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Photocatalytic removal of monoterpenes in the gas phase. Activity and regeneration

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We show the photocatalytic removal of various monoterpenes such as β-pinene, α-pinene, camphene and limonene in the gas phase as a function of the reaction temperature, from room temperature to 80 °C, taking also into account the thermal catalytic isomerization occurring on TiO_2 surfaces. The *on-stream* behaviour showed an initial plateau with total monoterpene removal followed by a progressive deactivation, associated to the surface poisoning by partially oxidized intermediates. Effective regenerative treatment could be performed under UV-A illumination with an oxidative humid air flow, for oxidizing the detrimental organic reaction intermediates into CO_2. Deactivation phenomena were studied as well as the optimization of regeneration treatments, both depending on the surface density of the TiO_2 coating, and we proposed that non-illuminated TiO_2 layers could be involved for explaining the interesting activity/deactivation behaviour pattern observed. We tried to evidence that reaction–regeneration cycles could be put forward to hold a continuous high efficiency monoterpene removal.

1. Introduction

More than 22,000 individual terpenoids are known at present, making them the largest group of natural products. Monoterpenes in plants are known to have mainly ecological roles, by acting as deterrents against feeding by herbivores, as antifungal defenses and as attractants for pollinators.[1] Terpenes can also act in the prevention and the therapy of several diseases including cancer, as natural insecticides and antimicrobial agents, as sprouting inhibitor during agricultural produce storage and as building blocks for the synthesis of many high value compounds.[2] Terpene hydrocarbons are also the main component of natural resins. In addition, terpenes such as limonene are essential for the industrial production of thin films such as plasma TV and remain strategic molecules for device production.

However, in parallel to the above-mentioned positive influence of terpenes, terpenes negatively impact on many industrial fields using wood as a raw material, and eliminating terpenes takes on importance within such fields. This restriction results from the necessary control of irritant and odorous gas releases such as that of terpenes, and from environmental policy, with the actual and forthcoming environmental regulation towards industrial effluent releases. The regulation of Volatile Organic Compounds (VOCs, including the terpenoid class) emitted by industrial processes has indeed created a strong incentive for research in this area in the last few decades inside both industrial and academic communities involved in innovative sustainable environmental research.

Up to now, mainly liquid phase isomerization[3–5] and polymerization[6] processes have been reviewed for catalytically transforming pinene. Few papers concern the use of immobilised porphyrins as photosensitizers to promote singlet oxygen oxidation of mono-terpenes,[7] the use of ZnO or sensitizers for the photochemical hydroperoxidation of terpenes,[8] the photocatalytic oxygenation of α-pinene using tetraphenyl-porphinatomolybdenum and niobium complexes and molecular oxygen for forming pinene epoxide and oxygenated products.[9] The disappearance of α-pinene through an air purification photocatalytic system has been briefly mentioned by Kudo *et al.* within polluted indoor air containing 26 different VOCs,[10] whereas Salthammer and Furmann,[11] and Hodgson *et al.*[12] investigated, targeting some terpenoids among many VOCs, the cleaning of indoor air resulting from the use of photocatalytic wall paints and of a UV-A driven photocatalytic oxidation device, respectively. Over the past two decades, the gas-phase terpene oxidation reactions have been exclusively limited to non-catalytic tropospheric reactions involving reactive species present in the troposphere, like ozone (O_3), hydroxyl (OH) and nitrate (NO_3) radicals. Other studies have focused on the quantification of the aerosol formed during the simulated atmospheric oxidation of terpenes.[13,14]

Within the Advanced Oxidation Processes developed to meet the ever stricter anti-pollution legislation required by the environmental protection pressure, photocatalytic oxidation is very promising for purifying contaminated wastewater containing organic pollutants and removing contaminants as well as irritant and odorous gas from air.[15–17] Photocatalysis is advantageous because the energy required is supplied by the direct absorption of light at room temperature, which thus requires the use of semiconductor materials with adequate band gaps as photocatalysts. Amongst the used semiconductors, titanium dioxide (TiO_2) is up to now the most attractive and efficient one, due to a high photocatalytic efficiency, its stability towards photocorrosion

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and chemicals, its insolubility in water, a low toxicity and low costs. Its band gap energy of 3.2 eV leads to photoexcitation requiring wavelengths less than *ca.* 385 nm corresponding to a near UV illumination.

