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Purification/deodorization of indoor air and gaseous effluents by TiO_2 photocatalysis

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Abstract

Our objective was to further assess the capabilities of TiO_2 to purify/deodorize indoor air and industrial gaseous effluents. Using a laboratory photoreactor including a lamp emitting around 365 nm and a TiO_2-coated fiber glass mesh, we first determined that the removal rate of three very different pollutants (CO, *n*-octane, pyridine) was 5–10 μmol per Wh consumed by the lamp for 50–2000 ppmv concentrations and 25–50 $l\,h^{-1}$ flow rates (dry air or O_2). We inferred that this order of magnitude allows, by use of a reasonable-size apparatus, the abatement of pollutants in constantly renewed indoor air, except CO and CH_4 that are too concentrated. Using a TiO_2 photocatalysis-based individual air purifier prototype, we showed, through distinctive analytical measurements, that the average concentrations of benzene, toluene and xylenes were indeed reduced by a factor of 2–3 in an ordinary non-airtight room. We also showed that O_3 addition in O_2 very markedly increases the mineralization percentage of *n*-octane, under otherwise identical conditions, in the laboratory photoreactor without photoexcitation of O_3; this property of O_3 can expand the application field of photocatalytic air purification in industry, at least in some cases.

Keywords: Purification; Deodorization; TiO_2 photocatalysis; Indoor air

1. Introduction

Treatment of air at room temperature, particularly indoor air in housings, by heterogeneous catalysis involves heating which can be prohibitory; the use of mere adsorbents, such as activated carbon, implies the change, disposal or regeneration of the adsorbents. Therefore, photocatalysis over TiO_2 [1] appears attractive in this field.

In this study, we have first determined, by use of an appropriate laboratory photoreactor, the order of magnitude of the photocatalytic degradation rate (expressed in μmol per Wh of electrical energy consumed by the UV lamp) of three very chemically different air pollutants. From this data, we concluded that the concentrations of most indoor air pollutants can be reduced by TiO_2 photocatalysis. This was checked, at much higher air flow rates than in the laboratory photoreactor, by measuring the effect of a TiO_2 photocatalysis-based prototype air purifier upon the concentrations of typical aromatic pollutants in an ordinary room under usual conditions. For that, we used novel analytical means. Concerning the photocatalytic treatment of industrial gaseous effluents, we have shown that the addition of ozone to dioxygen allows one to achieve the mineralization of *n*-octane, chosen as a model pollutant, whereas the mineralization was incomplete with dioxygen alone in the same photoreactor under otherwise identical conditions. Until now, the effect of O_3 in photocatalytic air purification was assessed only for removing

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[1] As most recent reviews see, e.g., [1,25–27].

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an organic pollutant and not for reaching a higher percentage of transformation into CO_2 of a pollutant containing several C atoms, which is of greater interest.

2. Experimental

2.1. Materials

In the laboratory photoreactor, we used the TiO_2-coated fiber glass mesh (ca. $65\,g\,m^{-2}$) produced by Matrix Photocatalytic [2]. The TiO_2 weight percentage was ca. 6.8.

Ahlstrom Paper Group Research and Competence Center [3] supplied the TiO_2-coated fibrous material employed in the prototype air purifier. The pristine material ($50\,g\,m^{-2}$) was first impregnated with an aqueous suspension of TiO_2 and colloidal SiO_2 by use of a size press and then dried in ambient conditions. The coating corresponded to a TiO_2 mass of $20\,g\,m^{-2}$ and to a TiO_2/SiO_2 ratio equal to 1. TiO_2 was prepared by Rhodia from $TiOSO_4$: it was anatase with a surface area of $320\,m^2\,g^{-1}$.

2.2. Photoreactors

The laboratory photoreactor (Fig. 1) comprised a Philips PLS 9W/10 UV lamp, emitting 2.2 W around 365 nm surrounded by an optimized number of layers of the Matrix material corresponding to a total geometric area of ca. $1300\,cm^2$, so that the air flow was turbulent and the radiant flux emitted by the lamp was completely absorbed/diffracted by the Matrix material. We also used, in the case of O_3 decomposition, a photoreactor with the same configuration and which includes two jackets, one external, the other around the lamp enabling one to vary the temperature. Ozone was generated in a BMT 802 ozoner fed with O_2 at a pressure of 187 Pa.

