



Gas phase adsorption of volatile organic compounds onto titanium dioxide photocatalysts

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ABSTRACT

Adsorption of pollutants onto photocatalyst surface plays a critical role in the efficacy of photocatalytic oxidation (PCO) technology for air purification applications. In this article, gas phase adsorption of toluene and methyl ethyl ketone (MEK) was studied using a small-scale single-pass continuous flow system. Equilibrium adsorption isotherms for toluene and MEK on six commercially available TiO₂ photocatalysts (P25, PC500, PC105, UV100, PC-S7, and S5-300A) coated on nickel foam substrates were determined. The selected photocatalysts cover a wide range of important photocatalytic properties including surface area, porosity, acidity, and population of surface hydroxyl groups. The TiO₂ coated filters were characterized by SEM technique to evaluate the quality of coating and homogeneity of titania powder on the support material. Furthermore, a thorough Fourier transform infrared spectroscopy (FTIR) was performed to investigate the nature of surface hydroxyl (OH) groups on various photocatalysts. Using the adsorption isotherm data, Langmuir model adsorption coefficients for toluene and MEK on various photocatalysts and humidity levels have been determined. Additionally, the impacts of challenge compound polarity and air relative humidity (RH) on the adsorption efficiency and Langmuir constants were assessed. The adsorption capacity for MEK (a highly polar compound) was much higher than that of toluene (a non-polar compound) on all photocatalysts, regardless of the humidity content. The results vividly showed that the relative humidity negatively affects the adsorption capacity for both MEK and toluene, however to different extents due to the differences in water solubility and polarity. FTIR characterization of MEK/toluene saturated titania samples revealed that isolated OH groups (both terminal (Ti-OH) and bridged (Ti-OH-Ti)) serve as highly active adsorption sites for volatile organic compound (VOC) molecules.

1. Introduction

In recent years, increased awareness regarding the impact of indoor air quality (IAQ) on human health and productivity, and the growing need for energy efficient buildings have resulted in a great deal of research in the field of indoor air purification. Among various methods developed to improve IAQ, photocatalytic oxidation has gained considerable attention owing to its superior features including room temperature process, medium to high efficiency, low energy consumption, and durability. Basically, in PCO, a semiconductor catalyst (such as TiO₂) is illuminated by light with sufficient energy to generate electron-hole (e⁻-h⁺) pairs which then take part in a series of reduction-oxidation reactions and, eventually, resulting in the conversion of VOCs to innocuous CO₂, H₂O and other by-products [1].

Since TiO₂ industrial production in the early 20th century, TiO₂ materials have been used in many different fields ranging from environmental photocatalysis and photovoltaics (i.e. solar cells) to electrochemistry (e.g. battery and fuel cell) and sensors [2–4]. In the field of

PCO air purification, titanium dioxide is the most investigated photocatalyst because it is chemically inert, inexpensive, and active toward various classes of indoor air pollutants [5,6]. Nevertheless, one of the main shortcomings of TiO₂, as a catalyst, is its low adsorption capacity for capturing gaseous pollutants (especially hydrophobic compounds) compared to famous adsorbents such as activated carbon [7].

Adsorption of VOCs onto the photocatalyst surface is crucial for instigating photocatalytic decomposition. It is upon the adsorption on the surface that pollutant molecules come into contact with highly active species/radicals (such as OH[•], O₂^{-•}) and undergo photochemical reactions [8,9]. From another perspective, since the recombination of e⁻-h⁺ pairs takes places extremely fast (< 25 μs [10]), the species that can act as charge carrier traps must be pre-adsorbed on the surface in order to make interfacial carrier trapping kinetically competitive to e⁻-h⁺ recombination process.

To date, several studies have been conducted on evaluating the adsorption performance of TiO₂ for various VOCs [11–18]. Wang et al. [19] investigated the competitive adsorption of methanol and water on

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TiO₂ and reported that methanol adsorption on the surface is much stronger than that of water. In a comprehensive work, the adsorption performance of titania coated fiberglass fibers and titania coated carbon cloth fibers were measured for nine VOCs (toluene, p-xylene, ethanol, 1-butanol, MEK, acetone, hexane, octane, and limonene) at concentration of 0.5–5 ppm and 10–72% RH [12]. It was observed that the adsorption isotherms of all compounds at different humidity conditions are linear with respect to equilibrium concentration, indicating that the adsorption mechanism follows Henry adsorption model at low ppm concentration (< 5 ppm). Among various VOCs tested, 1-butanol and MEK possessed the highest adsorption coefficients, which could be attributed to their high molecular weight and polarity. In agreement with these results, in a study on the adsorption performance of P25, it was showed that alcohols possess higher adsorption efficiency compared to ketones, aromatics, and alkanes [20]. Boulamanti et al. [21] examined the adsorption of aromatic VOCs on P25 and reported that the adsorption constants calculated from Langmuir-Hinshelwood model follow the order: ethyl-benzene < benzene < o-xylene < p-xylene ~ m-xylene ~ toluene. The low adsorption of ethyl-benzene and o-xylene was partly ascribed to their molecular structures, which give rise to bigger stereochemical hindrance during adsorption.

