Photodegradation of the indoor organic pollutants by UV irradiation using TiO$_2$ catalysts

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Abstract. Volatile organic compounds (VOCs) are a major environmental concern, because of their carcinogenic and toxic effects on human health. The most frequent types of VOCs found in indoor air are, according to literature, Chloroform, p-dichlorbenzene, tetrachloroethylene, formaldehyde, NOx. Another VOCs found very often mentioned in the literature are ethanol and acetone or BTEX compounds. The investigated compounds used in this work for studying the photodegradation effect are toluene and chlorobenzene. In the present work were calculated the photodegradation rates of the compounds mentioned above using UV radiation and TiO$_2$, as catalyst. The obtained results are discussed based on comparative values of removal quantities for few time intervals for different types of catalysts based on TiO$_2$ aerogel.

1. Introduction
Photocatalytic oxidation process has been intense studied and is a promising method for removing and destroying various VOCs [1, 2, 3] in the polluted air. This technique using TiO$_2$ is cheap and doesn’t require special conditions, the experiment is made usually at room temperature and pressure and the catalyst is stable. According to previous literature, using TiO$_2$ for organic pollutants degradation proved to be very efficient [4, 5, 6].

In this paper we studied the photodegradation of toluene and chlorobenzene compounds which are often found in the indoor air. Source materials for toluene vapors are paints, adhesives, gasoline and combustion sources, but for chlorobenzene are pesticides, plasticizers, preservatives, dyes and disinfectants manufactures [7, 8]. All experiments were made in a home made glass reactor.

2. Experimental
The used reactor volume was of 44 l, it had an air-blower, which maintained the homogenization of the compounds during the experiment. At the bottom of the reactor are two evacuation valves used for elimination of sample after every experiment. At the top there is a septum system for introduction of sample and collection of sample at determined time intervals. The reactor is provided with a UV source, which emits light in the range of 350-380 nm at a power of 60 W.

Usually in previous studies of photocatalytic degradation processes, several types of catalyst have been reported, such as: TiO$_2$, ZnO, Fe$_2$O$_3$ or ZnS [10]. In our experiments three different types of catalysts based on TiO$_2$ was used: TiO$_2$ Degussa P25, TiO$_2$-N doped and TiO$_2$-N doped thermic treated at 450°C (TiO$_2$-N doped TT). Catalyst support was glass plates having the 2 mm thickness, and 10x15 cm surface. The support plates were covered with three layers: first one of TiO$_2$ (for a good adhesion),
the next two TiO$_2$ aerogels (doped or undoped). The experiment was performed on pairs of plates with catalysts, total area of 300 cm$^2$ at room temperature (22°C) and humidity (around of 35% RH).

The initial concentration of compounds was 200 ppm. The measurements were made in a time interval of 300 min, the samples being collected from reactor at every 30 min. For quantitative determinations 1 ml of gas sample was injected into a Perkin Elmer 990 model gas-chromatograph equipped with a polar column of 6 m length and 3 mm inside diameter, made from stainless steel. The column temperature was programmed from 75°C to 200°C. The concentrations left in the photoreactor were obtained from chromatogram peak area having FID as detector.

3. Results and discussions

In the early reported studies of the photocatalytic processes was shown that based on oxidation and reduction reaction as final compounds result CO$_2$ and H$_2$O respectively [10]. The major physical parameters that have influenced the photocatalytic kinetics are: wavelength, concentrations of reactants, temperatures and the radiant flux [8].

According to the literature [11] the intermediate products detected from the UV photodegradation of gaseous chlorobenzene included hydrochloric acid, acetic acid, formic acid, phenol and chlorophenol. In the toluene photodegradation process as intermediate compounds were shown benzaldehyde and $p$-methylphenol [12].

We made four experiments: the first one was realized with no catalyst and we considered this as a blank experiment. In the next three experiments we tested the nanocatalysts that we have mentioned before. All the results are graphical represented in figure 1. Work conditions were as in section 2.

![graphs](image_url)

Figure 1. Toluene and Chlorobenzene photodegradation under UV light and TiO$_2$ catalysts. a) without catalyst; b) N-doped TiO$_2$ thermic treated; c) N-doped TiO$_2$; d) Degussa P25 catalyst.

Analyzing the above graphics as well as those obtained on blank samples (no UV or catalyst) we concluded that removal of compounds from photoreactor is due to two processes: adsorption on enclosure walls and the proper photodegradation.
The photodegradation process can be mathematically described by an exponential equation [13]:

\[ \ln C = \ln C_0 - k \cdot t \]  

where \( C \) is the removed concentration by photodegradation process, \( C_0 \) is the starting photodegradation concentration, \( k \) is the constant rate and \( t \) is time. Drawing the logarithm of concentrations obtained from experiment as a time function the photodegradation process (linear segment of drawing) can be separated of adsorption process. Table 1 lists some specific value, obtained for hourly time intervals.

| Time (min) | TiO\(_2\)-N doped TT | TiO\(_2\)-N doped CB | TiO\(_2\) Degussa P25 T | TiO\(_2\) Degussa P25 CB |
|-----------|----------------------|----------------------|-------------------------|-------------------------|
| 60        | 9.7                  | 13.9                 | 13.4                    | 13.2                    |
|           |                      |                      | 3.5                     | 6.02                    |
| 120       | 18.5                 | 26.4                 | 25.0                    | 26.2                    |
|           |                      |                      | 6.9                     | 13.3                    |
| 180       | 26.3                 | 37.0                 | 35.0                    | 37.2                    |
|           |                      |                      | 10.2                    | 19.3                    |

As can be seen in the table 1 the removal efficiency of compounds is improved by using N doped TiO\(_2\) catalyst relative to TiO\(_2\) Degussa P25. In the situation of N doped TiO\(_2\) thermal treated a discriminant effect of Chlorobenzene removal efficiency relative to Toluene must be mentioned. The effect can be explained based on stereo configuration of involved compounds.

4. Conclusions

Using TiO\(_2\) catalysts under UV light, a significant degradation of VOCs compounds was observed. Quantity of compound photodegradated depends of catalyst type and organic pollutant structure. Doping TiO\(_2\) is increasing the photocatalytic activity (in our case TiO\(_2\)-N doped is the most efficient catalyst). Usually a stronger photodegradation was observed for chlorobenzene comparing with toluene. When TiO\(_2\)-N doped is used the photodegradation rate values for both compounds are much closed.

All experiments were performed at normal conditions of temperature and humidity. At decreasing concentrations of compound two processes compete: adsorption and photodegradation.

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