Mass flowmeters were used to insure a constant flow ($6–24\,l\,h^{-1}$) of air containing a given concentration of the pollutant studied and, in some cases, of ozone.

The prototype air purifier (patent FR2774914) comprised a fan generating an air flow rate of $250\,m^3\,h^{-1}$, ca. $1300\,cm^2$ of the Ahlstrom material and two lamps of the same type as in the laboratory photoreactor with a total electrical power of 48 W.

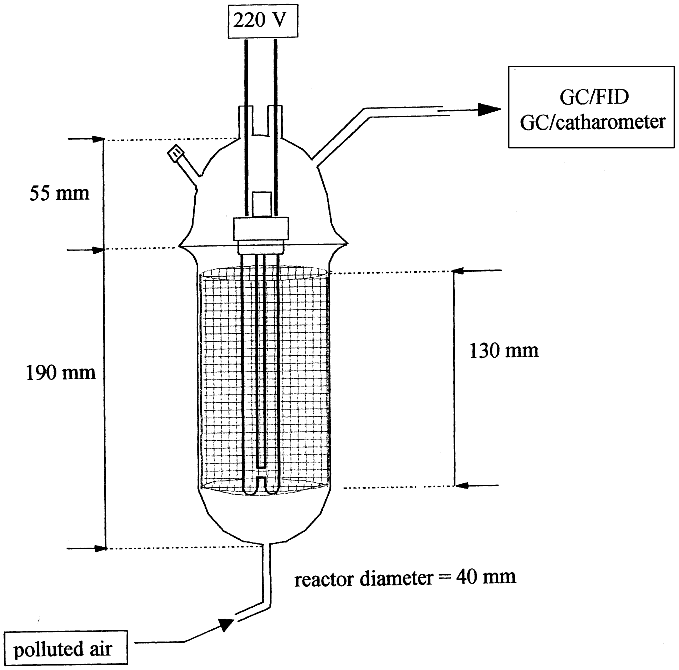

Fig. 1. Scheme of the laboratory photoreactor used in this work.

2.3. Analyzes

Analyzers based on IR and UV absorption measured CO and O_3 concentrations, respectively. Pyridine, *n*-octane and carbon dioxide were analyzed by gas chromatography (GC) with flame ionization (FID) or catharometer detectors.

Benzene, toluene and xylenes in ambient air were collected on a solid phase microextraction (SPME) fiber [4] exposed at the exit of the air purifier during 15 min. They were subsequently desorbed from the fiber directly at the entrance of the column of the GC–FID apparatus. Calibration was performed on the basis of the SPME–GC–FID analysis of the atmosphere obtained by introducing into a 6.275 l reservoir 1–5 μl of a 20–300 $\mu\text{mol}\,l^{-1}$ solution of each of these aromatics in diethylether which is poorly adsorbed on the SPME fiber. To our knowledge, these novel analytical procedures have never been used to estimate the efficacy of photocatalytic air purification under real conditions.

3. Results and discussion

3.1. TiO_2 photocatalytic efficiency from laboratory-scale experiments

To assess the capabilities of TiO_2 photocatalysis for air purification/deodorization, we used the laboratory photoreactor (see Section 2.2) whose electrical power corresponded to about one-fifth of what was thought reasonable to improve air quality in an individual room. The data thus obtained could also provide information regarding the treatment of industrial gaseous effluents.

The disadvantage of this type of photoreactor is that air flow rates are limited to a maximum of ca. 50 $l\,h^{-1}$. This requires increasing the pollutant concentration in order to operate with pollutant flow rates equivalent to those expected for indoor air decontamination. Consequently, the TiO_2 surface coverage by the pollutant is higher, which corresponds to the case of industrial effluents and not to that of indoor air.

For a wider significance of our results, we chose three structurally very different air pollutants, viz. carbon monoxide (yielding only one product which is volatile), *n*-octane (poorly adsorbed and producing many intermediate products) and pyridine (malodorous and relatively stable because of its aromaticity).

Our objective was not to provide various data corresponding to given conditions but to determine an order of magnitude for the removal rates of these pollutants at concentrations in the range 50–2000 ppmv in dry air or O_2 and flow rates comprised between 25 and 50 $l\,h^{-1}$. We found removal rates in the range 5–15 μmol per Wh consumed by the UV lamp. According to our own results — and considering literature data [5–16] obtained with other types of photoreactors and TiO_2-coated materials or TiO_2 powders — the changes caused by variations in the ambient humidity and temperature generally do not alter the order of magnitude. Also, for a large number of pollutants the relative photocatalytic removal rates [16–20] generally remain within an order of magnitude, with the exception of formaldehyde, which is very unstable, and some short chlorinated alkanes and alkenes for which contradictory results have been obtained.

