

Investigation of key parameters influencing the efficient photocatalytic oxidation of indoor volatile organic compounds (VOCs)

Natalia Quici¹, Daria Kibanova², María Laura Vera¹, Hyeok Choi³, Dionysios D. Dionysiou³, Marta I. Litter¹, Javiera Cervini-Silva², Alfred T. Hodgson^{4,φ} and Hugo Destailats^{4,5,*}

¹ Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

² Universidad Nacional Autónoma de México, Mexico City, Mexico

³ University of Cincinnati, Cincinnati, OH, USA

⁴ Lawrence Berkeley National Laboratory, Berkeley, CA, USA

⁵ Arizona State University, Phoenix, AZ, USA

^φ Current address: Berkeley Analytical Laboratories, LLC, Richmond CA, USA

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⁴Lawrence Berkeley National Laboratory, Berkeley, CA, USA

⁵Arizona State University, Phoenix, AZ, USA

^ϕCurrent address: Berkeley Analytical Laboratories, LLC, Richmond CA, USA

*Corresponding email: HDestailats@lbl.gov

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Introduction

Photocatalytic oxidation of indoor VOCs has the potential to eliminate pollutants from indoor environments, thus effectively improving and/or maintaining indoor air quality while reducing ventilation energy costs. Design and operation of UV photocatalytic oxidation (UVPCO) air cleaners requires optimization of various parameters to achieve highest pollutant removal efficiencies while avoiding the formation of harmful secondary byproducts and maximizing catalyst lifetime.

Materials and Methods

We evaluated the effect of key parameters on the performance of TiO₂-based photocatalysts in bench-scale experiments. A flow reactor was used to evaluate the effect of relative humidity, residence time, catalyst film thickness and UV frequency. The reactor operated at realistically low inlet toluene concentrations (~100 ppbv). Glass-supported photocatalyst samples were prepared using *dip-coating* and *sol-gel* methods, and irradiated with UV light under consistent reactor conditions. In each case, replicate samples were collected downstream of the reactor operating at steady state, with and without UV irradiation, to determine toluene removal ratios and byproduct yield. Toluene was sampled in Tenax sorbents and analyzed by thermal desorption/GC/MS; formaldehyde was derivatized with DNPH and analyzed by HPLC. In separate experiments, Fourier Transform Infrared Spectrometry (FTIR) using an Attenuated Total Reflection (ATR) flow cell was used for the evaluation of functional groups

formed or consumed during the irradiation of various model compounds (aromatic pollutants, terpenes, carboxylic acids) adsorbed onto a thin film of the photocatalyst.

Results and Discussion

In the bench-scale flow reactor, toluene removal efficiency was optimal for 10% RH and lower for higher humidity, suggesting a competitive displacement by water at the TiO₂ surface. At a long residence time (τ), toluene removal efficiency was higher than for shorter times (50-70% removal at $\tau=12$ ms vs. 18-35% removal for $\tau=3$ ms), and the yield of formaldehyde was significantly lower (<5% yield at $\tau=12$ ms vs. up to 20% yield for $\tau=3$ ms). This effect illustrates the critical effect of reactor design on the yield of undesired secondary byproducts. Upon increasing the TiO₂ film thickness, toluene removal efficiency increased linearly, reaching a maximum for 72 $\mu\text{g TiO}_2 \text{ cm}^{-2}$, corresponding to a film thickness of 350 nm. Thicker films did not result in additional efficiency.

FTIR analysis of the photocatalytic oxidation of 2-methylnaphthalene (2-MN) adsorbed on TiO₂ revealed the formation of stable intermediates exhibiting aldehyde, alcohol and carboxylic acid functionalities, which accumulated on the surface of the photocatalysts as 2-MN was degraded. Similarly, we analyzed the photo-oxidation of oxalic acid and gallic acid, two recalcitrant species which showed a significant degree of association with co-adsorbed water, and relatively slow degradation rates. The accumulation of these species in surface sites likely leads to inactivation of the photocatalyst.