Gas phase photocatalytic oxidation of VOC using TiO$_2$-containing paint: influence of NO and relative humidity

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Abstract

Advanced oxidation process (AOP) such as photocatalysis is a promising technology for air purification. It is the purpose of this study to investigate the photocatalytic removal of volatile organic compound (VOC) using TiO$_2$-containing paints. The photocatalytic activity of the paint was studied in a walk-in type environmental chamber (30 m^3) under a realistic level of irradiation, humidity and VOC amount with reference to a typical urban air pollutant concentration. The effects of concurrent photodegradation of NO and VOC as well as the effect of the relative humidity level were also investigated in order to evaluate the feasibility of the photocatalytic building material (paint) for air purification under real conditions. It was found that the presence of NO promoted the photodegradation of toluene, under low humidity levels (17% RH), up to 15%. It was suggested that the enhancement of toluene conversion was due to the generation of OH$^.$ radicals during the photodegradation of NO. Results were also showed that no photodegradation of toluene was found while increasing humidity up to 50%.
Keywords: photocatalysis, TiO$_2$, photocatalytic paint, VOCs, NO, air purification, relative humidity.

1   Introduction

Conventional methods for treating VOCs from gas streams, such as absorption, adsorption, condensation and thermal/catalytic incineration have inherent limitations and none of them is cost effectively. Therefore there is a demand for a relatively cheap and environmentally benign process of removing organic compounds in low concentration from gases (Wang and Ray [1], Zhao and Yang [2]). Heterogeneous photocatalytic oxidation (PCO) is useful for the treatment of air polluted with volatile organic compounds (VOCs). It allows the oxidation of airborne VOCs into carbon dioxide and water at room temperature in the presence of a semiconductor catalyst (e.g. TiO_2) and UV light source (Maira et al [3], Blanco et al [4]).

Light excitation of TiO_2 seminoconductor, under a wavelength between 360-380 nm, generates electrons and holes in the conduction and valence bands, respectively. These species are very reactive and can either recombine or diffuse to seminoconductor surface where they are trapped by adsorbed molecules of water and oxygen. They provoke the formation of hydroxyl radicals that attack pollutant molecules and thus degrade them (Riegel and Bolton [5]). Accordingly, materials that use photocatalyst have a semi-permanent capacity for removing VOCs from the air. Therefore, if photocatalysts can be used in roadway structures, as outer material on buildings along roadways etc., the building materials will have the capacity to clean the air along the roadways that is polluted by automobile exhaust gases, using only the solar energy (Fujishima et al [6], Strini et al [7])

Although a wide range of common organic pollutants can be treated by PCO the effectiveness of the process for pollution abatement seems to depend on the chemical nature of the pollutant molecule. For example the photocatalysis rates for aromatic compounds are relatively slow comparing with the complete oxidation of alcohols or chlorinated hydrocarbons (Maira et al [3]). Among numerous compounds which belong to VOCs, toluene is chosen for this study. The reason is that toluene is the major VOC found in indoor as well as urban outdoor environment.

Previous photocatalysis studies have mainly focused on the photodegradation mechanism, catalyst deactivation and catalyst preparation (Demeestere et al [8], Hashimoto et al [9], Cao et al [10]). The concentrations of pollutants used in most of the studies were very high (thousands of ppbs), rarely found in normal and polluted urban environments (Devahasdim et al [11], Hashimoto et al [9]).

It is the purpose of this study to measure the photocatalytic activity of commercial paint towards toluene at realistic level of irradiation, humidity and pollutants concentration. The photocatalytic materials are used under real scale so it is important to photo-induce air pollutants under realistic environmental indoor (Maggos et al [12]) or/and outdoor (Maggos et al [13]) conditions. TiO_2-containing paint was spread over the surface of glass panels and placed into a stainless steel (30 m^{-3}) walk-in type environmental chamber in order to verify their effectiveness in removing toluene under controlled environmental conditions. The depollution activity of the material is presented as the percentage

of the pollutant eliminated during the photocatalytic process and as the mass of the pollutant destroyed per second per square meter of exposed active surface (photocatalytic rate). The velocity (cm s^{-1}) of the photo-induced removal/degradation of the pollutant is also calculated.

