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Photocatalytic Oxidation of Volatile Organic Compounds for Cleaning Vehicle Cabin Air

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Abstract

The photocatalytic degradation of n-pentane in gas phase has been investigated under different conditions on a TiO_2 DEGUSSA P25 at room temperature, in dry air, in a flow through reactor. Several parameters have been studied such as the concentration of n-pentane [25-500]ppmv for a total flow of 120mL/min, the molar flow rate (0.10-2.5mmol/min), and the modulation of the irradiance at 365nm. The degradation and the mineralization into CO_2 were followed through a gas analysis with a GC/FID/Catalytic Methanizer. Preliminary results showed that a complete mineralization of n-pentane into CO_2 seems to be always achieved whatever the operating conditions. Moreover, the degradation rate of n-pentane reached about 0.05mmol/min. This work shows also that the a conversion rate of 44% is reached for a molar flow rate of 0.10mmol/min.

Keywords: VOC, n-pentane, photocatalysis, indoor air, vehicle, COV, n-pentane, photocatalyse, air intérieur, automobile

1 Introduction

The Volatile Organic Compounds (VOCs) represent a major health issue because of their important presence in the vehicle cabin air, a closed space in which people spent the most party of their time (Müller (2011)), causing allergies, respiratory and skin problems....

The most of the depollution systems are based on filtration or adsorption over active charcoal, cheap systems, which store the pollutants at the surface, requiring the regular change of them. In addition, Destaillats *et al.* (2011) showed that the VOCs adsorbed over those systems can produce secondary VOCs by reacting with atmospheric ozone, and so represent a supplementary risk for the human health.

On the other hand, some systems can degrade the VOCs such as ozonation systems, but represent a real danger for human health because ozone can react with lung tissues, and produce during the degradation other VOCs (EPA, 2005).

As a matter of fact, the photocatalysis, appears as a good alternative to those systems,

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because it's a well known sustainable way to degrade the major part of pollutants (Zhao, 2002).

The photocatalysis is based on the activation of a semi-conducting material upon irradiation providing an energy equal or superior to its band gap, which creates an electron and a hole in the bulk. After migration to the surface they react with the adsorbed molecules creating activated species such as $O_2^{\circ -}$ and HO°. Those radicals will finally react with the adsorbed pollutants at the surface and so degrade them (Linsebigler (1995), Herrmann (2005)).

It's quite difficult to give the exact composition of VOCs present in the vehicle cabin air, because of the impact of several parameters on their nature, such as the brand/ the model of the car, the interior of this one, the temperature, the relative humidity (r.h), the age of the vehicle (Muller (2011)).

However, 3 majors groups of VOCs are distinguishable: the cycloalkanes (533.5µg/m^3 either 19.8%), the aromatics (521,2µg/m^3 either 19.8%) and the alkanes (1363.5µg/ m^3 either 50.6%) (Faber (2013), Brodzik (2014), Yoshida (2006)). From these studies, it appears that alkanes are mainly represented in the vehicle cabin air. Among them, the n-pentane derivates are fully represented (Debono (2013)). To the best of our knowledge the degradation of the n-pentane by photocatalysis is not widely studied. That's why this preliminary work is focused on the photocatalytic degradation of the n-pentane under several conditions described below.

2 Objectives

The main objective of these preliminary works is to study the degradation of n-pentane in presence of TiO_2 under UV irradiation. Several parameters will be under study to understand how the n-pentane could be degraded by photocatalysis over a TiO_2. First, the impact of the concentration will be studied for a given total flow. From this result, the influence of the molar flow of n-pentane will be studied to allow us to work closer to the real conditions of a vehicle cabin air. Finally, the impact of the irradiance which plays an important role in photocatalysis will be considered.

3 Materials and Methods

Photocatalytic Reaction: The degradation of n-pentane was done at room temperature (~24°C) in dry air, in a flow through reactor equipped of an optical window of 4cm diameter which cut the wavelengths inferior at 340nm. The photocatalyst (30 mg of EVONIK® P25 powder, 86wt.% Anatase, 14wt.% Rutile) is deposed and scattered on a filter provided by Durapore® (Millipore, diameter: 5cm, porosity: 0.4µm) placed into the reactor.