Our purpose was to use the order of magnitude we measured to determine a priori whether an individual air purifier/deodorizer can be based on the same type of UV lamp and a similar TiO_2-coated fiber glass mesh. 10 μmol corresponds to about 10 ppbv in a room of ca. 24 m^3. Therefore, it is clear that an air purifier including UV lamps with an electrical power of some tens of W should very significantly decrease, within a reasonable period of time, the concentrations of almost all indoor air pollutants, since their concentrations are at most 100 ppbv [21], even though the removal rates are lower in the ppbv range compared with the ppmv range. This conclusion led us to participate in a project leading to the construction of an individual air purifier prototype (see Section 3.2). However, CO and CH_4 concentrations in ambient air are above 1 ppmv (CO concentration can even exceed 10 ppmv). Consequently, the order of magnitude we determined shows that even for a UV-lamp power in the range 50–100 W the concentrations of these pollutants will not be significantly affected by the air purifier, considering the permanent introduction of CH_4 and CO from outside and other rooms and possibly additional CO from tobacco smoke. For industrial effluents, although the extrapolation is presumably too large, the order of magnitude we determined indicates that UV lamps with an electrical power of 10 kW would be required to eliminate a pollutant at a concentration of ca. 25 ppmv in an air flow of 100 $m^3 h^{-1}$. This value may serve as a rough guidance to estimate whether a given air flow can be treated by TiO_2 photocatalysis. Clearly, as many very malodorous compounds have olfactory thresholds in the ppbv range, photocatalytic deodorization should be effective in the cases where the concentrations do not exceed the olfactory thresholds too much.

3.2. Evaluation of a prototype air purifier

The prototype air purifier/deodorizer was placed in a non-air tight room having a volume of 83 m^3. Outdoor air was admitted in this room before each experiment for 15 min. Then, the windows were closed and the air purifier fan was switched on to homogenize the air. After 1 h, the SPME fiber was exposed for 15 min and the collected BTX (benzene, toluene, *m*- and *p*-xylene (together), and *o*-xylene) were analyzed. The same SPME fiber was used to analyze the air after various periods during which the air purifier UV lamps were on. These experiments were repeated several times to take into account the variations in the initial BTX concentrations from day to day and even within the same day.

Fig. 2 gives an example of the results obtained for a day corresponding to high concentrations of BTX (and other pollutants as well, such as SO_2 according to the local weather reports). This figure clearly shows that the concentrations of all BTX were decreased by a factor of ca. 2 by the photocatalytic process to reach, within the first hour, equilibrium levels corresponding to equal rates of BTX photocatalytic removal and BTX introduction from outdoor, the corridor and the neighboring rooms. As TiO_2 photocatalysis (see Footnote 1) is effective for the degradation of any type of organic compound, except chlorofluorocarbons and *s*-triazine, qualitatively similar results would be obtained with the prototype air purifier for other pollutants having concentrations on the same order of magnitude. For still less-concentrated pollutants the photocatalytic elimination rates will be lower because of the lower TiO_2 surface coverage (Langmuir–Hinshelwood kinetic model), however, decreases in the equilibrium concentrations of these pollutants will also be observed.

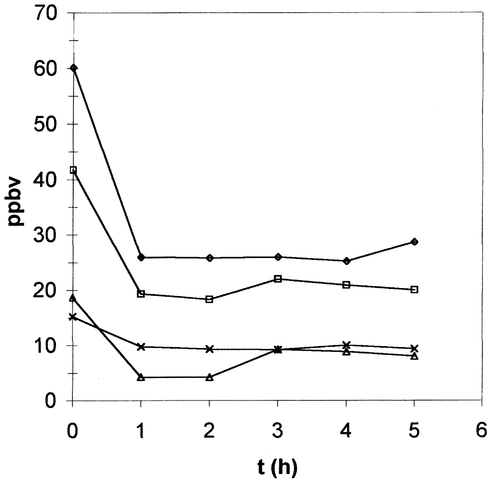

Fig. 2. Decreases in the concentrations of benzene (crosses), toluene (diamonds), *o*-xylene (triangles) and both *m*- and *p*-xylene (squares) in a non-air tight room caused by the prototype air purifier; $t = o$ refers to the concentrations before the purifier UV lamps were switched on.