Previous studies have reported the significant impact of relative humidity and inorganic pollutants presence on the rate of VOCs photooxidation (Ao et al [14]). For that purpose, the photocatalytic degradation of toluene under different humidity levels and the effect of the presence of NO were investigated in this study.

2   Materials and methods

2.1   Experimental set up

Experiments were conducted in a 30 m^3 environmental chamber (Indoortron) made of stainless steel. Strict control of temperature, relative humidity as well as zero air quality was obtained in the chamber. The operating temperature was 23°C while the relative humidity (RH) was set to 20% or 50%. Three stainless steel fans ensured internal chamber air mixing. The U.V exposure unit consisted of four (4) U.V Osram Ultravitalux 300 W lamps fixed on a square support. The lamp set placed at 150 cm from the centre of the sample panel, in an upper position. The total U.V irradiance was 4.6 W/m^2 at the center and 2.1 W/m^2 at the corner of the sample panels (Maggos et al [15])

Controlled levels of polluted atmospheres were achieved by injecting directly in the chamber a known amount of concentrated pollutant. Toluene was injected in the chamber using a chromatographic grade compressed air stream (1 l/m for 10 minutes). VOC sampling was performed by means of tubes filled with carbopack and the analysis was performed using a GC-MSD (Gas chromatography – Mass Selective Detector) coupled with Automated Thermal Desorber (ATD).

2.2   Materials preparation

Two types of construction materials were tested. a) M1: mineral silicate paint treated with 10% TiO$_2$; and b) M2: water-based styrene acrylic paint treated with 10% TiO$_2$. Each sample set is composed of four 1 m^2 glass panels (total surface area 4 m^2).

The preparation of the test samples consisted of soaking, conditioning (drying) and activation with UV. At the end of the soaking process, aimed to remove salts from paints, panels were washed up with deionised water (Mill-Q grade) and placed in the Indoortron to be conditioned. The coated glass panels remained in the Indoortron at least 12 hours at 30 m^3/h air exchange rate, 23°C and 50% RH operating conditions for conditioning. After conditioning, samples were UV-activated for 8 hours using the experimental UV lamps unit described below. At the end of the activation process another conditioning cycle for at least 12 hours at 30 m^3 h^{-1}, 23°C and 50% RH conditions were performed. In order to

estimate VOCs emissions from the materials, air samples were taken during ventilation mode as well as after 7 hours in static mode. By the end of the preparation steps, samples were ready to be tested for their photocatalytic efficiency.

2.3 Catalytic activity calculations

The principle for the photocatalytic activity measurement is based on VOC loss. The VOC was introduced into the environmental chamber allowing toluene concentration of about 100 µg m^{-3}.

Inside the chamber, the incoming pollutant was consumed by four (4) mechanisms:

1. sink effect (on the walls of chamber);
2. absorption on the surface of the sample;
3. photolysis by U.V light;
4. photocatalysis by TiO$_2$ and U.V light.

Therefore, the measurement can give information on the TiO$_2$-material activity provided that the above side effects (1-3) have been taken into account. So, before performing the photocatalytic experiments, blank tests (material without TiO$_2$) were carried out in order to estimate the loss of VOCs due to side effects.

The following equations were used in order to estimate the catalytic activity of the materials.

(1) The percentage of VOC which were photo-removed was calculated by the following equation:

$$\% VOC_{photo-removed} = \left(\frac{[VOC]_{U.V} - [VOC]blank}{[VOC]_{U.V}} * 100 \right)$$

where:

[VOC]$_{U.V}$ = The amount of VOC removed/degraded during the irradiation of TiO$_2$ containing sample (µg m^{-3})

[VOC]$_{blank}$ = The amount of VOC removed during the blank experiment (due to side effects) (µg m^{-3})

(2) The photocatalytic/oxidation rate (PR, µg m^{-2} s^{-1}) is calculated taking the sample surface, the chamber volume and the duration of the experiment into account. Thus, it provides a more precise estimation of the depollution capacity of a material than the percentage of photo-removal.

