Using physical–chemical properties of reactants to estimate the performance of photocatalytic oxidation air cleaners

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A B S T R A C T

Various ultraviolet photocatalytic oxidation (UV–PCO) technologies are being used to eliminate or minimize different types of indoor air pollution, namely volatile organic compounds (VOCs). However, the removal efficiency of such air cleaning systems for different kind of VOCs could be challenging or completely unpredictable at different indoor environment conditions. This study presents a new systematic experimental method for measuring the performance of UV–PCO systems for different operational test conditions. The experiments were carried out using a continuous single pass system setup with three different types of TiO$_2$ catalysts at high airflow rate and ambient indoor air temperature and humidity levels. The adsorption isotherm for each catalyst was determined individually to find a correlation for each test compounds. The relationship between the PCO rate constant and ionization potential (IP), as a physical and chemical property of selected alcohols compounds was investigated at the steady-state condition. The developed reaction rate correlations can be used as a design parameter to quantify the removal efficiency of other VOCs with the tested experimental system setup.

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1. Introduction

Heterogenous ultraviolet photocatalytic oxidation (UV–PCO), has received wide interest as a reassuring catalytic process for the degradation of organic pollutants, with acceptable energy consumption and high efficiency for different residential, commercial and industrial applications. There has been an increase in the number of published papers related to PCO within these past few decades where many studies have focused on the gas-phase photo catalysis mainly because of high reaction rate of some vapor phase organic pollutants such as alcoholic and chlorinated organic compounds [1,2]. A photocatalytic oxidation system needs a semiconductor material with an ultraviolet or visible light irradiation to convert the adsorbed airborne emissions into benign substances such as water and carbon dioxide. It is known that the completeness of PCO reaction rates and formation and destruction rate of some intermediates depend on various experimental and environmental parameters [1,3]. Presently, the PCO reactions of more than sixty volatile organic compounds have been studied extensively including formaldehyde, ethylene, acetaldehyde, toluene,

hexane, benzene, and xylene [4–7]. While there is more than 300 organic compounds that are currently identified in indoors environment, and their effect needs to be considered on the design and scale-up of a PCO system [8–11]. The complexity of PCO kinetics with unforeseen byproducts, which can be generated from different PCO reactions, could make it very difficult to obtain an accurate prediction of efficiencies of PCO systems under various environmental conditions. All these factors suggest that the applicability of PCO systems, is still unclear and more research and development are required.

Photocatalytic oxidation is a process which involves seven different reaction steps, namely: adsorption, electron and hole migration, dehydrogenation, hydrogen transfer, oxidation, pollutant degradation and desorption. Whereas conventional catalysts use the thermal activation method, in which photocatalytic reactions employ the photonic activation method in which all reactions occur on the catalyst surface.

In the presence of humidity, adsorbed water molecules tend to react with holes and produce hydroxyl radicals that, in turn, can oxidize VOCs (Fig. 1). The produced oxygen and hydroxyl radicals are the most important electrophiles and nucleophiles species in the photocatalytic process. The adsorbed water molecules could act as traps for the generated holes and hinder the recombination of the active electron-holes. The following equations describe the

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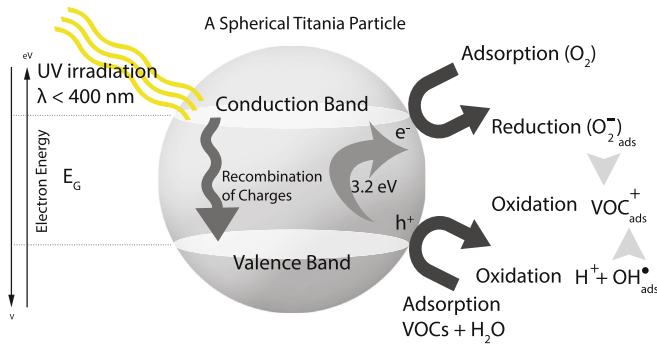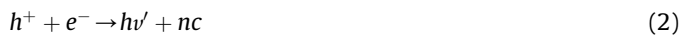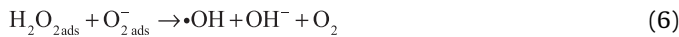 E-mail address: fariborz.haghighat@concordia.ca (F. Haghighat).

