Adsorption and photocatalytic oxidation of formaldehyde on a clay-TiO$_2$ composite

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ABSTRACT

We investigated the adsorption capacity and photocatalytic removal efficiency of formaldehyde using a hectorite-TiO$_2$ composite in a bench flow reactor. The same experimental conditions were applied to pure TiO$_2$ (Degussa P25) as a reference. The catalysts were irradiated with either a UVA lamp (365 nm) or with one of two UVC lamps of 254 nm and 254 + 185 nm, respectively. Formaldehyde was introduced upstream at concentrations of 100–500 ppb, with relative humidity (RH) in the range 0–66% and residence times between 50 and 500 ms. Under dry air and without illumination, saturation of catalyst surfaces was achieved after ∼200 min for P25 and ∼1000 min for hectorite-TiO$_2$. The formaldehyde uptake capacity by hectorite-TiO$_2$ was 4.1 times higher than that of P25, almost twice the BET surface area ratio. In the presence of humidity, the difference in uptake efficiency between both materials disappeared, and saturation was achieved faster (after ∼200 min at 10% RH and ∼60 min at 65% RH). Under irradiation with each of the three UV sources, removal efficiencies were proportional to the Ti content and increased with contact time. The removal efficiency decreased at high RH. A more complete elimination of formaldehyde was observed with the 254 + 185 nm UV source.

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1. Introduction

Formaldehyde (HCHO) is an ubiquitous indoor pollutant released from wood-based building products and furnishings, among other natural and anthropogenic sources [1]. Formaldehyde forms as a result of the oxidation of volatile organic compounds (VOCs) by either ozone or hydroxyl (OH•) radicals under atmospheric conditions [2,3]. Indoor exposure to HCHO is associated with increased risks of asthma and allergy [4]. Reportedly, observed changes in nasal lavage fluids during formaldehyde inhalation have been attributed to non-specific proinflammatory properties [5]. Asthma and allergies are reported to affect ca. 6% and 20% of the

89 million US workers in nonagricultural and nonindustrial indoor settings, respectively. Such health consequences stemming from formaldehyde inhalation in the workplace has been reported to cause productivity losses ranging from 20 to 70\$B yr^{-1} [6]. Furthermore, formaldehyde is listed by USEPA as a probable carcinogen (group B1, USEPA), and the World Health Organization has classified formaldehyde as a human carcinogen [7]. Surveys conducted in both US commercial buildings and homes showed mean indoor HCHO concentrations values ca. 11 and 17 ppbv, respectively. Such concentrations are higher than the 8-h reference exposure levels proposed by the California Environmental Protection Agency, i.e., 7 ppbv, and are close to the 8-h recommended level for occupational exposure in the US (16 ppbv) [8]. Current indoor-air pollutant exposure scenarios are likely to worsen in a near future provided that adaptation to climate change and urban heat island effects may lead to increases in the use of air conditioning, tighter building envelopes, as well as to lower air-exchange rates [9]. In addition, expanding urbanization and changes in land use patterns may contribute to increased surface-level concentrations of ozone, an indoor formaldehyde precursor [10].

Advanced indoor air cleaning technologies can play an important role in mitigating indoor exposures. In a related work we have tested prototype TiO$_2$ photocatalytic oxidation (PCO) air cleaners.

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Table 1
Preparation of photocatalyst-coated Raschig rings.

Material	m_f (mg)	TiO$_2$ content[a] (%)	$m_{f\text{-TiO}_2}$ (mg)	BET surface area[a] (m^2 g^{-1})	Average pore volume[a] (cm^3 g^{-1})
Hecto-TiO$_2$	1.03	60.8	0.626	140	0.457
P25	0.762	100	0.762	60.7	0.308

[a] Data taken from Ref. [14].

The results have showed promise in the simultaneous abatement of VOCs present in multi-component mixtures at typical indoor levels [11–13]. We observed single-pass conversion efficiencies better than 20% for most VOCs, reaching in some cases as much as 80% removal. Although volatile aldehydes can be eliminated by PCO at rates comparable to those for other VOCs, incomplete mineralization of a few target compounds present in the mixtures (alcohols, terpenes) results in the formation of additional HCHO, acetaldehyde, and other partially oxidized byproducts. For the experimental conditions tested, HCHO outlet/inlet concentration ratios were between 1.9 and 7.2. Given the data variability observed, it becomes clear the need for improving experimental conditions towards PCO applications.

Clay-TiO$_2$ nanocomposites have been postulated as suitable alternative photocatalysts in environmental applications. In particular, for air treatment considerations, these materials offer a large porous structure for VOC adsorption and high adsorption capacity. Recently, we have synthesized hectorite-TiO$_2$ composite (hecto-TiO$_2$) [14], a titania-rich material (60% TiO$_2$) with significantly higher BET surface than Degussa P25 TiO$_2$ (BET$_{hecto-TiO_2}$/BET$_{P25}$ = 2.3). We tested the material towards toluene as probe compound. When challenged with toluene vapor, hecto-TiO$_2$ showed a performance comparable to P25 under air either under dry conditions or low relative humidity, ca. $\leq$10% RH. However, hecto-TiO$_2$ performance was found to become partially inhibited at higher humidity, ca. 33% and 66% RH [15]. These findings were explained as the consequence of water adsorption and condensation at nano-sized pores sites, which limits the access of hydrophobic compound molecules to TiO$_2$ active sites. In this study, we challenge hecto-TiO$_2$ under similar testing conditions with HCHO, a hydrophilic compound. The purpose is to explore the photocatalytic activity of surface clay-TiO$_2$ composites towards HCHO, and better understand the effect of water co-adsorption in photocatalytic efficiency.