To our knowledge, it is the first set of experiments demonstrating the effect of a photocatalytic purifier on the quality of ambient air under usual conditions. Previous demonstrations were based on bench-scale tests.

3.3. Effect of ozone

For a concentration of 130 ppmv of *n*-octane in O_2 the elimination percentage of C_8H_{18} was comprised between 97 and nearly 100% at stationary state for the flow rates indicated in Fig. 3; in other words, the maximum removal rate (mol per time unit) of *n*-octane achievable with our laboratory photoreactor was not attained under these conditions. This maximum would correspond to the case where the elimination percentage is low (higher *n*-octane flow rate).

By contrast, the percentage of CO_2 obtained with respect to complete mineralization of *n*-octane was comprised between ca. 25 and 50 for these flow rates (Fig. 3). The photoreactor length was insufficient to achieve mineralization of the intermediate products which compete with one another and with continuously introduced *n*-octane for the photocatalytically generated oxidizing species.

Since the amount of TiO_2-coated material was already optimized for the UV lamp used, adding O_3

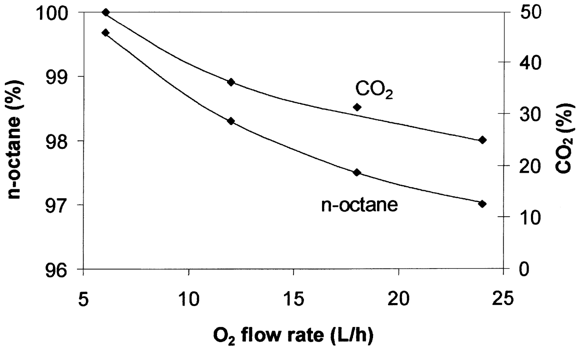

Fig. 3. Stationary-state percentages of C_8H_{18} eliminated and of CO_2 formed (with respect to total mineralization) for the photocatalytic treatment of oxygen containing 130 ppmv of *n*-octane in the laboratory photoreactor for various flow rates.

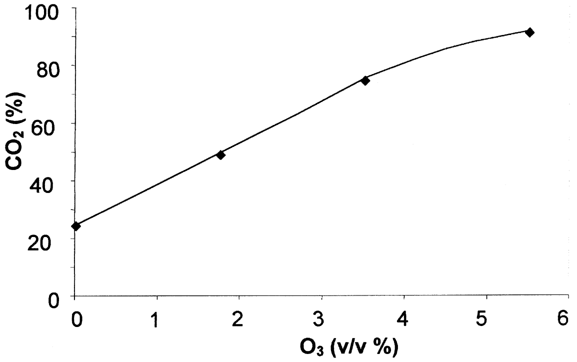

Fig. 4. Stationary-state percentages of CO_2 formed (with respect to total mineralization) for the photocatalytic treatment, in the laboratory photoreactor, of O_2 (flow rate: $24\,l\,h^{-1}$) containing various volumic percentages of O_3 and 130 ppmv of *n*-octane.

to O_2 appears as a means of increasing the density of these oxidizing species. Also, *n*-octane mineralization was deemed as a good test to assess to what extent the capabilities of TiO_2 photocatalysis can be improved by use of O_3 in order to eliminate not only an organic pollutant but also its numerous intermediate products.

Ozone does not absorb the wavelengths used in this study and is therefore stable in the absence of TiO_2. However, at room temperature it is partially split over the TiO_2-coated material in the dark [22], which, for a $24\,l\,h^{-1}$ flow rate and 3.5% (v/v) of O_3 in O_2, led to an almost complete removal of *n*-octane (130 ppmv), but to only a few percents of mineralization. Under the same conditions, the mineralization percentage reached ca. 75% when TiO_2 was UV-irradiated, ca. 90% when in addition the % (v/v) of O_3 was increased to 5.5 (Fig. 4), and 100% on decreasing the flow rate at this latter O_3/O_2 ratio.

Photocatalytic degradation of alkanes over TiO_2 yields carbonyl compounds and, to a lesser extent, alcohols and alkenes as intermediate products [23]. Ozone can directly react with alkenes but not with the other products. Therefore, the very substantial increase in *n*-octane mineralization cannot be attributed to a direct reaction of ozone.

