Are TiO$_2$-based exterior paints useful catalysts for gas-phase photooxidation processes? A case study on $n$-decane abatement for air detoxification

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Abstract

*n*-Decane is a saturated long-chain hydrocarbon, belonging to the family of the volatile organic compounds (VOCs), which is persistently present in indoor air of several industrial closed facilities. Due to the VOCs environmental impact, all efforts that have been made during the last decades to degrade this kind of air pollutants are extremely important. Accordingly, the present paper reports *n*-decane photooxidation studies carried out in an annular photoreactor under simulated solar irradiation and employing a catalytic bed made of cellulose acetate monoliths coated with a photocatalytic paint. The influence of the feed flow rate, *n*-decane concentration, relative humidity, and incident irradiance on the *n*-decane degradation kinetics was assessed. Within this work, *n*-decane photodegradations higher than 90% were achieved, depending on the experimental conditions. Additionally, a phenomenological reaction rate model of the *n*-decane photocatalytic oxidation was proposed and assessed. The proposed model assumes that *n*-decane and water molecules compete for different active sites on the catalyst surface. Finally, despite the high *n*-decane photodegradation achieved, reaction by-products were identified and, based on these compounds, a reaction mechanism was formulated.

Keywords: Photocatalysis; Air Decontamination; *n*-Decane; Photo-TiO$_2$ Paint; Acetate Cellulose Monoliths; Artificial Sunlight.
1. Introduction

For a long time, society has been debating indoor air pollution and its effect on human health whether in urban or industrial areas [1-4]. Today, 70-90% of our lifetime is spent at indoor environments [5, 6]. Incoming air filters or air cleaners based on ultraviolet germicidal irradiation, activated carbon, ionization, or ozone generation are the most used methods for air decontamination [3, 7]. Nevertheless, photocatalysis is now seen as a valuable option for de-polluting purposes [8-15], mainly because it: i) can be operated at room temperature [16]; ii) air (through water vapour and molecular oxygen) can be used as the source of oxidant [17], iii) degrades/mineralizes a wide range of organic pollutants into harmless or easily neutralized final products (CO₂, H₂O and mineral acids) [18]; iv) can take advantage of solar radiation for performing the charge separation at the semiconductor [19]. Furthermore, semiconductor titanium dioxide (TiO₂) is commonly employed as photocatalyst in photocatalytic oxidation (PCO) processes due to its inexpensiveness, resistance to photocorrosion, high oxidative power, and relatively low toxicity [20-22].

As reported in our previous work [23], high concentrations of n-decane (up to 300 μg m⁻³) were found in the indoor air of a WWTP with closed facilities at different sampling sites and campaigns; thus, n-decane was used as organic air pollutant model. The solar PCO of n-decane over TiO₂ for air detoxification can be represented by eq. 1 [10]:

\[
C_{10}H_{22}(g) + \frac{31}{2} O_2(g) \xrightarrow{\text{TiO}_2, h\nu} \text{intermediates} \xrightarrow{\text{TiO}_2, h\nu} 10 \text{CO}_2(g) + 11 \text{H}_2\text{O}(g) \quad (\text{eq. 1})
\]

and considering what is believed to be the initial stages of the photocatalytic process, the following equations are the most representative [24-27]:

\[
\text{TiO}_2 + h\nu \longrightarrow e^-_{\text{cb}}(\text{TiO}_2) + h^+_{\text{vb}}(\text{TiO}_2) \quad (\text{eq. 2})
\]

\[
h^+_{\text{vb}}(\text{TiO}_2) + \text{H}_2\text{O} \longrightarrow \text{HO}^+ + \text{H}^+ \quad (\text{eq. 3})
\]
Conduction-band electrons $e_{cb}^{-}(\text{TiO}_2)$ and valence-band holes $h_{vb}^{+}(\text{TiO}_2)$, i.e. electron-hole pairs, are generated when photons of energy $h\nu$ matching or exceeding the semiconductor band-gap energy are absorbed (eq. 2). Once at the surface of the semiconductor, and on the absence of any suitable acceptor (for $e_{cb}^{-}$) and donor (for $h_{vb}^{+}$) recombination will occur in a matter of nanoseconds; therefore no reaction occurs [16, 27]. Hydroxyl anions and water molecules adsorbed on TiO$_2$ surface, act as electron donors, while molecular oxygen acts as electron acceptor, leading to the formation of hydroxyl ($\text{HO}^*$) and superoxide ($\text{O}_2^{*-}$) radicals [24-26] (see eq. 3-5). When an organic molecule (RH) is adsorbed onto semiconductor surface, the reaction with hydroxyl radical occur, followed by structural breakdown into several intermediates until, eventually, total mineralization (see eq. 6) [10, 28]. The photogenerated holes due to the high oxidation potential can also participate in the direct oxidation of the organic pollutants (eq. 7) [29, 30]. Peroxide (HOO$^*$) radical can also be generated from the protonation of $\text{O}_2^{*-}$ radical and subsequently form hydrogen peroxide (see eq. 8-9).

TiO$_2$ powders have been incorporated as white pigment in different applications from ancient times [31]. As early as 1929, Kiedel [32] stated that titanium white pigment, under sunlight irradiation, was responsible for paint chalking because the photodegradation of organic binder. In 1938, Goodeve et al. [33] reported that UV
absorption produces active oxygen species on the TiO$_2$ surface that cause dyes to photobleach.

Although, it was during the 1960s that, for the first time, TiO$_2$ photochemical effect was used to induce chemical reactions [34, 35]. Mashio and coworkers [36] in 1956 conducted several studies regarding oxidation induced by TiO$_2$ under illumination. These works concluded that anatase is more photoactive than rutile. However, the first contribution for understanding the heterogeneous photocatalytic effect was in 1972 with the pioneer work by Fujishima and Honda [37]. These authors investigated the electrochemical photolysis of water using a single TiO$_2$-rutile crystal (n-type) as photoanode and a Pt counter electrode. This work opened the frontiers for the use of titania for photocatalysis and other applications.