This article reports on the use of UV-A photocatalysis for degrading β-pinene and its isomers α-pinene, camphene and limonene. It evidences the possible setting of a continuous high efficiency monoterpene removal process by designing an optimized reaction/regeneration cycle procedure.

2. Experimental

2.1. Experimental set-up and procedures

The TiO$_2$ photocatalyst was commercially available Hombikat UV100 (Sachtleben), named UV100. It had a non- microporous BET specific surface area of 309 m^2/g.

The photocatalytic activity measurements were carried out in an annular Pyrex reactor (300 mm length and 35 mm internal diameter), made of two coaxial tubes 4 mm apart, between which the reactant mixture was passing through. Details concerning both photocatalytic reactor and set-up can be found elsewhere.[18] The TiO$_2$ photocatalyst was evenly coated on the internal side of the external tube of the coaxial reactor by evaporating to dryness an aqueous slurry of TiO$_2$ and the coated reactor was further dried at 110 °C for 1 h in air. The annular reactor was thus classically working *on-stream* in a seep mode, with a direct illumination from the inner central lamp radially illuminating the photocatalytic coating. β-Pinene (Aldrich, > 99.5%) and water were fed at ambient temperature and atmospheric pressure by bubbling air through two saturators respectively, and mixed with additional air to obtain the required pinene–water–air ratios with a constant total air flow of 200 cm^3/min. The relative humidity was set at 50%, whereas the pinene content was set at 200 ppm, corresponding to 1.22 g/m^3 of pinene per m^3 of flowing air. This high and unusual value for photocatalysis for carrying out the experiments resulted from *on-line* and *on-site* measurements performed at the outlet of an air effluent containing terpenes within a paper-maker factory. The surface density of the TiO$_2$ coating corresponds to the amount of TiO$_2$ deposited per cm^2 of glass reactor wall.

A cylindrical furnace surrounding the photoreactor 1 mm apart was used for performing the photocatalytic tests at temperatures up to 80 °C. Two procedures described in a further section were investigated using or not a pre-adsorption step prior to switching on the UV-A illumination. UV-A illumination was provided by commercial 8 W (for test), and 8 W or 15 W (for regeneration) black light tubes with a spectral peak centred around 380 nm, and located inside the inner tube of the reactor.

The reaction products were analyzed *on-line* on a micro-gas chromatography (M200H, HP) equipped with thermal conductivity detectors, and coupled when necessary to mass spectrometry. Pure β-pinene, α-pinene, camphene and limonene were used for calibration.

The regeneration phases were performed at 80 °C for a duration ranging from 2 h to 12 h under 8 W or 15 W UV-A illumination using humid air as oxidative flow at 200 cm^3/min, *i.e.* in fully similar conditions than those of the tests, except the absence of any β-pinene flow.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was carried out with a Bruker IFS-66.

3. Results and discussion

3.1. Thermal catalytic activity

The catalytic isomerization of the β-pinene reactant is observed in the dark on UV100 TiO$_2$ powder, with the formation of α-pinene, camphene and limonene at 60 °C and 80 °C, as represented in Scheme 1 (Fig. 1). Thermal isomerization reactions did not occur at room temperature, whereas the β-pinene/α-pinene/camphene/limonene ratio was depending on the temperature. This seems to be related to the surface acidity of the oxide,[4] since basic MgO did not show any isomerization, whereas we observed it at different extents over γ-Al$_2$O$_3$ and SiO$_2$ (not reported). Indeed, the selectivity of the terpene isomerization is known to vary with the catalyst acid strength, with weak acids favouring the formation of polycyclic camphene, and stronger acids resulting in monocyclic products such as limonene.[19,20] The rearrangement of α-pinene is indeed selected to probe the effect of acid strength on catalytic performances.[17] It is known that the isomerization of β-pinene into α-pinene occurs through thermally-activated acid/base solid catalysis. The acid-catalysed rearrangement of α-pinene proceeds *via* two parallel pathways, one by ring expansion giving rise to polycyclic products such as camphene, and another yielding monocyclic
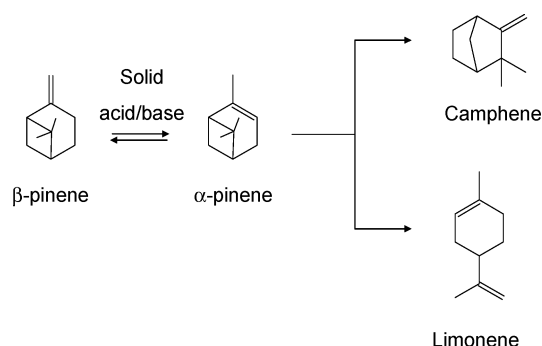
Scheme 1 The most common isomers formed starting from β-pinene, adapted from ref. 4 evidencing both monocyclic and polycyclic pathways.
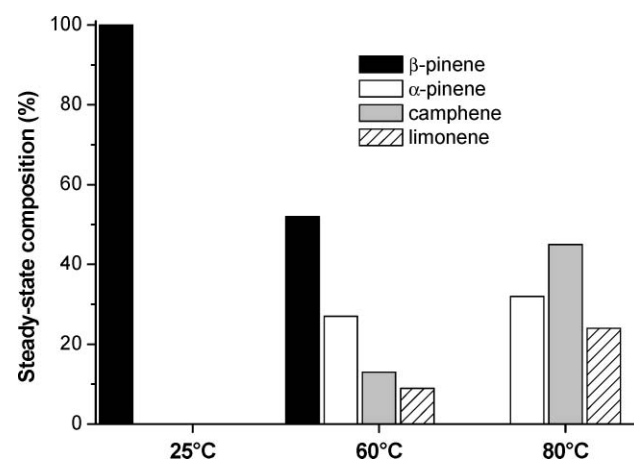