Considering the fact that indoor air can contain numerous chemical gas pollutants, some researchers have focused on the competitive adsorption of VOCs on titania surface [11,22]. Adsorption of 2-propanol/toluene binary mixtures (80–400 ppb concentration and 0–60% RH) on PC500 was studied by Vildoza et al. [22]. Their findings revealed that given the large surface area of the catalyst the competition for PC500 active sites is negligible at dry conditions while under 60% RH the adsorption efficiency substantially declined from 100% to 50% and 70% to 5% for 2-propanol and toluene, respectively. A similar behavior was noted in the co-adsorption of methanol and benzene on P25 upon using humid air, which was attributed to the competitive adsorption between VOCs and water molecules and the lower mass transfer due to the water layer formed on titania surface [17]. Zhong et al. [11] explored the competitive adsorption of binary mixtures of toluene, p-xylene, MEK, and acetone on silica fibers loaded with TiO₂. Based on the obtained results, it was concluded that for the non-polar mixture of p-xylene and toluene and the polar/non-polar mixture of MEK and p-xylene, the presence of a second compound always has an inhibitory effect on the adsorption capacity. However, in the case of MEK-acetone mixture at a specific concentration ratio (MEK/Acetone = 0.6), an improvement in the adsorbed amount with regard to the single compound adsorption was seen.

Regarding the influential parameters in the adsorption process, Nagao and Suda [16] studied the adsorption of benzene, toluene, and chlorobenzene on TiO₂ with rutile crystal phase and noted that the amount of irreversible adsorption for all pollutants declined linearly with increasing the concentration of surface hydroxyl groups. In another work, by analyzing the FTIR spectra of P25 and PC500 in contact with acetaldehyde, Verbruggen et al. [23] proposed that the adsorption of acetaldehyde can occur via H-bridge with a surface hydroxyl group

(CH₃CH=O...HO-Ti) and carbonyl bonding with a cation Ti⁴⁺ surface group (CH₃CH=O...Ti⁴⁺). Kirchnerova et al. [24] investigated the adsorption of n-butanol (580 ppm) over P25 and UV100 in humid air (1.7% water) and highlighted the direct correlation between the catalyst surface area and the adsorbed amount of n-butanol. On the contrary, Suligoj et al. [25] achieved higher toluene adsorption over P25 than over PC500 (12.6% vs. 7.1%), in spite of the fact that PC500 surface area is nearly six fold of that of P25.

Although a great number of articles have been published on the performance of PCO systems, photocatalyst fabrication, and simulation of PCO processes, only a few studies have specifically focused on the adsorption efficiency of photocatalysts for VOC removal. More importantly, in most of the experiments dedicated to study the adsorption of VOCs on photocatalysts, the impact of relative humidity on the adsorption isotherms has not been fully investigated. Motivated by this research gap, the main objective of the present work is to provide a systematic adsorption study of toluene and MEK over titanium dioxide at different levels of relative humidity (0, 20, and 50%). The adsorption performances of six commercially available titanium dioxide photocatalysts (P25, PC500, PC105, UV100, PC-S7, and S5-300A) have been evaluated and adsorption isotherms are presented. Knowing the importance of hydroxyl groups in the adsorption process, FTIR analysis was employed to study the type and concentration of OH groups on titania surface and subsequently determine the contribution of these groups to the adsorption of VOC molecules. Based on the structural properties of selected photocatalysts and the results obtained from FTIR analyses, attempts are made to provide clear explanations for different adsorption trends observed for each titania sample and connect the key properties of the air filter and the adsorption capacity for toluene and MEK.

2. Methodology

2.1. Materials and instrumentation

P25 from Evonik®, PC500, PC105, PC-S7 and S5-300A from Cristal Global Companies, and UV100 from Hombikat® are selected titanium dioxide photocatalysts in this study. Some of the main characteristics of the photocatalysts are tabulated in Table 1 [25–27]. Nickel foam filter (Shanghai Tankii Alloy Material Co.) was used as support material for photocatalyst nano-powders. The width, height, and thickness of the Ni filter are 10, 10, and 0.1 cm, respectively. The morphology of the TiO₂-coated Ni-foam filters was studied by scanning electron microscope (SEM, Hitachi S-4700 Model) at the acceleration voltage of 15 kV. FTIR analyses were carried out using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific). Spectra were recorded in a range of 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹ and an absorbance detection limit of 0.001 a.u. Air spectrum, as background, was always subtracted from the obtained FTIR spectra in all experiments. Toluene (99.9%) and MEK (99.9%) (Fisher Scientific Inc., Canada) were chosen as air contaminants and the relevant physical properties of these compounds are

Table 1
Characteristics of titanium dioxide photocatalysts.

Photocatalyst	Properties			Other remarks	Reference
	BET (m ² /g)	Mean pore radius (nm)	Crystalline phase		
P25	50	–	Anatase (80%) and Rutile (20%)	Non-porous material with interparticle pores (meso and macropore)	[26]
PC500	276	6.1	Anatase	Type IV sorption isotherms indicates the presence of mesopores	[25]
PC105	80	15.3	Anatase	–	[27]
PC-S7	300	–	Anatase	Neutral to moderately alkaline pH	Manufacturer
S5-300A	330	–	Anatase	Acidic	Manufacturer
UV100	330	< 5	Anatase	Agglomeration of small subparticles into round-shaped particles generates high density small pores with characteristic of microporous materials	[26]

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