Construction materials can be used to support photocatalytic TiO$_2$ nanoparticles and used as depolluting agents [31, 38-44]. Paint coatings, among all construction materials, are especially attractive as support for photocatalytic TiO$_2$ since almost all surfaces in urban areas can be painted. Bygott et al. [38], for instance, report a field trial in London, close to a school children playground, where an area of 300 m$^2$ of walls was painted with a silicate-based paint incorporating 7.5 wt.% of photocatalytic TiO$_2$. The results showed a daily NO$_x$ abatement of ca. 4.5 g in about 10 000 m$^3$ of air around the school children playground [38]. Maggos et al. [44] report NO$_x$ depollution tests in an artificially closed parking area, which was polluted by a car exhaust during the testing period; they observed a reduction of 19 % and 20 % for NO and NO$_2$, respectively. Salthammer and Fuhrmann [43] studied the photocatalytic efficiency of two different types of commercially available wall paints in a 1 m$^3$ test chamber with and without air exchange using artificial daylight. The results showed that formaldehyde was
photooxidise under static conditions. In contrast, for typical VOCs, under dynamic conditions, no significant photocatalytic effect was observed.

Several studies indicate that paint components can impair the photoactivity of paint films [42-50]. For example, Allen et al. [46] studied the effect of different paint components on the photoactivity of these paints. The results showed that the porosity, which is related to the particulated paint components (pigments and extenders) concentration, has a positive effect on photoactivity. However, higher content in CaCO$_3$ and high porosity makes paints prone to self-degradation. In the same line, Mendes and co-workers [41, 51, 52] developed a vinyl exterior paint modified with several TiO$_2$ photocatalysts: P25 (Evonik/Degussa), PC50 (Millennium), PC105 (Millennium), PC500 (Millennium), ANX type PA (Kemira), UV100 (Sachtleben), AMT100 (Tayca), UVLP7500 (Kronos), VLP7000 (Kronos), and VLP7101 (Kronos); the authors stated that paint pigmentary TiO$_2$ is the most critical component affecting the photocatalytic activity for NO$_x$ abatement due to its competitive absorption of the UV radiation. Considering the results reported by these authors, the highest yields towards NO$_x$ photocatalytic oxidation are obtained when incorporating in paint formulations photocatalysts PC500 (Millennium), PC105 (Millennium), and UV100 (Sachtleben) [41, 51, 52]

Although the potential of photocatalytic paints to detoxify air is very promising, several studies demonstrate the formation of by-products that may be harmful for humans [45, 53-55]. For example, Uhde and Salthammer [54] reported that UV-irradiated paints produce undesired and highly toxic by-products such as formaldehyde, acetaldehyde, ethylacrolein, pentanal, 1-hydroxy-butanone, and hexanal. This observation was further emphasized by Kolarik and Toftum [53]. Auvinen et al. [45] and Geiss et al. [55] found that relatively high amounts of organic compounds, such as aldehydes and ketones, are formed from the decomposition of binders and additives. Auvinen et al. [45] also stated
that photocatalytic surface aging and the use of different substrates (glass, gypsum or polymeric plaster) do not have a noteworthy influence on the paint photocatalytic activity.

Disinfection of air using photocatalytic paints was the focus of other research groups [47, 50, 56]. According to Hochmannova and Vytrasova [47], UV light emitted from normal domestic fluorescent lights is capable to ensure the photocatalytic and antimicrobial effects of paints incorporating nanoparticles of zinc oxide. Later, Sousa et al. [50] showed microorganism photoinactivation over a photocatalytic paint under UVA irradiation.

Although photocatalytic paints have been showing very promising results concerning the photodegradation of air pollutants and the photoinactivation of microorganisms, it is necessary to keep improving their performance paints as well as understand the phenomena behind their photoactivity. This paper presents a study on gas-phase solar photooxidation of n-decane over a TiO$_2$-containing paint, using a lab-scale continuous-flow annular photoreactor with a compound parabolic collector. To the best of our knowledge, this is the first time that the performance of TiO$_2$-based exterior paints and their applicability on gas-phase photooxidation processes for n-decane abatement is evaluated. The photocatalytic oxidation of n-decane was studied for different operating conditions, such as feed flow rate, n-decane concentration, feed relative humidity and incident irradiance. The n-decane degradation reaction behaviour in the continuous system was modelled considering different Langmuir-Hinshelwood kinetic-based reaction rate equations. It considers that PCO of n-decane is not influenced by reaction intermediates and/or products and n-decane and water are the major species. In addition, a reaction mechanism was proposed for n-decane PCO considering the degradation by-products identified by GC/MSD.
2. Experimental

2.1. Materials and chemicals

Mendes and co-workers [41, 51, 52] reported a water-based vinyl paint loaded with TiO\textsubscript{2} photocatalyst PC500 (Millennium) that produced high NO conversions among several other commercially available photocatalysts. For this reason, the same modified vinyl paint with photo-TiO\textsubscript{2} PC500 was selected. The PC500 photocatalyst properties are detailed in Table 1. Cellulose acetate monoliths (named C: TIMax CA50-9/S – $L_{C} = 80$ mm, $d_{ch}^2 = 9$ mm $\times$ 9 mm, $e_{w,ch} = 0.1$ mm; Wacotech GmbH & Co. KG.) were used to support the catalytic paint. For the generation of humidified air streams contaminated with $n$-decane, deionized water and $n$-decane ($\geq 94\%$; CAS no. 124-18-5; Merck) were used without further purification. Air Liquide provided all gases, with minimum total purities of 99.999%: helium N50, nitrogen N50, and synthetic air N50 ($O_2$: 20 ± 1%; $H_2O$: $< 3$ ppm; $C_nH_m$: $< 0.1$ ppm; $CO_2$: $< 1$ ppm; CO: $< 1$ ppm).