Fig. 1 Distribution at steady-state of the isomers obtained from β-pinene on the UV100 TiO$_2$ samples at 25 °C, 60 °C and 80 °C.

products such as limonene.[4,6,20–22] It should be mentioned that at 60 °C–80 °C, the carbon balance was closed by the different isomerization products.

At high temperature, thermal catalytic isomerization thus happens together with the UV-A photocatalytic reaction, with formation of α-pinene, camphene and limonene isomers. As a result, the observed removal performances are further expressed in terms of (total) terpene removal and not of β-pinene removal. Therefore, a terpene removal efficiency of 100% means that 100% of the terpene reactants (including the different isomers formed) have been removed. It was important to note that independently to the reactor temperature, the inlet total terpene concentration was 200 ppm. At room temperature, the terpene removal corresponded to the β-pinene removal due to the absence of any thermal reactions over TiO_2.

3.2. Photocatalytic oxidation/deactivation/regeneration

The photocatalytic behaviour shown by the commercially available UV100 TiO_2 was studied from room temperature up to 80 °C. The influence of the catalyst surface coverage, *i.e.* the TiO_2 surface density, on the pinene removal and on the *on-stream* deactivation was only investigated at a temperature of 80 °C, because it appeared that increasing the reaction temperature was beneficial to the terpene removal efficiency. In addition to that, it must be noted that from an industrial application point of view, for which the removal of pinenes and most generally of terpenes from post-process tail-gas effluents is targeted (such as factories using wood as raw material), the temperature of such tail-gas effluents containing those VOC pollutants is usually close to 80 °C, as measured by *on-site* analysis. A reaction/regeneration cyclic procedure has also been optimized in order to maintain a total removal efficiency over a long period.

The temperature of the reactor was first increased to 80 °C before two different testing procedures were applied, consisting of : (i) a first dark adsorption step followed by the photocatalytic step when switching on the UV-A lamp and (ii) the direct photocatalytic step without waiting for any adsorption/desorption dark equilibrium. It could be noted that within the whole reaction temperature range, no photolysis phenomena occurred under UV-A illumination for both photocatalytic test procedures.

3.2.1 Using a first dark adsorption step of β-pinene followed by photooxidation.

Activity. As shown in the previous sub-section, mainly thermal isomerization reactions occurred in the dark, with the main formation of α-pinene, limonene and camphene. Thus, proceeding with a first dark adsorption of β-pinene molecules at 60 °C and 80 °C (until reaching the adsorption equilibrium), led to performing the photocatalytic removal of a mixture of terpenes, instead of that of pure β-pinene, with an inlet flow containing a mixture of β-pinene, α-pinene, camphene and limonene terpenes rather than pure β-pinene. It should be noted that removing a mixture of terpenes was in agreement with the problematic of some industrial fields, such as those using wood as raw material, which are concerned with polluted effluents containing terpene mixtures and not only β-pinene. As a result, the observed removal performances were expressed in term of (total) terpene removal and not of β-pinene removal. At room

temperature, the terpene removal corresponds to the β-pinene removal due to the absence of any thermal reactions over TiO_2.