The irradiation is performed by a Philips Mercury Lamp PL-L 18 W, with a major irradiation in UV-A (315-400nm), placed directly on the reactor's window. The irradiance is measured by a radiometer at the outlet of the lamp.

VOC generation: In order to generate the n-pentane at different concentrations, a n-pentane cylinder provided by Air Liquide®, at 1000ppmv in air (with 959±29 mol-ppm of n-pentane and 19.94±0.40mol-% of O_2) is used. The dilutions are performed with a dry air flow composed by 300ppbv of CO_2 (obtained by an air compressor equipped by particles/CO_2/relative humidity filters) *via* a Brooks Instrument® mass flow controller.

Photocatalytic degradation measurements: All the gases were analysed by a GC-Flame Ionization Detector GC CP-3800 Varian equipped with a catalytic methanizer for the CO_2 detection. The separation is performed by two capillary columns in series: a CPSIL-5 and a PLOTQ provided by Agilent®.

A first analysis is done by by-passing the reactor to have the blank of the mixture sent into the reactor. Then, a second analysis is done to observe the adsorption of n-pentane on TiO_2 in dark (without irradiation). Finally, a last analysis is done upon irradiation in the reactor. For all the analysis the stationary state is reached.

Tested conditions: The impact of the n-pentane concentration has been tested for a total flow of 120mL/min, and irradiation power of 5mW/cm² for the following range: [25-500]ppmv. The experiments are performed at room temperature, in dry air.

Then, different molar flows, from 0.10 to 2.50mmol/min, were tested in order to be closer to the real conditions in vehicle cabin air. Indeed, if we consider that in a vehicle cabin, the averaged concentration of a specific pollutant is around 100ppb (Faber (2013)), and that the usual air flow used by the usual ventilation system is superior or equal to 20m^3/h, which corresponds to a molar flow of the pollutant superior or equal to 1.37mmol/min. At the same time, the irradiance has been modulated from 5mW/cm² to 0.5mW/cm².

The conversion rate of n-pentane and the mineralization into CO_2 of the degraded n-pentane are calculated by the followed equations:

$$\tau_{C_5H_{12}} = \left(\frac{n_{(C_5H_{12})i} - n_{(C_5H_{12})f}}{n_{(C_5H_{12})i}} \right) \times 100 \qquad \nu_{CO_2} = \left(\frac{n_{(CO_2)f}}{5n_{(C_5H_{12})i}} \right) \times 100$$

with:

τ_{C5H12}: the conversion rate of n-pentane during the photoxidation

ν_{CO2} : the conversion into CO_2 of the degraded n-pentane during the photoxidation

$n_{(C5H12)i}$: the initial number of moles of n-pentane

$n_{(C5H12)f}$: the final number of moles of n-pentane

$n_{(CO2)f}$: the final number of mole of CO_2

Impact of the concentration: The degradation rate of n-pentane and the production rate of CO_2 under different concentrations are presented in Figure 1.

It appears that for low concentrations the degradation rate increases, and reaches a plateau at a value of about 0.05mmol/min. The photocatalysis following a Langmuir-Hinshelwood model (Herrmann (2005)), the reaction rate is directly dependent of the surface coverage Θ of the catalyst by the molecules of pollutant (if we neglect the adsorption of O_2 and of reaction products). At low concentrations of reactant, the coverage rate is less than 1, and the degradation rate is directly related to the pollutant concentration (apparent order reaction 1). At higher concentrations, the coverage rate is nearly 1, the surface is saturated, and the degradation rate is no more dependent of the reactant adsorption (apparent order reaction 0).

Moreover, a complete mineralization seems to be always achieved whatever the initial concentration. Indeed, the production rate of CO_2 is equal to around 5 times to the degradation rate of n-pentane confirming the equation of n-pentane oxidation:

$$C_5H_{12} + 8O_2 \xrightarrow{h\nu / TiO_2} 5CO_2 + 6H_2O$$

From these results it also appears that for an initial concentration of n-pentane of 25ppmv, a conversion of 23% is reached. As expected, the conversion rate is decreasing when the concentration increases.