2.2. Photocatalytic films preparation and characterization

Photo-TiO\textsubscript{2} PC500 from Millennium) was used to modify a commercially available exterior water-based vinyl paint. The catalyst and paint properties are summarized in Table 1 [52]. From the original exterior water-based vinyl paint, half of the pigmentary TiO\textsubscript{2} (9 wt.% in wet base) was removed; the photocatalytic paint (henceforth named as P) was, subsequently, formulated by adding 9 wt.% of photo-TiO\textsubscript{2} PC500 (ca. 50 cm$^3$ of paint without 50% of pigmentary TiO\textsubscript{2} and mixing for 30 min at 300 rpm in a 100 cm$^3$ stainless steel vessel), as reported by Águia et al. [41]. The final photo-TiO\textsubscript{2} PC500 and pigmentary TiO\textsubscript{2} content was 9 wt.% in wet basis (ca. 17 wt.% in dry basis) (see Table 1).

Cellulose acetate monoliths were coated with a thin film of the photocatalytic paint P using the dip-coating method (Dip-Coater RDC21-K, Bungard Elektronik GmbH
Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis was performed in a FEI Quanta 400 FEG ESEM / EDAX Genesis X4M apparatus equipped with a Schottky field emission gun (for optimal spatial resolution) for the characterization of the surface morphology of PC500 powder, fresh PC, and used PC samples (after more than 50 h of PCO experiments) as well as their chemical composition. Each sample was mounted on a double-sided adhesive tape made of carbon for its surface observation at different magnifications; the cross-section of the fresh PC sample was also measured by this technique. These SEM/EDX analyses were made at CEMUP (Centro de Materiais da Universidade do Porto).

2.3. **Experimental setup**

The experimental setup is depicted in Fig. 1. A full description of the whole apparatus is given elsewhere [58]. The feed generator is composed by three mass flow controllers (MFC, El-Flow, Bronkhorst High-Tech B.V.), which allow the generation of humid air streams contaminated with $n$-decane by flowing air through distinct Woullf
bottles (Normax, Lda.), one containing $n$-decane and another filled with deionized water
(Fig. 1a). The photocatalytic system comprises (Fig. 1b): i) a solar simulator (Atlas, model
Suntest XLS+) with a working area of 0.110 m$^2$, a 1.7 kW air-cooled xenon arc lamp, a
daylight filter and quartz filter with infrared coating; ii) a compound parabolic collector
with 0.023 m$^2$ of illuminated area with electropolished anodized aluminium reflectors (to
use both direct and diffuse irradiation as well to uniform it throughout the bed); iii)
photoreactor composed by two concentric and axially centred tubes (the outer tube made
of Pyrex-glass, Duran borosilicate glass 3.3, cut-off at 280 nm, Schott-Rohrglas GmbH,
and the inner tube made of quartz, Quarzglas-Rohr Quarzglastechnik, GmbH & Co.); iv)
an actinic lamp (Actinic BL TL 6 W, Koninklijke Philips Electronics N.V.) for catalyst
degassing and activation purposes, placed inside and axially centred in the inner tube
(peak at 365 nm – UVA radiation). Both inlet and outlet caps of the photoreactor have
four equidistant inlets to ensure a better distribution of the feed stream to the reactor. Note
that the tubing for inlets and outlets are made of PTFE (supplied by Vidrolab2, S.A.) that
minimizes the adsorption of VOCs. Table 1 also shows the tube dimensions of the
photoreactor; Figs. 1b1 and 1b2 schematically represent the continuous-flow photoreactor
from a side and frontal point of view, respectively.

$n$-Decane concentration histories were monitored using a gas chromatograph
(MGC Fast GC, Dani Instruments S.p.A.) equipped with a flame ionisation detector (FID)
and a Volcol capillary column (20 m $\times$ 0.18 mm $\times$ 1.00 µm; Supelco, Sigma-Aldrich Co.
LLC.) (see Fig. 1c). The experimental setup was connected to a computer and controlled
using a data acquisition board system and an in-house program developed routine written
in Labview environment (NI Corporation). All connections are of 1/16” stainless steel
tubing (Swagelok Company) to reduce dead volumes.

Additionally, by-products from the $n$-decane photooxidation were analysed at
steady-state, sampling the photoreactor exit stream to a Tedlar bag (232-05SKC, SKC Inc.) and then transferring the sample to stainless steel tubes with Tenax TA60/80 mesh (Supelco, Sigma-Aldrich Co. LLC.). After sampling, identification and quantification of the reaction products was performed with a thermal desorption system (SDT 33.50, Dani Instruments S.p.A.) working in line with a GC/MSD device (a gas chromatograph GC 6890N coupled to a mass spectrometer detector MSD 5973, Agilent Technologies, Inc.). The response factor of toluene (ISO 16000-6 [59]) was used to determine the concentration of the major products (while for n-decane, specific response factor were used).

2.4. Photocatalytic experiments

All experiments were carried inside the chamber of the aforementioned solar simulator, which can simulate a spectrum similar to that of sunlight within $300 < \lambda < 800$ nm. The incident irradiance was measured using a broadband UV radiometer (CUV 5, Kipp & Zonen B.V.), placed on the outside of the outer tube and at the same height, within a spectral range of 280 to 400 nm corresponding to the UV fraction of the solar irradiation.

At steady-state, n-decane photodegradation fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$, where $C_{\text{dec, feed}}$ and $C_{\text{dec, exit}}$ in ppm are the pollutant concentration on the feed and exit streams, respectively) was studied for several experimental conditions: feed flow rate (75–300 cm$^3$ min$^{-1}$, measured at 1 bar and 298 K), pollutant concentration (40-138 ppm), feed relative humidity (3-40%, measured at 1 bar and 298 K), and incident irradiance (18.9-38.4 W m$^{-2}$, measured for the spectral range between 280-400 nm: UV fraction of the incident sunlight). Table 2 summarizes all the experiment conditions. Prior to all experiments, the catalytic bed was degassed and the photocatalytic paint coat activated under UV radiation and by flowing 30 mL min$^{-1}$ (measured at 1 bar and 298 K) of synthetic air with 40 % of relative humidity for 24 h (similar conditions as described...
elsewhere [41]). Before turning on the solar simulator, the catalytic bed was continuously
fed and, by means of outlet stream sampling analysis, the feed composition steadiness
was checked.