The TiO_2 photocatalyst—independently of the reaction temperature and the testing procedure—displayed firstly a period with a total terpene removal, *i.e.* a 100% removal efficiency with no terpene release, before *on-stream* deactivation occurred. Therefore, the initial period during which 100% of terpene removal was observed (characterized by the Duration of Complete Terpene Removal, DCTP, and expressed in minutes) was an important parameter to take into account. Fig. 2 shows the DCTP as a function of the reaction temperature on the commercial UV100 TiO_2 photocatalyst, obtained with a first dark adsorption period and with a reactor surface coverage of 1.2 mg/cm^2. The catalyst showed a DCTP of 40 min at 25 °C, whereas the DCTP increased to reach durations longer than 100–110 min at 60–80 °C. This was in agreement with the usual optimal operating range of photocatalysis, reported to be 20–80 °C with a slight increase in the photoactivity with the temperature within this range, due to the very small apparent activation energy in this medium range.[23] Since the terpene containing tail-gas effluents released in some industrial applications are generally at temperatures close to 80 °C, further investigations have been performed at this temperature. CO_2 was the sole reaction product detected in the outlet stream, no gaseous intermediate by-products being observed, thus indicating that partially oxidized by-products remained adsorbed at the TiO_2 surface, as shown later by DRIFT.
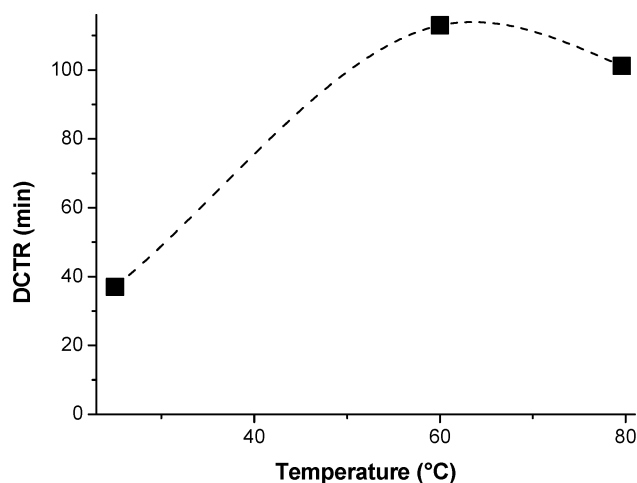

Fig. 2 DCTR (in minutes) as a function of the reaction temperature on UV100 TiO_2 at 1.2 mg/cm^2 surface coverage, with a prior dark adsorption period, and an 8 W UV-A light.

The influence of the TiO_2 surface density on the *on-stream* terpene removal is reported in Fig. 3. It could be observed that increasing the reactor surface coverage from 0.6 to 1.2 mg/cm^2 led to extending from 50 min to 100 min, the initial period during which complete terpene removal was observed, whereas this duration remained at about 100 min when increasing the TiO_2 loading further up to 14.3 mg/cm^2. This led to estimating the VOC conversion before deactivation occurred at 50 mg$_{terpenes}$/g$_{TiO2}$, 48 mg$_{terpenes}$/g$_{TiO2}$, 23 mg$_{terpenes}$/g$_{TiO2}$, 14 mg$_{terpenes}$/g$_{TiO2}$ and 4 mg$_{terpenes}$/g$_{TiO2}$ for TiO_2 loadings of 0.6 mg/cm^2, 1.2 mg/cm^2, 2.4 mg/cm^2, 4.7 mg/cm^2 and
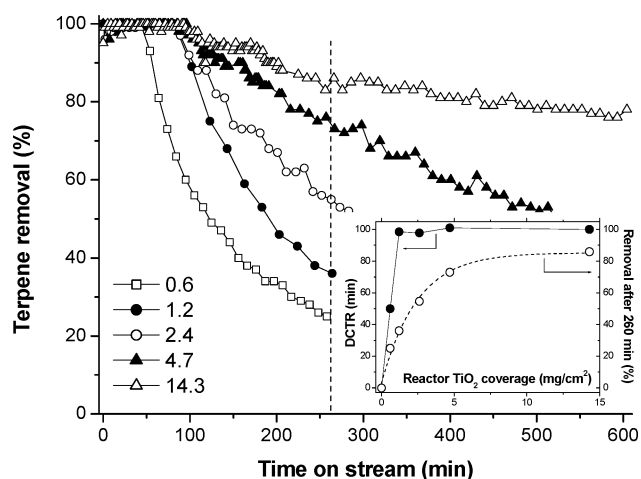
Fig. 3 Terpene removal with time on stream at 80 °C as a function of the TiO$_2$ reactor surface coverage in mg/cm^2, on UV100 TiO$_2$, with prior dark adsorption period. Inset : DCTR (min) and removal efficiency at 260 min, as a function of the reactor TiO$_2$ coverage in mg/cm^2.