However, as PR is dependent on the concentration of the pollutant and as this concentration decreases with time, PR also decreases with time. Consequently, PR is in practice always calculated on basis of the first hour measurement.

$$Photooxidation-rate(PR) = \left(\frac{V * [VOC]_{TiO_2UV}}{A * t} \right)$$

where:

[VOC]$_{TiO_2 \, U.V}$ = The amount of VOC removed photocatalytically from the system due to TiO$_2$ effect (μg m^{-3})

   V = the volume of the experimental chamber (m^3)

   A = Sample surface (m^2)

   T = Irradiation time (s)

(3) The deposition velocity was also calculated in order to describe the photocatalytic activity independently of the pollutant concentration.

$$Photocatalytic\text{-}Velocity(PV) = \left(\frac{PR}{\dfrac{[VOC]_{in} + [VOC]_{uv}}{2}} \right)$$

where:

   PR: The photocatalytic rate (μg m^{-2} s^{-1})

   [VOC]$_{in}$ = The initial amount of VOC before turn on UV light (μg m^{-3})

   [VOC]$_{uv}$ = The VOC concentration during irradiation phase (μg m^{-3}).

3   Results and discussion

3.1 VOC degradation activity

As shown in Table 1, styrene acrylic paint (M2) presents better photocatalytic properties than mineral silicate paint (M1). Approximately 8% of toluene is photocatalytically eliminated due to M1 TiO$_2$-containing paint while the corresponding value for M2 is more than 46%. Accordingly, the rate (μg m^{-2} s^{-1}) and velocity (cm s^{-1}) that toluene photo-induced were higher while using M2 paint.

Table 1:   Toluene photocatalytic parameters.

Material	% Toluene Reduction	Photocatalytic rate (μg m^{-2} s^{-1})	Photocatalytic Velocity (cm s^{-1})
M1	8.46	0.011	0.008
M2	32.5	0.015	0.013

   The results presented in Table 1 were obtained under experimental conditions of 23°C and 20% RH while no other compound was co-injected in the chamber than toluene.

3.2 Relative humidity effect

Figure 1 shows the impact of humidity on toluene photocatalytic elimination on both paints (M1, M2). The photocatlytic degradation of toluene decreases while increasing humidity from 20% to 50%. Actually, the photocatalytic activity was turned to zero regarding M1 paint while it was significant eliminated as far as M2 is concerned. In particular, the photocatalytic rate and velocity of toluene on M2 was reduced from 0.015 to 0.003 $\mu g\ m^{-2}\ s^{-1}$ and from 0.013 to 0.003 $cm\ s^{-1}$ respectively. This is probably due to the fact that as the humidity increases, more water vapor adsorbed on the TiO_2 surface, increasing competition for adsorption sites. It has been reported that humidity could have both positive and negative effects on the photooxidation rate of a pollutant (Einaga et al [16]). It is well known that water plays an important role in the photooxidation process since it contributes in the formation of active species (OH radicals etc.). However, the effect of humidity on the conversion of a pollutant also depends on its concentration (Ao et al [14]). At very low levels of pollutant (the case of this study) the competition for adsorption sites between toluene and water vapor is thousand times more than applying ppm level pollutants and only a small amount of water vapor is sufficient for the generation of OH radicals. Thus the photocatalytic activity decreases.
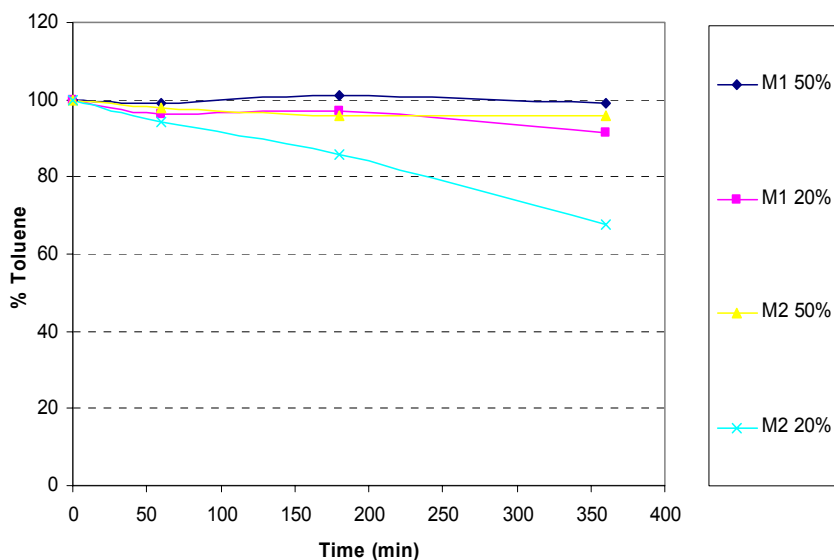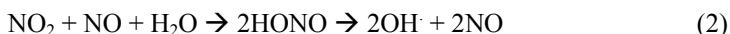

Figure 1:   Photocatalytic degradation of toluene on M1 and M2 paints under different relative humidity levels.