3. Results and discussion

3.1. Photochemical oxidation of n-decane

A blank test consisting in an experiment without photocatalyst was performed,
showing no measurable n-decane concentration decrease (data not presented; operating
conditions reported in Table 2: run 1).

3.2. Photocatalytic oxidation of n-decane

3.2.1. Surface characterization of photo-TiO$_2$ powder and PC samples

The surface morphology of PC500 powder sample and its chemical composition
were determined by SEM/EDX. The SEM micrograph (Supplementary Data: Fig. A.1)
shows an estimated size of the photo-TiO$_2$ agglomerates of ca. 600-1500 nm. According
to this image, the dimension of the agglomerates range from half size up to the values
provided by the manufacturer (see Table 1); similar sizes are displayed in SEM pictures
of photocatalytic paint films loaded with the same photocatalyst and reported by Águia
et al. [51]. As previously mentioned by the same authors [51], EDX analysis of PC500
powder (Supplementary Data: Fig. A.2) indicates that both agglomerates and individual
particles are only made of TiO$_2$.

The surface morphology and chemical composition of PC samples was also
determined by SEM/EDX. SEM micrographs of fresh PC and used PC samples (with
50 h+ of use in PCO of n-decane) at three different magnifications are shown in Figs. 2a
to 2d. The fresh PC images (Figs. 2a and 2c) show that the photocatalytic paint was
homogeneously coated on the cellulose acetate monolith. After its use on the PCO
experiments (Figs. 2b and 2d), SEM micrographs suggest that the film structure was not
significantly affected despite the harsh operating conditions employed. This conclusion was also supported by EDX analysis of both fresh and used samples (shown in Figs. 2e and 2f, respectively). According to the EDX spectra, the proportion of each element remained approximately the same after the photocatalytic experiments. From SEM images (Fig. 3) it was also possible to estimate the paint film thickness (ca. 5-10 µm) and the cellulose acetate monolith thickness (ca. 50 µm). Contrarily to what have been observed by Lopes et al. [60] when using TiO₂ sol-gel films supported on cellulose acetate monoliths, paint films are approximately 25-fold thicker (and more resistant) than TiO₂ sol-gel films. These properties significantly prevent film fissures, delamination, and/or degradation. Thus, the use of paint films reveals to be an advantage in the prevention of the catalyst/support aging.

3.2.2. Operating parameters effect on n-decane photodegradation

At steady-state conditions, n-decane photodegradation fraction \( C_{\text{dec, exit}} / C_{\text{dec, feed}} \) was obtained for four experimental conditions (Figs. 4-6). Fig. 4 shows the effect of the feed flow rate \( Q_{\text{feed}} \) on the n-decane photodegradation fraction. n-decane photodegradation decreases as \( Q_{\text{feed}} \) increases, since a higher feed flow rate results in a lower residence time, reducing the pollutant-catalyst contact period. Thereby, for a 4-fold increase in \( Q_{\text{feed}} \), the photocatalytic process is 1.6, 1.9, and 2.3 times less effective, respectively, for incident irradiances of 38.4, 29.1 and 18.9 W m⁻² (Table 2: runs 4 and 7, runs 5 and 8, and runs 6 and 9, respectively). This also means that, for a higher feed flow rate the incident irradiance on the catalyst surface becomes more relevant for the PCO of n-decane: the electron-hole pairs formation is favoured by higher incident irradiances.

In Fig. 5 is shown the influence of the feed concentration on the n-decane photodegradation fraction. Results show a decrease in the photodegradation fraction with an increase of n-decane concentration. In fact, for a 3.4-fold increase in n-decane
concentration, 1.8, 2.4, and 3.6 times lower photodegradation fractions were observed for incident irradiances of 38.4, 29.1 and 18.9 W m\(^{-2}\), respectively (Table 2: runs 4 and 7, runs 5 and 8, and runs 6 and 9, respectively). So, increasing the number of \(n\)-decane molecules that enters the reactor per unit of time, a higher number of photons/hydroxyl radicals are necessary to achieve the same photodegradation. Furthermore, the results above suggest that the feed concentration has a more important influence on the PCO of \(n\)-decane than the feed flow rate for the same organic load, most likely due to the considerably lower surface area “usefully” available for the photocatalytic reaction. In other words, despite the equivalent UV-irradiated surface area, there are more VOC molecules adsorbed per surface area, restricting the generation of oxidant species from adsorbed water and oxygen (namely, hydroxyl radicals, peroxide radicals, and superoxide radicals).

Although there are plenty of studies describing the influence of feed relative humidity on the photodegradation of alkanes, conclusions are still not clear [10, 61]. Twesme et al. [62] and Zhang and Liu [63] pointed out 40% and 20% of relative humidity, respectively, as the optimum conditions regarding water content to obtain the highest degradation rates in their studies. Shang et al. [64] demonstrated in their studies that the degradation rate of \(n\)-heptane decreases as the relative humidity was increased from 0 to 60%. In fact, the presence of vapour water molecules has two opposing effects: i) inhibits the degradation by competitive adsorption to the photocatalyst surface (for feed streams with high water vapour content) [6, 65]; ii) accelerates the degradation by promoting hydroxyl radicals formation [25]. Fig. 6 shows a slight relative increase (3%) of the \(n\)-decane photodegradation for the highest irradiance value (38.4 W m\(^{-2}\)) and within the relative humidity range of 3 % to 40 %.

On the other hand, it was found that for the lower irradiance values, particularly for 18.9 W m\(^{-2}\), its effect on the \(n\)-decane photodegradation...
becomes more relevant: for the same relative humidity increment, the $n$-decane photodegradation is 3% (from run 16 to run 1) to 25% (from run 18 to run 3) more efficient with a 2-fold reduction of the incident irradiation (from 38.4 to 18.9 W m$^{-2}$). This supports the important role of hydroxyl radicals in photocatalytic processes due to the lower amount of surface electron-hole pairs available on the catalyst surface to react with the pollutant molecules.