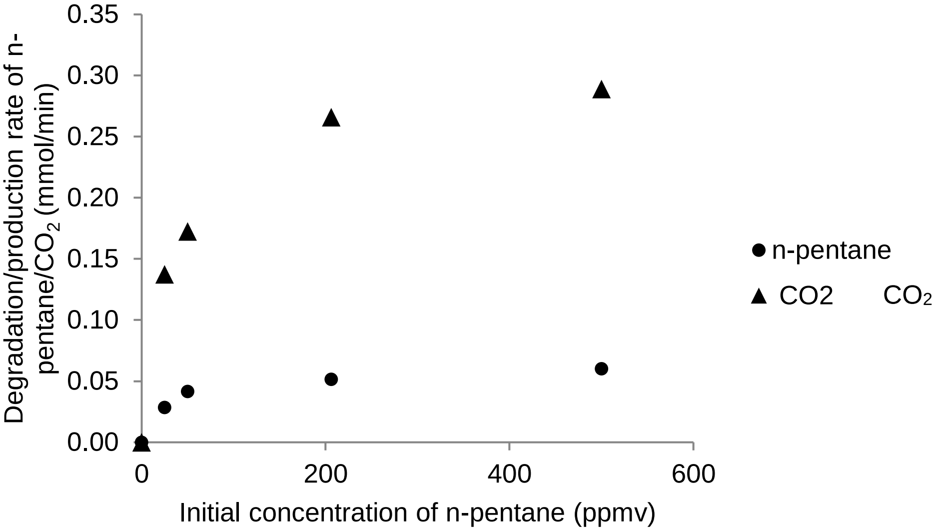

Figure 1: Degradation rate of n-pentane (dots) and production rate of CO_2 (triangles) as a function of the initial concentration of n-pentane.
Total flow: 120mL/min. Irradiance: 5mW/cm^2.

Impact of molar flow: In the same way, different molar flows have been tested; the results are represented in the Figure 2. When the molar flow increases, the conversion rate is decreasing. Indeed, the contact time decreases. A conversion rate of 44% is reached for a molar flow of 0.10mmol/min corresponding to a degradation rate of 0.05mmol/min, maximal degradation rate of n-pentane obtained in presence of 30 mg of TiO_2 P25 and under 5mW/cm^2 of irradiance.

This study highlights an important result: for a molar flow close to the real conditions 1.03mmol/min or more, the degradation rate is about 0.05mmol/min. It means that in a recirculation system of indoor air, to degrade a molar flow of pollutant (n-pentane) of 1.03mmol/min, it requires in these conditions about 20 minutes.

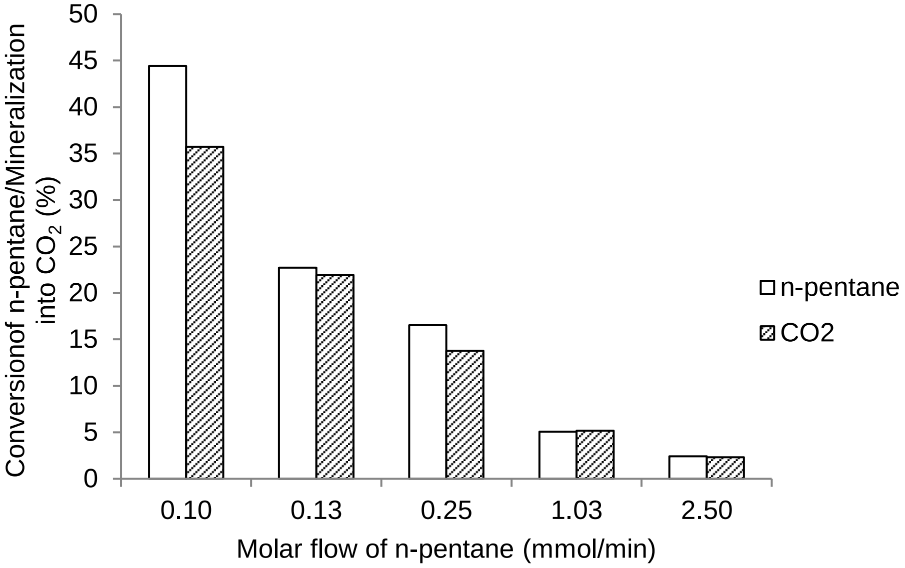

Figure 2: Conversion of n-pentane (unshaded) and percentage of mineralization into CO_2 (shaded) as a function of the molar flow of n-pentane. Irradiance: 5mW/cm².