14.3 mg/cm^2 respectively. Indeed, it is known that the photocatalytic activity first linearly increases with the surface covering ratio, due to the increase in the amount of TiO$_2$ in which all the particles, *i.e.* all the surfaces exposed—are totally illuminated.[23] For higher amounts of catalyst, a screening effect of excess particles occurs, which masks part of the photosensitive semiconductor surface, due to the limited penetration thickness of UV-A illumination. The value obtained, 1.2 mg/cm^2, in agreement with that reported by Herrmann, was found equal to 1.3 mg TiO$_2$/cm^2 for a fixed bed. However, whereas the DCTR remained around 100 min, increasing the TiO$_2$ surface density up to 14.3 mg/cm^2 allowed the catalyst deactivation to be strongly slowed down, the system loaded at 14.3 mg/cm^2 maintaining a terpene removal of 84% and 80% after 260 min and 600 min on stream respectively. By contrast, a lower surface density resulted in a quicker deactivation, a 1.2 mg/cm^2 coverage leading to a terpene removal around 35% after 260 min on stream.

This unusual behaviour led to putting forward the involvement of non-illuminated TiO$_2$ semi-conductor particles. As the thickness of the TiO$_2$ coatings used in this study was strongly larger than the UV-A penetration thickness, we assumed that non-illuminated TiO$_2$ particles could participate in the overall process. It was proposed that they could allow a possible storage of poisoning reaction intermediates at the surface of non-illuminated TiO$_2$ particles, and/or that they could artificially increase the residence time within the TiO$_2$ coating, thus increasing the contact probability with photocatalytic sites.

Deactivation/regeneration. Using a 1.2 mg/cm^2 surface coverage (considered as the reference coverage), continuous deactivation of the photocatalyst occurred till reaching a near-zero activity after 12 h on stream under UV-A illumination. Fig. 4A shows the influence on the photocatalyst efficiency, of the regeneration duration after complete deactivation. Recovering of the catalyst efficiency, *i.e.* recovery of an initial 100% terpene removal, could be obtained by performing a 8 W UV-A oxidative regeneration for 12 h under a 50% relative humidity air stream at 80 °C in the absence of any terpene reactant. Shorter regeneration periods led to the partial recovery of the terpene
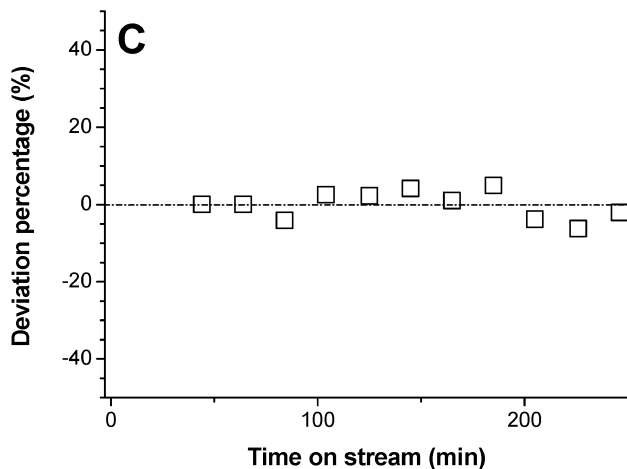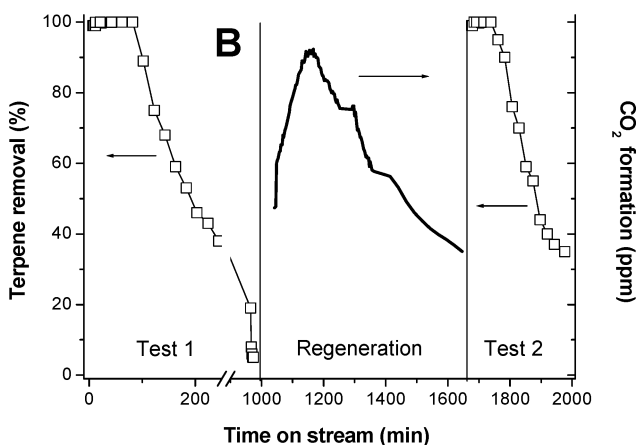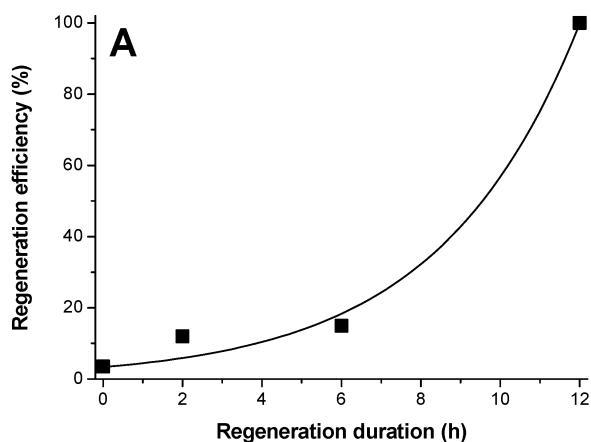