It should be pointed out that after 50 h under simulated solar irradiation and continuous feed (humid air contaminated with $n$-decane), similar photodegradations were obtained under the same operating conditions (data not shown). Considering the up-stated for SEM analysis (see section 3.2.1), it is suggested that PC deterioration was negligible.

### 3.2.3. Simulation and predictive studies of $n$-decane kinetics through PCO

Several models have been proposed in the literature for simulating VOC photocatalytic oxidation kinetics [58, 60]. Table 3 describes the complete mathematical model combined with three different Langmuir-Hinshelwood reactions rate expressions. The numerical solution of the mathematical model was performed in gPROMS environment (Process System Enterprise, London, UK) using the orthogonal collocation on finite elements method. The number of elements used was 90 with two interior collocation points (third order polynomials) in each element of the photocatalytic bed. The simulations were performed with an absolute and relative tolerance of $1 \times 10^{-5}$. First, parameters were estimated using a sequential quadratic programming algorithm [60]; then, the mathematical model was employed for simulating the PCO of $n$-decane. Table 3 reports the estimated kinetic and adsorption equilibrium parameters.

Results shows that the mathematical model with the Langmuir-Hinshelwood kinetic reaction rate expression RE-3 (bimolecular competitive two types of sites rate expression) generally produced better fitting results within the operational conditions.
studied than models RE-1 or RE-2 (bimolecular competitive one type of sites or
bimolecular non-competitive two types of sites rate expressions) (Figs. 4-6). This means
that both \textit{n}-decane and water molecules must be considered independent and targeting
different active sites of the catalyst surface. The surface active sites competition between
the two types of molecules cannot be disregarded because, despite the higher number of
parameters required by RE-3, this rate expression is more suitable to describe the
experimental data (see the statistical analysis reported in Table 3). Contrarily to the
previous reported models of PCO [58, 60], it was necessary to include an incident
irradiance exponential order constant \((n)\). The radial effect of the UV irradiation passing
through the PC samples and its consequent reflection and refraction were not considered;
moreover, the mathematical model neglects any partial UV absorption by the PC samples.
Nevertheless, the UV irradiance on PCO of \textit{n}-decane could be fitted by an irradiance
exponential order constant \(n = 0.8\), as can be seen throughout the paper (Figs. 4-6).

The closest results to our data regarding gas-phase PCO of \textit{n}-decane were obtained
by Debono \textit{et al.} [66]. However, these authors performed UVA-photocatalytic
experiments of \textit{n}-decane over TiO\textsubscript{2} powder dispersed at the bottom of a batch reactor, and
employing \textit{n}-decane-polluted air stream at ppb level. Therefore and only for these
conditions Debono \textit{et al.} [66] were able to provide a photocatalytic lab-scale setup
effective for complete \textit{n}-decane photodegradation.

Considering that the mathematical model described successfully the reported
experiments, simulations can now be performed to obtain insights concerning the effect
of each operating variable on the process performance. The effect of the lab-unit
geometrical parameters on the PCO of \textit{n}-decane was assessed \((\text{e.g., photoreactor length}
\textit{L}R)\) within the operating condition studied, aiming unit geometric optimization and re-
scaling. Fig. 7 shows the \textit{n}-decane photodegradation fraction profiles, considering
photoreactors of different lengths ($L_R$). It can be seen that, when the operating conditions of run 3 are employed (lowest incident irradiance, and intermediate feed flow rate and $n$-decane concentration), a 1.5-fold increase of the photoreactor length yields to a $n$-decane photodegradation enhancement of 85% (see Fig. 7a). Moreover, for a photoreactor 2× longer, complete $n$-decane photodegradation is attained (Fig. 7a). On the other hand, Fig. 7b predicts how $n$-decane photodegradation fraction is affected as a function of the photoreactor length when the highest incident irradiance and feed flow rate are employed (run 7). For a 1.5 times longer photoreactor than the experimentally employed, a 76% $n$-decane photodegradation enhancement is observed. If the reactor is twice the length ($L_R = 0.32$ m), only 1% of $n$-decane feed is predictively unreacted; complete $n$-decane photodegradation is attained when using a ~3 times longer photoreactor.

3.3. Reaction mechanism for the PCO of $n$-decane

The degradation mechanisms of alkanes and the corresponding formation of its by-products have been studied recently [61, 64, 66-69]. According to the previously cited authors it was found that ketones and aldehydes are the main intermediates of $n$-decane photochemical reaction. Minabe et al. [70] reported that gas-phase photooxidation of long organic chains over TiO$_2$ thin-films only produces CO$_2$ and H$_2$O. It was suggested that both reactants and intermediates were continuously adsorbed on the TiO$_2$ surface. Within this work, identification and quantification of the $n$-decane photocatalytic reaction by-products were monitored by GC/MSD (Supplementary Data: Table A.1), for the experimental conditions of run 1 (previously described in Table 2). The identified by-products (and their concentration) were: unreacted $n$-decane (4.32 ppm), $n$-hexane (0.035 ppm), $n$-heptane (0.028 ppm), $n$-octane (0.007 ppm), $n$-nonane (0.036 ppm), $n$-undecane (0.005 ppm), 4-methylnonane (0.006 ppm), 2,6-dimethyloctane (0.009 ppm), butanoic
acid (0.022 ppm), propanoic acid (0.072 ppm), and butanal (0.016 ppm). Therefore and based on the nature of the identified compounds, a reaction mechanism under wet air (40%) is proposed and schematized in scheme 1. According to scheme 1, n-decane undergoes a cleavage into radicals – cracking – by a hydroxyl radical. Taking into consideration that alkyl radical stability increases along the series from methyl to primary, followed by secondary, and then by tertiary carbon, the energy required to create them decreases [71]. So, in the case of straight-chain alkanes, secondary carbons are oxidized by hydroxyl radical rather than primary ones. Nonetheless, from scheme 1 and supported by literature [64, 71-73], it is assumed the formation of both primary and secondary alkyl radicals. After homolytic cleavage of n-decane four paths can take place: 1) radical recombination generating new alkane hydrocarbons such as n-hexane, n-octane, or 2,6-dimethyloctane (Table 3); 2) hydrogen abstraction reactions leading to the formation of alkanes and alkenes; 3) reaction with adsorbed O$_2$ producing a highly reactive superoxide radicals; 4) oxidation by hydroxyl radicals forming alcohols.