3.3 Mixture effect

The effect of concurrent photodegradation of toluene and NO was investigated as both of them usually co-exist in indoor and urban environment. It was found that NO (~220 ppb) promoted the photodegradation of toluene on both samples under 23°C and 20% RH (Figure 2). NO presence increase toluene photodegradation from 8% to 14% on M1 while the increase for M2 was from 32% to 46.8%.

The enhancement of toluene conversion is due to the generation of hydroxyl radicals (OH$^.$) during the photodegradation of NO as shown in eqs (1, 2):

$$NO + HO_2^. \rightarrow NO_2 + OH^. \qquad\qquad (1)$$

$$NO_2 + NO + H_2O \rightarrow 2HONO \rightarrow 2OH^. + 2NO \qquad (2)$$

Thereafter, OH$^.$ radicals react with toluene (adduction of OH radical to the aromatic ring) increasing the photocatalytic degradation of the pollutant (Ao et al [14]).
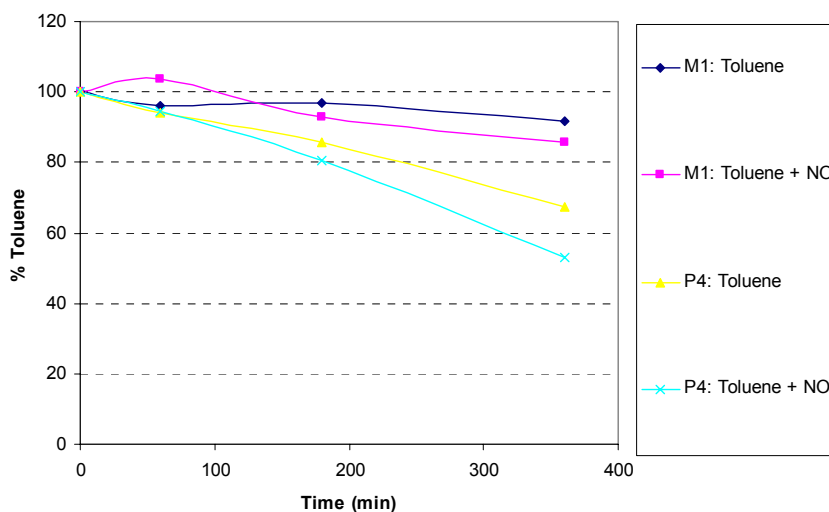

Figure 2:   Photocatalytic degradation of toluene on M1 and M2 paints with and without the presence of NO (200ppb).

4   Conclusions

Two types of TiO$_2$-containing paints were tested for their ability to photo-induce VOC. The 8.46% and 32.5% of toluene were removed photocatalytically on M1 (mineral silicate paint) and M2 (styrene acrylic paint) samples respectively. Photocatalytic rate (μg m^{-2} s^{-1}) and velocity (cm s^{-1}) of toluene were also calculated for both samples. M2 sample presented better photocatalytic

properties than M1. The rate M1 degrades the organic pollutant was calculated up to 0.011 µg m^{-2} s^{-1} while the corresponding value for M2 were 0.015 µg m^{-2}s^{-1}. Humidity was found to significantly affect toluene photodegradation. An increase in humidity level from 20% to 50% inhibited the photooxidation of toluene on samples surface. In that case the photocatalytic rate decreased from 0.015 µg m^{-2} s^{-1} to 0.003 µg m^{-2} s^{-1} on M2 sample while the photo efficiency of M1 was totally eliminated.

On the other hand, the presence of NO enhanced the photodegradation of toluene on both samples. Co-injecting NO and toluene in the chamber increased the photocatalytic degradation of the organic pollutant on M1 and M2 sample from 8% to 14% and from 32% to 46.8% respectively. The formation of OH radicals, from the photocatalytic degradation of NO, consist the main parameter for the promotion effect of NO.

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