The electron affinity of O_3 is 2.1 eV compared with 0.44 eV for O_2. Consequently, in the presence of ozone, the electrons photopromoted to the TiO_2 conduction band can more easily be captured, either directly

$$e^- + O_3 \rightarrow O^{o-} + O_2 \quad (k = 1.8 \times 10^9\,l\,mol^{-1}\,s^{-1})$$

or indirectly

$$e^- + O_2 \rightarrow O_2{}^{o-} \quad \text{and} \quad O_2{}^{o-} + O_3 \rightarrow O_2 + O_3{}^{o-} \quad (k = 2.11 \times 10^{11}\,l\,mol^{-1}\,s^{-1})$$

The above rate constants are given as an indication, they refer to the gas phase in the presence of an electrical field [24]. The radical anion $O_3{}^{o-}$ is still more unstable than O_3 and can presumably easily split at the surface of TiO_2

$$O_3{}^{o-} \underset{TiO_2}{\rightarrow} O^{o-} + O_2$$

Alternatively, it might react with water adsorbed at the surface of TiO_2, since the photocatalyst was not thermally pretreated and since H_2O is formed by *n*-octane degradation

$$O_3{}^{o-} + H_2O \underset{TiO_2}{\rightarrow} OH^o + OH^- + O_3$$

Furthermore, the increase in the scavenging rate of photoproduced electrons resulting from the presence of ozone should decrease the recombination rate of electrons and holes h^+ and accordingly augment the formation rate of hydroxyl radicals from basic OH surface groups

$$OH_s{}^- + h^+ \rightarrow OH^o$$

In all cases, very oxidizing species, viz. O^{o-} and OH^o, would thus be generated.

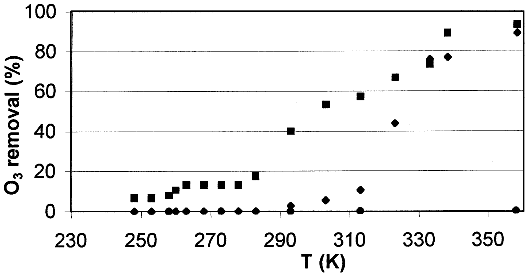

Fig. 5. Stationary-state percentages of O_3 removal in the thermostated laboratory photoreactor as a function of the temperature with the TiO_2-coated Matrix fiber glass mesh in the dark (diamonds) and under UV-irradiation (squares). Circles refer to the UV-irradiated uncoated fiber glass mesh. Flow rate of O_2 containing 4.5% (v/v) of O_3: $23\,l\,h^{-1}$. Note that the radiant flux at and below 273 and at 343 K was decreased by a factor of ca. 1.5 with respect to the temperature range 293–313 K.

The effect of UV irradiation on the decomposition of O_3 over TiO_2 was investigated in the temperature range 248–358 K. Fig. 5 shows that for 4.5% (v/v) of O_3 in O_2 no dark decomposition was observed below ca. 290 K, whereas UV-irradiation caused decomposition even at 248 K despite a radiant flux lowered by a factor of ca. 1.5 with respect to room temperature. Clearly, the difference between the photoinduced and dark decomposition percentages of O_3 over TiO_2 is very significant at near-room temperature. These results are consistent with the above reasoning proposing the easy scavenging by O_3 of the electrons photopromoted to the TiO_2 conduction band.

In conclusion, as ozone is employed in various industrial processes, such as paper bleaching, TiO_2 photocatalysis could be of interest both for exploiting the presence of ozone to mineralize air pollutants at higher rates while removing excess ozone. In cases where O_3 is not already used, the cost of its generation can be prohibitive; the interest of adding O_3 will obviously depend on the particular case and on the regulations.

4. Conclusions

Laboratory measurements have allowed us to evaluate the order of magnitude of pollutant removal rate per electrical power unit that can be expected from available UV lamps and TiO_2-coated material. General conclusions are drawn about the capabilities of TiO_2 photocatalysis for treating air. The efficacy of a prototype to purify/deodorize air in an ordinary room was assessed through the use of adsorbent-coated fibers to collect pollutants in ambient air, a procedure which had not been previously used for that purpose. Another part of this study has shown that even under conditions where the photocatalytic elimination of a hydrocarbon with a relatively long chain is satisfactory, adding O_3 enables one to increase the efficiency for mineralization. This may be an alternative to increasing the reactor size. At least, that result draws the attention on a means to benefit from excess O_3 in processes that use this oxidizing agent.

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