Several authors [24, 64, 67, 73] reported the rapidly dehydration of alcohols into alkenes or oxidation into corresponding ketones or aldehydes (see scheme 1, path 4); alkenes could be degraded into aldehydes as reported by Djeghri and Teichner [72] whereas aldehydes could suffer double oxidation by hydroxyl radicals into carboxylic acid [24, 74, 75] as it was detected the presence of propanoic and butanoic acid. An alternative approach was suggested by Kominami et al. [76] after observing the formation of an ester from the recombination of the aldehyde and its intermediate. Then, according to Augugliaro et al. and Peral et al. [24, 25], ester could be adsorbed on the TiO$_2$ surface where it would be dissociated into alkoxy and carboxylate radical. The alkoxy form an aldehyde and the carboxylate radical could produce alkyl radicals and carbon dioxide leading to alkanes after radical recombination or alkenes after hydrogen abstraction.
reaction. Carboxylate radical could also be formed by oxidation by hydroxyl radical of carboxylic acid which would lead to the formation of alkyl radicals and CO₂ in a process called decarboxylative dimerization. On the other hand, several authors [77-79] have proposed the reaction between ketones and adsorbed O₂, forming an unstable ketone diolate complex onto the TiO₂ surface. Consequently, the diolate complex would rapidly be dissociated into carboxylate which would lead to the formation of alkyl radicals and carbon dioxide. These radicals would be rapidly oxidized into alcohols and, then, aldehydes [80]. This approach may explain the absence of ketones and presence of butanal.

Considering that \( C_{i, \text{dec}} \) refers to the carbon atoms concentration of compound \( i \) formed by \( n \)-decane photodegradation (all unreacted \( n \)-decane and its by-products produced), it can be defined as:

\[
C_{i, \text{dec}} = \frac{C_i}{M_i} \cdot n(C) \cdot M(C)
\]  
(eq. 8)

where \( C_i \) [ppm] and \( M_i \) [g mol\(^{-1}\)] are the gas phase concentration and molecular weight of compound \( i \), respectively, \( n(C) \) is the number of carbon atoms of each component \( i \) molecule, and \( M(C) \) [g mol\(^{-1}\)] is the molecular weight of a carbon atom. Thus, the mineralization efficiency \( (\eta_{\text{min}} \text{ in } \%) \) can be determined through eq. 9.

\[
\eta_{\text{min}} \text{[%]} = \left[ 1 - \frac{\sum_i (C_{i, \text{dec}})_{\text{exit}}}{\sum_i (C_{i, \text{dec}})_{\text{feed}}} \right]
\]  
(eq. 9)

Thus, considering the carbon atoms concentration of each identified and quantified by-product resulting from the \( n \)-decane molecules photodegradation (experimental conditions reported in Table 1: run 1) more than 99% of the \( n \)-decane degraded (~94% of \( n \)-decane fed) was completely mineralized into CO₂ and H₂O. This result is in agreement to what Debono et al. [66] disclosed in their previous work: the total carbon atoms concentration of all by-products formed by \( n \)-decane photodegradation is lower than 5%.
4. Conclusion

The use of an annular lab-photoreactor under simulated solar irradiation has shown to be inefficient for the photochemical reaction of gaseous \( n \)-decane and extremely effective on the photocatalytic process over a photo-TiO\(_2\) paint. Under simulated solar irradiation, the gas-phase photocatalytic experiments showed that highest \( n \)-decane photodegradation (98\%) was attained at the lowest \( Q_{\text{feed}} \) (75 cm\(^3\) min\(^{-1}\)) and \( C_{\text{dec, feed}} \) (41 ppm), and highest \( RH_{\text{feed}} \) (40\%) and \( I \) (38.4 W m\(^{-2}\)). Feeding the photoreactor with the double flow rate, the \( n \)-decane photodegradation decreases from 96 to 62\% (run 1 and 7). Alternatively, when the \( n \)-decane concentration on the feed stream is doubled, the remaining unreacted \( n \)-decane fed drops from 4 to 46\% (run 1 and 13). It was also observed that the water vapour content effect on the PCO of \( n \)-decane is more pronounced under lower irradiances, i.e., from ~71 to 56\% (run 3 and 18).

A phenomenological model, assuming a Langmuir-Hinshelwood mechanism (bimolecular competitive with two types of sites) was able to describe the \( n \)-decane photodegradation. It was observed proposed that both species compete for adsorption within different specific active sites (type 1 and 2) of the catalyst surface. Considering the type of by-products identified, a reaction mechanism for \( n \)-decane photodegradation under the conditions used was proposed.

For all reasons stated before and considering the well-known wide range of paint applications, the results reported seem quite promising for the treatment of indoor and outdoor air. Further research should focus in studying the role of interfering pollutants, as \( \text{NO}_2 \), and also the eventual production of acetaldehyde and formaldehyde as sub-products.
Acknowledgements

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Appendix A. Supplementary Data
References


E. Keidel, Furben Zeitung 34 (1929) 1242.


Table captions

Table 1. Catalyst and paint properties; catalytic bed characteristics; photoreactor dimensions employed in the gas-phase PCO of \(n\)-decane under simulated solar irradiation.

Table 2. Experimental conditions employed in the study of \(n\)-decane photodegradation.

