STUDIA UBB CHEMIA, LVII, 3, 2012 (p. 15 – 21)
(RECOMMENDED CITATION)

PHOTODEGRADATION STUDY OF SOME INDOOR AIR POLLUTANTS IN THE PRESENCE OF UV-VIS IRRADIATION AND TIO_2 PHOTOCATALYST

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ABSTRACT. In the present study, two selected volatile organic compounds (VOCs) were exposed to UV-VIS irradiation – produced by common fluorescent tubes - under controlled humidity and different temperature conditions and their photocatalytic oxidation was quantitatively studied in the presence of TiO_2. Using the inexpensive UV-VIS light source a significant photochemical degradation of toluene and chlorobenzene was obtained. The removal of studied compounds was investigated, in the presence of two different TiO_2 catalysts (Degussa P25 TiO_2 and aerogel TiO_2), whose activity was not affected by the high humidity conditions. In all experiments the degradation rate for toluene was higher than for chlorobenzene. At 70 % relative humidity and room temperature conditions, Degussa P25 TiO_2 shows a major photodegradation effect, comparatively to aerogel TiO_2. Increasing the temperature up to 50 °C and maintaining the relative humidity at the same level, the photocatalytic degradation in the presence of the aerogel TiO_2 increase significantly, therefore the photocatalytic activities for both TiO_2 catalysts are comparable, as well in the case of toluene as for chlorobenzene.

Keywords: *photocatalytic oxidation, toluene, chlorobenzene, degradation rate*

INTRODUCTION

Common indoor air pollutants, namely volatile organic compounds (VOCs) arise from paints, solvents, preservatives, automobile exhaust gas, industrial facilities et al and they are found in the indoor air of residences as well as in office buildings. Due to the absence of air current and aeration of the indoors, the concentration of the total VOCs can be 2-5 fold higher than

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in outdoor air and can have unwholesome effects [1]. The destruction of various VOCs from polluted air can be performed in different ways: activated carbon adsorption methods, photochemical oxidation and photocatalytic oxidation (PCO) [1-3].

Recently, titanium dioxide(TiO_2)-mediated photocatalysis used to achieve the degradation of VOCs pollutants has been receiving an accentuated attention [1, 4, 5]. The pollutants were fairly decomposed by ozone and hydroxyl radicals produced by UV irradiation [6], and the photodegradation was enhanced by the presence of TiO_2. Semiconductors, in our cause TiO_2 are widely used as photocatalysts, due to their specific characteristics: photochemical stability, lack of toxicity and low cost. Another advantage of the TiO_2 assisted photodegradation is the possibility to operate under atmospheric pressure and room temperature. Despite these advantages, the application of photocatalytic oxidation has some concerns. A limiting factor of the PCO is that one compound may promote or inhibit the removal rate of other compounds [7-9]. In literature contradictory results are presented on: the inhibitory effect of water molecules, which can be attributed to the competition for adsorption on semiconductor surface between pollutants and water molecules [10, 11], respectively the enhancement effect of H_2O, due to formation of active species of hydroxyl radicals, which inhibit deactivation of catalyst [1, 2, 12, 13].

Toluene is a major indoor air pollutant and extensively studied. It is frequently used as an industrial feedstock and as a solvent. For toluene low degradation rates were reported, due to catalyst deactivation [14, 15], in spite of humid air conditions, namely the water molecules can assist to the regeneration of surface: under UV irradiation give rise the highly oxidative hydroxyl radicals involved in the photocatalytic oxidation process [12]. Chlorobenzene is a typical halogenated aromatic VOC that is widely used in industrial fields and in agriculture [16], and the removal rate and the quantum yield could be enhanced working under higher air humidity conditions [17].

The aim of the present paper was to investigate the removal efficiency by photochemical oxidation and photocatalysis of toluene and chlorobenzene under different experimental conditions, using the UV-VIS irradiation. Generally UV irradiation is used for PCO studies, but in the present paper UV-VIS light was used, because it is a very common illumination system of indoors. The photodegradation under controlled humid air conditions at 25 °C and at 50 °C, and the photocatalytic oxidation on the TiO_2 Degussa P25 and TiO_2 aerogel surfaces were investigated and compared. The high humidity condition was chosen to study the role of water molecules in the PCO process. The photochemical oxidation was also evaluated in the presence of irradiation with UV-VIS light, without photocatalyst, too, in order to verify the efficiency of the irradiation with UV-VIS light.

RESULTS AND DISCUSSION

Under dry air condition, reactive oxygen species are generated due to exposure to UV-VIS light, via gas-phase reaction [1]. The generated oxygen species react with the H_2O molecules from humid air, in this way a large number of hydroxyl radicals are formed. The formation of hydroxyl radicals takes place by direct interaction of the H_2O molecules with the irradiation. The generated reactive species, having a strong oxidative effect, induce the photochemical oxidation of the VOCs in the gas phase. The experiments performed confirm the theory about the enhancement effect of water, therefore in this paper are presented results obtained for high (70 %) relative humidity (RH) conditions.

