocatalytic Air-Cleaning Technologies*

Pichat et al. (2000) have shown that ozone can be directly eliminated by TiO_2 nanoparticles in a process that is promoted by both heat (in the ambient temperature range of 0° to 50°C) and by UV light. Further examination of this process seems warranted. Other alternative approaches may emerge as well.

4.0 Conclusions

The performance of high-quality photocatalytic materials has been characterized in terms of *catalytic activity*, which is the volume of air that can be cleaned in a given time by a unit area of surface. Catalytic activity is a key figure of merit that can be measured in laboratory experiments and that can be used as a key input to meteorological simulations of smog formation, transport, and destruction.

Photocatalytic reduction of air pollution using titanium dioxide nanoparticles is technically feasible, since the catalytic activity is not zero. However, accomplishing this goal in a cost-effective manner will be challenging, since large volumes of air must be processed. Needed are meteorological simulations of pollutant generation, transport, and destruction in order to optimize photocatalysis deployment; and further improvements in the catalytic activity of the materials.

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Appendix A – Workshop Brochure

Workshop on

Passive Photocatalytic Oxidation of Air Pollution

Friday, June 29, 2007
9 am - 5 pm

Perseverance Hall
Lawrence Berkeley National Laboratory
Berkeley, California · USA

Abstract

This workshop is intended to provide a roadmap for the development of a program using titanium dioxide nanoparticles to reduce air pollution in California cities. We focus on *passive* Photo-Catalytic Oxidation (PCO) strategies in which the catalytic particles are supported by building materials and irradiated by sunlight. We will review current technical knowledge and identify problems that must be solved with applied research in order to enable eventual deployment of the technology.

Background

Small particles of titanium dioxide act to catalyze oxidation of adsorbed molecules in the presence of above-bandgap ultraviolet (UV) light. Research is underway to characterize the rates and reaction pathways for various volatile organic compounds (VOCs, such as benzene, toluene, terpenes, etc.) that can produce toxic ozone when irradiated in the presence of NO_x. Oxides of nitrogen and sulfur can also be removed. Research is also identifying improved catalysts, mostly variants of anatase TiO_2 particles. The size of the ongoing research effort is indicated by a literature search, using the terms photocatalysis and TiO_2, which identifies 3,000 publications in the past ten years.

The Heat Island Group (of the Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory) has been investigating and assisting with the commercialization of novel infrared-reflecting cool roofing materials for the past decade. We have recently contracted with the California Energy Commission to examine the feasibility of novel roofing and other construction materials that may clean the ambient air.

At the workshop, speakers will summarize the current state of the art. Then, discussion will focus on the identification of the most important problems that need to be addressed before the technology can be deployed. Below is a list of key issues identified so far.

Who should attend?

- Scientists with information on the efficacy of passive PCO
- Representatives of companies manufacturing or deploying catalysts
- Representatives of public agencies with an interest in abating air pollution such as the California Energy Commission, USEPA, USDOE, California Air Resources Board, Air Pollution Control Districts, etc.

If you wish to speak at the workshop, please make advance arrangements with Paul Berdahl or Hashem Akbari. Additionally, Maya Minamihara can accept registrations and arrange for site access.

Workshop Contacts:

Paul Berdahl, +1-510-486-5278, PHBerdahl@LBL.gov
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Administrative contact Maya Minamihara, +1-510-486-6845, +1-510-486-6996 (fax), MMinamihara@LBL.gov

Further workshop details will be posted to http://coolcolors.LBL.gov/pco-workshop .

Questions for future applied research on passive PCO

We take as given that continuing basic research will seek improved catalytic materials such as doped TiO_2 and mixtures of catalytic oxides with metals. Nanoparticle anatase TiO_2, however, provides a baseline material for applications. So the most pressing issue is: Can passive PCO deployment provide significantly cleaner air at an acceptable cost?

(1) *Material Options*. What are the most attractive options for deployment? These may include cement concrete walls, roads, polymeric coatings, window coatings, etc.

(2) *Material design*. As an additive to cement at the 1 – 10 % level, anatase works as a photocatalyst. However, can the catalytic particles be integrated into a porous surface layer and thereby improve performance? How should the nanoparticles be supported? A related issue is optimizing the use of the available UV flux.