Impact of the irradiance on the mineralization rate: The impact of the irradiance power has been tested for a same molar flow of 0.10mmol/min. We clearly observed after a diminution of 90% of the irradiance power, a diminution of more or less 90% of the conversion rate (44% to 4%), and a complete oxidation of n-pentane seems to be still observed. In photocatalysis, the conversion rate is directly depending on the irradiance power of the irradiation source, because it's related to the number of electron/hole pairs formed. The more the irradiance power is, the more the number of electron/hole pairs increases and the photocatalytic activity increases

Table 1. Impact of the irradiance on the conversion rate of the n-pentane by photocatalysis

Irradiance Power (mW/cm²)	**Molar flow (mmol/min)**	**Conversion (%)**	**Mineralization into CO_2 (%)**	**Rate (mmol/min)**
5	0.10	44	80	0.05
0.5	0.10	4	100	0.01

4 Conclusions

The photocatalytic oxidation of n-pentane on TiO_2 P25 was investigated under different conditions in dry air, at room temperature in a flow through reactor. A complete mineralization seems to be always achieved whatever the investigated operating conditions. No reaction intermediates were detected.

The impact of the concentration and molar flow of n-pentane have been demonstrated.

Due to surface saturation, the degradation rate of n-pentane (production rate of CO_2) remains constant for high hydrocarbon concentrations, or high molar flows, and reaches a degradation rate of 0.05 mmol/min. Moreover, a maximum conversion of 44% is achieved for a molar flow of 0.10 mmol/min of n-pentane. Increasing the contact time could probably enhance the hydrocarbon conversion. This study also highlighted that even if the irradiance is decreased by 90% leading to similar drop of the conversion, a total mineralization was still achieved.

According to these results, the required time to clean a cabin air vehicle exposed to 100 ppb of n-pentane can be estimated at around 20 and 200 minutes under an irradiation of $5mW/cm^2$ and $0.5mW/cm^2$, respectively. This estimation takes into account a photocatalytic device equipped with a ventilation system delivering a flow of $20m^3/h$, and 30mg of TiO_2 P25. This preliminary work seems to show that the n-pentane can be degraded and mineralized in conditions close to the real operations.

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References

[1] Brodzik K., J. Faber, D. Lomankiewicz & A. Golda-Kopek (2014): In vehicle VOCs composition of unconditionned newly producted cars. J. Environ. Sci., vol. 26, p 1052-1061

[2] Debono O., F. Thévenet, P. Gravejat, V. Héquet, C. Raillard, L. Le Coq & N. Locoge (2013): Gas phase photocatalytic oxidation of decane at ppb levels: removal kinetics, reaction intermediates and carbon mass balance, J. Photoch. Photobio. A, vol. 258, p 17–29

[3] Destaillats H., W. Chen M. G. Apte, N. Li , M. Spears , J. Almosni, G. Brunner, J.J. Zhang & W. J. Fisk (2011): Secondary pollutants from ozone reactions with ventilation filters and degradation of filter media additives. Atmos. Environ., vol. 45, p 3561-3568

[4] Faber J., K. Brodzik, A. Golda-Kopek & D. Lomankiewicz, (2013): Air pollution in new vehicle as a result of VOC emissions from interior materials. Pol. J. Environ. Stud.,vol. 22, n°6, p 1701-1709

[5] Herrmann J-M., (2005): Heterogeneous photocatalysis: state of the art and present applications. Topics in Catalysis, vol. 34, n°1-4, p 49-65

[6] Linsebigler A.L., G. Lu & J.T. Yates, Jr, (1995): Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chem. Rev., vol. 95, p 735-758

[7] Müller D., D. Klingelhöfer, S. Uibel & D. A. Groneberg, (2011): Car indoor air polllution-analysis of potential sources. J Occup Med Toxicol, vol. 6, p 1701-1709

[8] United States Environmental Protection Agency (EPA), Residential Air Cleaners. Indoor Air Quality,EPA report, Second Ed., 402-F-09-002, 2009

[9] Yoshida T. & I. Matsunaga, (2006) : A case study on identification of airborne organic compounds and of their concentrations in the cabin of a new car for private use. Environ. Int., vol. 32, p 58-79

[10] Zhao J. & X. Yang, (2003): Photocatalytic oxidation for indoor air purification: a literature review . Build. Environ., vol. 38, p 645-654.