In case of experiments performed at 25 °C, in the absence of TiO_2 and after 150 min irradiation a significant removal of toluene (20.3 %) was observed (see **Table 1.**). This photochemical degradation can be attributed to the oxidation effects of reactive radicals formed in humid air conditions under UV-VIS irradiation. For chlorobenzene the degradation rate under UV-VIS light treatment was lower relative to toluene (8.1 %, after 150 min irradiation), which can be correlated with the chemical structure of the compounds. Therefore the common fluorescent tubes can produce a significant degradation of the studied VOCs and the costs are much lower, than in the case of ozone producing UV lamps.

On the other hand, in the reaction of TiO_2 with UV-VIS light there are photoinduced electrons (e^-) and positive holes (h^+) on the semiconductor surface [18]. The electrons and holes produced can further generate hydroxyl and oxygen reactive species, under appropriate conditions. Due to the high reactivity of the generated species, the mechanism is contributing to the oxidation of organic pollutants and leads to the photocatalytic oxidation of VOCs. In the present study the activity of two different TiO_2 was evaluated: the commercial available Degussa P25 and aerogel TiO_2.

In the presence of photocatalyst and UV-VIS light, according to the theory described above, a significant enhancement of the photodegradation is expected. The degradation rate in photocatalytic oxidation of studied compounds is relevant at 25 °C temperature, in the presence of the commercial semiconductor, Degussa P25 TiO_2. In spite of high humidity conditions (RH=70%), no deactivation of TiO_2 was observed. Under these experimental conditions for toluene the degradation rate, attributed to the photocatalytic oxidation activity of the Degussa P25 TiO_2, was increased by 10.4 %, as compared to photochemical oxidation (without TiO_2), and for chlorobenzene by 9.4 % (see **Table 1.**).

By increasing the photoreactor temperature up to 50 °C, the photocatalytic activity of Degussa P25 TiO_2 did not change, the removal of toluene (31.1 % degradation, after 150 min) and chlorobenzene (17.1 % degradation, after 150 min) remaining at about the same level as for 25 °C (see **Table 1**). The Degussa P25 TiO_2 photocatalytic activity was not affected by a 25 °C increase of temperature, so in these conditions the semiconductor properties were conserved.

Table 1. Photodegradation of toluene and chlorobenzene under UV-VIS irradiation, after 150 min exposure, at 70 % RH, for different temperature conditions (25 °C and 50 °C), in the presence of two type of photocatalyst (Degussa P25 and Aerogel), respectively in the absence of photocatalyst (without TiO_2)

Compound	Photoreactor temperature [ºC]	TiO_2 Photocatalyst	Degdaration rate at 150 min [%]
Toluene	25	Degussa P25	30.7
		Aerogel	22.4
		without TiO_2	20.3
	50	Degussa P25	31.1
		Aerogel	28.6
		without TiO_2	20.9
Chlorobenzene	25	Degussa P25	17.5
		Aerogel	10.7
		without TiO_2	8.1
	50	Degussa P25	17.1
		Aerogel	16.2
		without TiO_2	9.0

The photocatalytic activity of the second semiconductor, aerogel TiO_2 catalyst under UV-VIS light, at 25 °C was much lower than the Degussa P25 TiO_2 activity under the same experimental conditions. The toluene photodegradation, by UV-VIS irradiation and in the presence of aerogel TiO_2 after 150 min, was 22.4 %, by 8.3 % less than in the case of Degussa P25 TiO_2, and being just by 2.1 % higher than in the absence of photocatalyst. The photodegradation rate by UV-VIS light and aerogel TiO_2, for chlorobenzene was 10.7 %, a much lower value in comparison with photocatalytic activity of Degussa P25 TiO_2 (17.5 %), and only little higher than under UV-VIS irradiation (8.1 %). It may be concluded that the photocatalytic activity of aerogel TiO_2 semiconductor is the same for toluene and chlorobenzene degradation. The differences between the degradation rate for toluene and chlorobenzene were attributed to the differences in the chemical structures of the studied VOCs.

The photocatalytic activity of the aerogel TiO_2 under UV-VIS light exposure was significantly increased by the temperature increase of the photoreactor (**Figure 1.**) and was comparable with the photocatalytic activity of Degussa P25 TiO_2. For high humidity condition (RH = 70 %), at 50 °C, under UV-VIS irradiation the photocatalytic activity of aerogel TiO_2 for the toluene degradation was 28.6 %, and for chlorobenzene degradation 16.2 %. The degradation rates presented were very similar to those reported for Degussa P25 TiO_2 under similar conditions. The higher photocatalytic activity of aerogel TiO_2 at 50 °C can be correlated with a structural modification of the titanium dioxide following an increase in temperature.