2. Experimental

2.1. Preparation of clay-supported TiO$_2$

Hectorite (Na$_{0.4}$Mg$_{2.7}$Li$_{0.3}$Si$_4$O$_{10}$(OH)$_2$; SHCa-1) from San Bernardino County, CA, USA, was purchased from the Source Clays Repository of the Clay Minerals Society (West Lafayette, IN), and used as received. A description of the synthesis and characterization of the TiO$_2$–clay nanocomposites has been reported previously [14]. Briefly, a 1% (w/w) clay–water suspension was stirred for 2 h. A TiO$_2$ sol–gel solution was prepared by mixing titanium tetraisopropoxide Ti(OC$_3$H$_7$)$_4$ (97%, Sigma–Aldrich, Milwaukee, WI) with hydrochloric acid (37%, reagent grade, Aldrich, Milwaukee, WI), de-ionized water (17.6 MΩ cm, Millipore) and absolute ethanol ($\geq$98%, Riedel-de Haen, Switzerland). The concentration of Ti(OC$_3$H$_7$)$_4$ in the sol–gel solution (Solution A) was 0.4 M. The H$_2$O/Ti(OC$_3$H$_7$)$_4$ molar ratio for Solution A was adjusted to 0.82, and the pH was 1.27. Solution A was diluted with absolute ethanol to obtain a Ti(OC$_3$H$_7$)$_4$ concentration ca. 0.05 M (Solution B). An aliquot of Solution B was added to the clay suspension to adjust the TiO$_2$ content in suspension ca. 70% (w/w). The resulting suspension was stirred for 24 h, and then centrifuged at 3800 rpm for 10 min. The solid phase was recovered and washed three times with de-ionized water. The hectorite-TiO$_2$ composite was dispersed in

a 1:1 water:ethanol solution, and then exposed to hydrothermal treatment at 180 °C for 5 h. The product was centrifuged once again at 3800 rpm for 15 min, and re-suspended in absolute ethanol (Solution C).

2.2. Preparation of photocatalyst-coated Raschig rings

Fifty Raschig glass rings (5 mm OD × 5 mm length; Ace Glass, Vineland, NJ) were coated with hecto-TiO$_2$ composite and fifty more were coated with P25 (TiO$_2$, Degussa, Germany). Before coating, the rings were initially sonicated for 5 min in acetone (J.T. Baker), and for 5 min in de-ionized water; and oven-dried at 60 °C for 1 h. Each ring was dip-coated for 5 s in suspensions containing (a) Solution C or (b) P25 suspended in ethanol. Coated rings were placed in an oven at 110 °C for 5 h to evaporate the solvent. Dried-coated rings were stored in ambient conditions prior to use.

The average mass of the photocatalytic material deposited in each ring was determined as follows:

$$m_f = \frac{(m_c - m_g)}{50} \tag{1}$$

where m_f is the average mass of photocatalytic material per ring; m_c is the mass of 50 coated rings; and m_g is the mass of the same 50 rings determined before coating. Shown in Table 1 are data for average mass (m_f), average mass of TiO$_2$ deposited per ring ($m_{f\text{-TiO}_2}$), as well as BET surface area for each catalyst, average pore area for hecto-TiO$_2$ and equivalent average pore area for P25, as determined by the BJH method.

2.3. Photocatalytic reactor and experimental methods

2.3.1. Photocatalytic reactor and UV lamps

The photocatalytic flow reactor used in the experiments has been described previously [15,16]. Briefly, the reactor consisted of a cylindrical-quartz tube containing a variable number of coated or uncoated-Raschig rings, which were irradiated by a UV-lamp and placed parallel to the tube at a constant distance ca. 25 mm. Three-different lamps were used: a UVA lamp with λ_{max} = 365 nm and irradiance I_{365} = 0.77 mW cm^{-2} (UVP Model 90-0019-01), a UVC lamp (UVC/O$_3$) with λ_{max} = 254 nm and secondary emission at 185 nm with an irradiance I_{254} = 2.8 mW cm^{-2} (UVP Model 90-0004-01) and a second UVC lamp (Spectroline Model 11SC-1 OF) with λ_{max} = 254 nm and an irradiance I_{254} = 4.45 mW cm^{-2}. The magnitude for the irradiance of the lamps at 25 mm from the source was determined with a UVP radiometer calibrated at 365 nm and 254 nm, respectively.

2.3.2. Formaldehyde source

Paraformaldehyde (J.T. Baker, Phillipsburg, NJ) was used to generate a constant flow of formaldehyde [17]. A constant airflow of "zero" quality air of 300 mL min^{-1} was circulated through the diffusion vial containing paraformaldehyde placed in a water bath at constant temperature (20 ± 1 °C). The generated formaldehyde concentration at the source outlet varied between 530 and 650 ppbv. A 100 mL min^{-1} flow was diverted from the source outlet and diluted with either dry or humid air. The flow and concentration of formaldehyde at the reactor inlet were adjusted to ca. f = 500 mL min^{-1} and [HCHO]$_{inlet}$ = 110–130 ppbv, respectively.