Fig. 1. Reaction mechanisms of the PCO on catalyst particle.

possible photoelectronic reactions on the catalyst surface, which include photo generated holes (h^+) [12]:

$$hv + TiO_2 \rightarrow TiO_2 \left(h^+ + e^- \right) \tag{1}$$

$$h^+ + e^- \rightarrow hv' + nc \tag{2}$$

$$h^+ + H_2O_{ads} \rightarrow HO^{\bullet}_{ads} + H^+ \tag{3}$$

$$h^+ + OH^-_{surf} \rightarrow HO^{\bullet}_{ads} \tag{4}$$

$$h^+ + VOC \rightarrow VOC^+_{ads} \tag{5}$$

The produced hydroxyl peroxides react with adsorbed oxygen and available photo electron-holes:

$$H_2O_{2ads} + O^-_{2\,ads} \rightarrow \bullet OH + OH^- + O_2 \tag{6}$$

$$H_2O_{2ads} + e^- \rightarrow \bullet OH + OH^- \tag{7}$$

$$H_2O_{2ads} + hv \rightarrow 2\bullet OH \tag{8}$$

Hydroxyl radicals are also capable of migrating and carrying out the direct destruction of absorbed VOCs on the catalyst surface:

$$\bullet OH + VOC_{ads} \rightarrow VOC_{oxd} + H_2O \tag{9}$$

Accordingly, it is obvious that the PCO mechanism is based on hydroxyl radical attacks and •OH radicals play an important role in the oxidizing organic compounds. The hydroxyl radicals are the most reactive elements and able to virtually oxidize most VOC molecules and degrade them to harmless products such as CO and H_2O.

Although, there is much information about hydroxyl radical activity and organic compounds, the kinetics and mechanisms of reactions are still not fully understood which prevents the development of a comprehensive model. Therefore, it is essential to develop a systematic procedure to identify this kinetic behavior, which allows predicting PCO reaction rates of the VOCs.

1.1. Ionization potential (IP)

Ionization potential (IP)[1] is known as the amount of energy required to ionize a molecule. Ionization generally occurs when the adsorbed energy of molecule is larger than the molecule's energy of

ionization. Therefore, in order to ionize VOCs, the output energy from UV lamps in the system should be higher than IP of the molecules. Since IP is a measure of the electronic density of a molecule, theoretically a higher IP value means that the molecule requires more energy to be ionized. It also has an inverse relation with the PCO rate constants, k_{PCO}, and is a descriptive example of a *structure reactivity relationship* (SRR). Gaffney and Levine [13] used the molecular physical properties of organic compounds, such as *linear free energy*, *bond association energy* in order to correlate the IP and hydroxyl radicals reaction rate of reactants (k_{OH}) together.

Sattler and Liljestrand [14] studied the relationship between the reaction rate constant, k_{PCO}, IP and hydroxyl reaction rate constant of VOCs, k_{OH}, by developing a model based on pseudo-first order L–H mechanism to predict photocatalytic reaction rates for selected class of compounds. However, the correlation between PCO rate constants and IP and OH radical rate constants were found only at the high initial concentration rates. Their experiments were performed using a small batch reactor and at high and low ppm levels of VOCs concentrations and over-saturated humidity (>100% RH). Similarly, Yu et al. also investigated the relationship between the VOCs hydroxyl radicals constant and PCO reaction rates based on Sattler's experimental model; but their experiments were carried out under different conditions (0.1–9.0 ppm for VOCs, RH 20,50, 80%) [15]. They used the Henry's law constant of VOCs to determine the Langmuir adsorption constants: Their PCO kinetic results were followed mono and bimolecular L–H models.

In this study, a series of experiments were carried out in order to establish a correlation between the IP as physical and chemical properties of a class of VOCs and PCO reaction rates. Five VOC compounds (ethanol, n-propanol, 1-butanol, sec-butanol and 3-pentanol) were selected and tested with three different types of catalysts in a four parallel UV–PCO duct system that was especially designed to evaluate different types of PCO systems under similar operational test conditions. The adsorption isotherm and kinetics of individual VOCs were also determined in order to examine the relationship of the IP and the PCO reaction rate for each individual test compound. The effect of humidity on the removal efficiency of UV–PCO systems was also studied in detail.

1.2. Kinetic modeling of PCO

The understating of surface reactions and their kinetics are crucial to successfully predict the removal rate of contaminants in a PCO system. The kinetic of reactions can generally be determined experimentally using reactor, which is operated either in single-pass or multi-pass. First, it is necessary to define efficiency (η):

$$\eta\% = \left(1 - \frac{C_A}{C_{A0}} \right) \times 100 \tag{10}$$

where, C_A, C_{A0} are the outlet and inlet concentration of the reactant species, respectively. The L–H model has been successfully applied to predict the kinetics of PCO reactions in many different PCO research studies [16]. The L–H model consists of adsorption from the gas phase and desorption to the gas phase, separating species on the surface and reactions between adsorbed species on the catalyst surface. The kinetics of photocatalysis generally follows the first order unimolecular L–H model:

$$\frac{1}{r} = \left(\frac{1}{kKC} + \frac{1}{k} \right) \tag{11}$$

A linear regression analysis of the initial rate ($1/r$) versus the initial concentration of VOC ($1/C_{A0}$) gives the k and K values as the reaction rate constant and Langmuir adsorption constant of the

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[1] Ionization potential also known as Ionization Energy (IE).