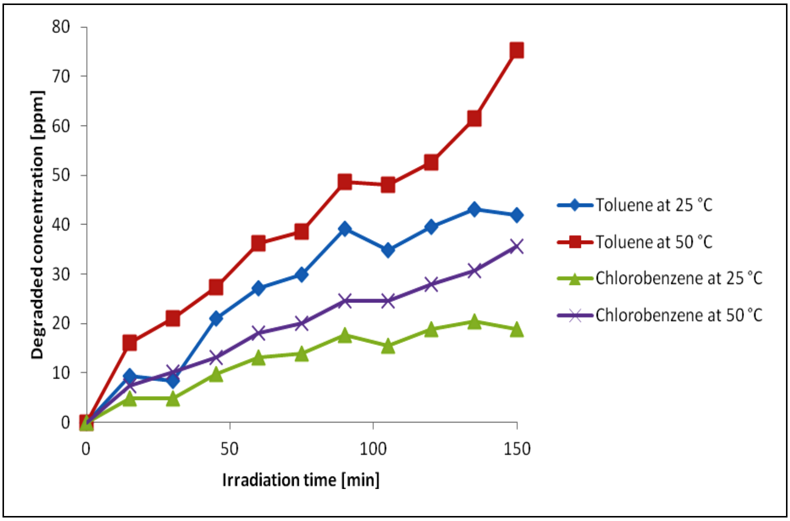

Figure 1. Evaluation as a function of time (from 0 min to 150 min irradiation) of the photocatalytic activity of aerogel TiO_2 for toluene and chlorobenzen at different temperature conditions (25 °C and 50 °C)

CONCLUSIONS

Using common UV-VIS emitting fluorescent tubes a relevant degradation of toluene and chlorobenzene was obtained, permitting also a significant reduction of costs. Higher removal was observed in the presence of semiconductors: Degussa P25 and aerogel; and the high humidity conditions did not produce a TiO_2 deactivation. Due to the chemical structure differences between toluene and chlorobenzene, for toluene a higher degradation rate was found, in all experimental conditions.

For the closed photoreactor operated at 25 °C the degradation rate in the presence of Degussa P25 was much higher than the degradation in the presence of aerogel TiO_2. By increasing the temperature of the reactor up to 50 °C, an increase in the photocatalytic activity of the aerogel TiO_2 was observed. It may be concluded that Degussa P25 has a stable semiconductore structure, while the aerogel TiO_2 photocatalyst structure was modified due to 25 °C temperature increasing.

EXPERIMENTAL SECTION

A closed photoreactor (0.410 l volume) of cylindrical shape, having an internal air-blower - which maintains a homogenous flow of the compounds - was used. In opposite position to the air-blower was set a sample collection point with a rubber septum system. The dipping procedure – repeated at nine times - was used to deposit the Degussa P25 TiO_2 catalyst and aerogel TiO_2 catalyst on the surface of three glass plates, followed by a drying procedure. The glass plates having a total area of 250 cm^2 coated with the TiO_2 catalyst, were located in the center of the reactor.

Irradiation was made with two straight fluorescent daylight 13W tubes, situated at the two opposite parts of the glass plates, in order to obtain an adequate illumination. Irradiation with fluorescent lamps, instead of UV irradiation was preferred, because in case of extension of the method to a large scale, it can reduce significantly the costs. On the other hand the fluorescent tube has an intensive emission at 434 nm, which contribute to electron transfer from the valence band to the conduction band, on the TiO_2 semiconductor surface [19].

The experiments were carried out at a temperature of 25 °C measured inside of the photoreactor. The temperature of 25 °C was obtained using a cooling air stream. Without air cooling, the temperature increases and stabilizes at 50 °C. Photocatalysis was studied under both temperature conditions.

The relative humidity (RH) was maintained at constant level, RH = 70 % by introducing a suitable quantity of water into the reactor, to supply the H_2O molecules as needed. The initial concentrations of toluene and chlorobenzene in the photoreactor were 400 ppm (v/v) of each compound. After equilibration, 0.2 ml of gas samples were collected from the reactor for analysis at every 15 min intervals and the concentration measurements of the target compound were performed over a time interval of 150 min. The quantitative determination was achieved using a Perkin Elmer Gas Chromatograph (GC), equipped with a flame ionization detector (FID). A stainless steel column with a phenyl-methyl silicone packing was used, of 2 m length and 2.2 mm i. d., maintained in isothermal conditions at 125 °C. The temperatures of injector and manifold were set to 225 °C. The concentrations of the studied compounds were calculated from chromatographic peak areas.

ACKNOWLEDGMENTS

This study was supported by a National Plan II Programmers' Grant (No. 71-136) from the Ministry of Education and Research, National Authority for Scientific Research (ANCS). The authors thank Dr. Nicolae Palibroda for his valuable comments and suggestions.

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