(3) *NOx reaction rates*. Removal of NO_x may be the most important asset of passive PCO. Its reaction produces reactive nitric acid, and in the presence of calcium ions, water soluble calcium nitrate. What are the reaction rates currently achievable, and what are the theoretical limits of performance? [One estimate (J. C. Yu) is that a 1 m^2 area can remove 0.1 g of NO_x during a 12-hour day.]

(4) *Overall effects of passive PCO deployment*. What are the current pollutant levels in cities and how can widespread PCO alter the concentrations and species? Reaction rates depend on UV flux, reactant levels, temperature, and humidity. The recent European PICADA program demonstrated a favorable impact on NO_x and some VOCs in outdoor experiments. Also, the relationship between laboratory experiments and corresponding outdoor experiments was investigated. However, other work shows that partial oxidation of some VOCs leads to toxic products such as formaldehyde. Is this a show-stopper?

(5) *Durability.* The practical utility of passive PCO requires demonstrations that catalyst deactivation is a minor issue or one that can be managed.

(6) *Cost.* Technology for source control of NO_x costs roughly $2,000 to $10,000 per metric ton. How cost effective is passive PCO?

(7) *Patent issues*. It has been pointed out that a large number of patents have been issued. Do companies entering the field have to license technology from Japanese and European firms?

(8) *Standards*. We need simple standard tests suitable for rating (for example) the ability of paving tiles to destroy NOx and VOCs. Despite work on this issue in Japan and Europe, this issue appears unresolved.

(9) *Other items as suggested by Workshop participants*

Appendix B – Workshop Agenda

Agenda for Workshop on

Passive Photocatalytic Oxidation of Air Pollution

Friday, June 29, 2007
9 am - 5 pm

Perseverance Hall
Lawrence Berkeley National Laboratory (LBNL)
Berkeley, California · USA

9:00 Welcome and Introductions

9:15 Workshop Overview – Hashem Akbari, LBNL

9:35 Health benefits of reducing air pollution in California – Lori Miyasato, California Air Resources Board

10:05 Overview of O3/NOx/VOC production and transport in Northern and Central California, Shaheen Tonse, Atmospheric Sciences group, LBNL

10:25 – 10:40 Break

10: 40 Recent European R & D – The PICADA project – Pierre Pichat, CNRS, Ecole Centrale de Lyon

11:20 R & D in Texas – Robert L. Yuan, Civil Eng. Dept., Lamar Univ., Beaumont Texas

11:50 Summary of R & D in Japan – Paul Berdahl, LBNL

12:20 – 1:20 Lunch (provided on-site)

1:20 Status of active photocatalytic air cleaners – Hugo Destaillats, LBNL

Design of a Program for California

Topic discussions based on the questions in the workshop brochure

1:40 Material deployment strategies and material design

2:10 NO_x reaction rates

2:40 Overall effects of passive PCO deployment; undesired reaction products

3:10 – 3:15 Break

3:15 Cost and durability; Will dry California summers impair catalyst regeneration?

3:45 Patent issues; Standards

4:15 Outline of a California Program

Appendix C – List of Workshop Attendees

Attendees at Workshop on Passive Photocatalytic Oxidation of Air Pollution
Lawrence Berkeley National Laboratory
June 29, 2007

Hashem Akbari, LBNL (Lawrence Berkeley National Laboratory)

Gina Barkalow, CEC (California Energy Commission)

Paul Berdahl, LBNL

Judith Bergland, SSAI (Support Systems Associates, Inc.), NASA (National Aeronautics and Space Administration), SSC (Stennis Space Center).

Hugo Destaillats, LBNL

Scott R. Frerichs, Dupont

Racheal Gould, 3M

Lara Gundel, LBNL

Daria Kibanova, LBNL guest

Tom Kirchstetter, LBNL

Alfred T Hodgson, LBNL

Hong, Keith C., Saint Gobain

Ash Lashgari, ARB (California Air Resources Board)

Ronnen Levinson, LBNL

Lori Miyasato, ARB-RD (Air Resources Board-Research Division)

Marla Mueller, CEC

Pierre Pichat, CNRS (Centre National de la Recherche Scientifique), and Ecole Centrale de Lyon, France

Linda Smith, ARB-RD

Shaheen Tonse, LBNL

Edward Vine, CIEE

Robert Yuan, Lamar Univ. Beaumont, Texas

Staff: Maya Minamihara, LBNL