Table 3. Mathematical model, boundary conditions, kinetic reaction rate expressions used for estimation of the kinetic and adsorption equilibrium parameters of the PCO of \(n\)-decane; Estimated kinetic and adsorption equilibrium parameters of the mathematical model.
Figure Captions

Fig. 1. Schematic representation of the experimental set-up and the continuous-flow photoreactor: a) lab-scale unit used for the generation of air streams containing n-decane and water vapour; b) sunlight simulator containing the photoreactor: b1) from a side point of view and b2) from a frontal point of view; c) master gas chromatograph analytic system used for the analysis of the photoreactor feed and exit streams. Reprinted (adapted) with permission from Lopes et al. [58]. Copyright © 2012, Elsevier.

Fig. 2. SEM micrographs (a-d) and EDX spectra (e, f) of PC before (left-side images) and after 50 h+ of use (right-side images) in PCO of n-decane.

Fig. 3. Photographs (a-b) and SEM micrographs (c-d) of PC after 50 h+ of use in PCO of n-decane.

Fig. 4. Influence of feed flow rate ($Q_{\text{feed}}$) on n-decane photodegradation fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$, at steady-state conditions): experimental points for incident irradiances measured within 280-400 nm (sunlight UV fraction) of 38.4 W·m⁻² (◆), 29.1 W·m⁻² (□), and 18.9 W·m⁻² (▲), and RE-1 (- - -), RE-2 (— - —), and RE-3 (——); $C_{\text{dec, feed}} = 73$ ppm, $RH_{\text{feed}}^a = 40\%$, and $T = 298$ K; operation conditions reported in Table 1; * measured at 298 K and 1 bar.

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Fig. 6. Influence of the feed relative humidity ($RH_{\text{feed}}$) on n-decane photodegradation fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$, at steady-state conditions): experimental points for incident
irradiances measured within 280-400 nm (sunlight UV fraction) of 38.4 ( ), 29.1 ( ), and 18.9 W·m⁻² ( ), and RE-1 ( - - - ), RE-2 ( - - - - ), and RE-3 ( — — — — );

$Q_{\text{feed}}^* = 150 \text{ cm}^3\cdot\text{min}^{-1}$, $C_{\text{dec, feed}} = 73 \text{ ppm}$, and $T = 298 \text{ K}$; operation conditions reported in Table 2; * measured at 298 K and 1 bar.

**Fig. 7.** $n$-Decane photodegradation fraction profiles ($C_{\text{dec, exit}}/C_{\text{dec, feed}}$, at steady-state conditions) for photoreactors with different lengths [$L_R$]: 0.16 ( — ), 0.24 ( — — — ), 0.32 ( - - - ), and 0.48 m ( · · · ); (a) $C_{\text{dec, feed}} = 73 \text{ ppm}$, $Q_{\text{feed}}^* = 150 \text{ mL min}^{-1}$, and $I = 18.9 \text{ W m}^{-2}$ (measured within 280-400 nm: sunlight UV fraction); (b) $C_{\text{dec, feed}} = 73 \text{ ppm}$, $Q_{\text{feed}}^* = 300 \text{ mL min}^{-1}$, and $I = 38.4 \text{ W m}^{-2}$ (measured within 280–400 nm: sunlight UV fraction); $RH_{\text{feed}}^* = 30\%$, and $T = 298 \text{ K}$; operation conditions reported in Table 2 (runs 3 and 7, respectively) (* measured at 298 K and 1 bar); experimental data (points); mathematical modelling with RE-3 (lines).
Scheme Captions

Scheme 1. Schematic representation of the reaction pathways proposed for the gas-phase degradation of \textit{n}-decane under simulated solar irradiation (R: alkyl roots or hydrogen).
Table 1
Catalyst and paint properties; catalytic bed characteristics; photoreactor dimensions employed in the gas-phase PCO of \( n \)-decane under simulated solar irradiation.

| Catalyst and Paint [51, 52] | | |
|----------------------------|----------------------------|
| Manufacturer | PC500 (Millennium) |
| Crystal structure | >99% Anatase |
| Crystal size [nm] | 5-10 |
| Shape | Agglomerates |
| Surface area [m\(^2\) g\(^{-1}\)] | 345 |
| Agglomerate size [µm] | 1.2-1.7 |
| Shape | Agglomerates |

| Exterior water-based vinyl paint | | |
|---------------------------------|----------------------------|
| Pigmentary TiO\(_2\) | 18 wt.% (wet basis) |
| Water | 30 wt.% (wet basis) |
| Extenders (CaCO\(_3\) and silicates) | 18 wt.% (wet basis) |
| Polymer extender slurry | 8 wt.% (wet basis) |
| Binder slurry | 20 wt.% (wet basis) |
| Additives (in slurry) | 6 wt.% (wet basis) |

| Catalytic bed (PC) | | |
|--------------------|----------------------------|
| TiO\(_2\) content (wet basis) | | |
| Pigmentary | 9 wt.% (wet basis) |
| PC500 | 9 wt.% (wet basis) |

| Thin-film properties | | |
|----------------------|----------------------------|
| \( m_P \) [g] | 1.052 |
| \( \rho_P \) [g cm\(^{-3}\)] | 2.61 |

| Support (C) | | |
|-------------|----------------------------|
| \( m_C \) [g] | 2.006 |
| \( \rho_C \) [g cm\(^{-3}\)] | 1.30 |
| \( d_{ch} \) [cm] | 0.9 |

| Porosity | \( \varepsilon \) | 0.991 |

| Photoreactor | | |
|-------------|----------------------------|
| Outer tube (Pyrex-glass) | | |
| \( d_{ot,e} \) [cm] | 5.00 |
| \( d_{ot,i} \) [cm] | 4.64 |
| Inner tube (quartz) | | |
| \( d_{in,e} \) [cm] | 2.00 |
| \( d_{in,i} \) [cm] | 1.64 |
| Photoreactor | | |
| \( L_R \) [cm] | 16.0 |
| \( V_R \) [cm\(^3\)] | 220 |
Table 2
Experimental conditions employed in the study of \( n \)-decane photodegradation.

<table>
<thead>
<tr>
<th>Run</th>
<th>( Q_{\text{feed}} ) [^{\text{a}}] [^{\text{b}}] [cm(^3) min(^{-1})]</th>
<th>( C_{\text{dec, feed}} ) [^{\text{c}}] [ppm]</th>
<th>( RH_{\text{feed}} ) [^{\text{d}}] [^{\text{e}}] [%]</th>
<th>( I ) [^{\text{f}}] [^{\text{g}}] [W m(^{-2})]</th>
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<tr>
<td>1(^{\text{a}})</td>
<td>150</td>
<td>73</td>
<td>40</td>
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<td>73</td>
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<td>18.9</td>
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<tr>
<td>18</td>
<td>150</td>
<td>73</td>
<td>3</td>
<td>18.9</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) Measured at 298 K and 1 bar.

\(^{\text{b}}\) Measured within 280–400 nm (sunlight UV fraction).

\(^{\text{c}}\) Operating conditions used for photochemical experiment.
Table 3
Mathematical model, boundary conditions, kinetic reaction rate expressions used for estimation of the kinetic and adsorption equilibrium parameters of the PCO of n-decane; Estimated kinetic and adsorption equilibrium parameters resulting from the mathematical model.

<table>
<thead>
<tr>
<th>Mathematical model, correlations, parameters, and boundary conditions [58, 60]</th>
</tr>
</thead>
</table>
| Material balance for each component $i$:  
\[
\frac{d}{dz} \left( \varepsilon D_{ax} \frac{dC_i}{dz} \right) - \frac{d}{dz} \left( \bar{u}_{0,ch} C_i \right) - v_r = 0
\]  |
| Axial dispersion (laminar flow) [81-84]:  
\[
D_{ax} = D_m + \frac{1}{192} \left( \frac{\varepsilon^2 d_{ch}^2}{\varepsilon D_m} \right)
\]  |
| Molecular diffusivity of the mixture:  
\[
D_m \approx \frac{1}{N} \sum_{i=1}^{N} D_{m,i}, \quad \text{with} \quad D_{m,i} = (1 - y_i) \sum_{j=1}^{n} \frac{D_{g}}{y_i}
\]  |
| Binary diffusion coefficient [85-88]:  
\[
D_g = \frac{1.41 \times 10^{-7} T^{1.75}}{\rho \left( \Sigma _{\varepsilon} \right)^{1.5}}
\]  |
| Superficial velocity (in the cross-section of each channel):  
\[
\bar{u}_{0,\text{ch}} = \frac{Q_{\text{feed}}}{2 \pi \left( \frac{\varepsilon d_{\text{ch}}}{2} \right) \left( \frac{\varepsilon d_{\text{ch}}}{2} \right)^{1/2}}
\]  |

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<tr>
<th>Component $i$</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>$H_2O$</th>
<th>dec</th>
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<tbody>
<tr>
<td>$M_i$ [g·mol⁻¹]</td>
<td>28.01</td>
<td>32.00</td>
<td>18.02</td>
<td>142.28</td>
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<tr>
<td>$\left(\Sigma\varepsilon\right)_i$</td>
<td>18.5</td>
<td>16.3</td>
<td>13.1</td>
<td>209.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Photoreactor feed ($z = 0$)</th>
</tr>
</thead>
</table>
| Boundary conditions:  
\[
\bar{u}_{0,\text{feed}}C_{i,\text{feed}} = \bar{u}_{0,\text{ch}} C_i - \varepsilon D_{ax} \frac{dC_i}{dz} \bigg|_{z=0} = 0
\]  |

<table>
<thead>
<tr>
<th>Kinetic reaction rate expressions [3, 6, 58, 60, 89-95]</th>
</tr>
</thead>
</table>
| RE-1:  
\[
r_{\text{dec}} = I^n \cdot k \left( \frac{K_{\text{dec}} K_{H_2O} C_{\text{dec}} C_{H_2O}}{1 + K_{\text{dec}} K_{H_2O} C_{\text{dec}} C_{H_2O}} \right)
\]  |
| Langmuir-Hinshelwood bimolecular competitive one type of sites |
| RE-2:  
\[
r_{\text{dec}} = I^n \cdot k \left( \frac{K_{\text{dec}} C_{\text{dec}}}{1 + K_{\text{dec}} C_{\text{dec}}} \right) \left( \frac{K_{H_2O} C_{H_2O}}{1 + K_{H_2O} C_{H_2O}} \right)
\]  |
| Langmuir-Hinshelwood bimolecular non-competitive two types of sites |
| RE-3:  
\[
r_{\text{dec}} = I^n \cdot k \left( \frac{K_{\text{dec}} C_{\text{dec}}}{1 + K_{\text{dec}} C_{\text{dec}} + K_{H_2O} C_{H_2O}} \right) \left( \frac{K'_{H_2O} C_{H_2O}}{1 + K'_{\text{dec}} C_{\text{dec}} + K'_{H_2O} C_{H_2O}} \right)
\]  |
| Langmuir-Hinshelwood bimolecular competitive two types of sites |

<table>
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<th>Estimated parameters</th>
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<tr>
<td>Kinetic reaction rate expressions</td>
</tr>
<tr>
<td>$n$</td>
</tr>
<tr>
<td>$k$ [mol m⁻² s⁻¹ (W⁻¹ m²³)]</td>
</tr>
<tr>
<td>$K_{\text{dec}}$ [M⁻¹]</td>
</tr>
<tr>
<td>$K_{H_2O}$ [M⁻¹]</td>
</tr>
<tr>
<td>$K'_{\text{dec}}$ [M⁻¹]</td>
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<td>$K'_{H_2O}$ [M⁻¹]</td>
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<td>Statistics</td>
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<tr>
<td>$S^2_R \times 10^7$ [mol² m⁴ s⁻²]</td>
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</table>
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