Fig. 4 (A) Regeneration efficiency (in %) as a function of the duration of the 8 W UV-A regeneration at 80 °C performed after complete deactivation of the catalyst (12 h of test). (B) Cycles of alternative photocatalysis and regeneration steps : test #1 with complete deactivation being obtained after 12 h of test, followed by a 8W-UVA regeneration at 80 °C for 12 h, and finally test #2 performed in similar conditions to test #1. (C) Deviation percentage between tests #1 and #2, evidencing the efficiency of the regenerative treatment. This deviation percentage corresponds to the difference in efficiency between both fresh and regenerated photocatalysts relatively to the efficiency of the first test.
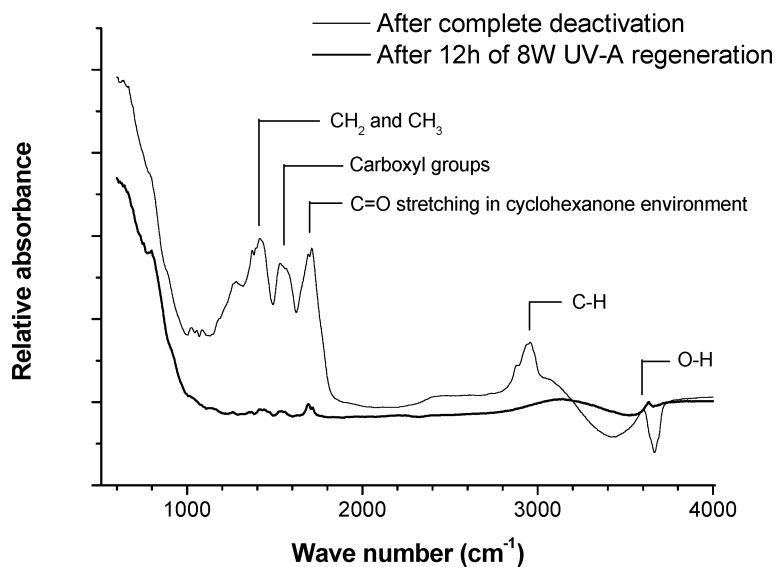
Fig. 5 DRIFT analyses of the TiO$_2$ photocatalyst after complete deactivation (overnight test) and after 12 h of 8 W UV-A regeneration.

removal efficiency, with regeneration efficiencies lower than 15% for regeneration durations shorter than 6 h. Regeneration conditions in terms of temperature, relative humidity and flow rate, were similar to those of the reaction step, in order to facilitate an efficient alternative switching between both test and regeneration periods. The recovery of the initial activity with a similar *on-stream* behaviour was confirmed by looking at Fig. 4A to 4C. No difference could be observed comparing the efficiency obtained on both fresh and regenerated photocatalysts. Indeed, by defining the deviation percentage as the difference in efficiency between both photocatalysts relatively to the efficiency of the initial test, this deviation percentage remained within a ±5% relative range as a function of time on stream (Fig. 4C). Poisoning of the photocatalyst surface by reaction intermediates was reversible, as observed by comparing DRIFT analyses performed after complete deactivation of the catalyst (*i.e.* after 12 h of test) and after a regeneration procedure of 12 h (Fig. 5). These reaction intermediates resulting from a partial oxidation process and acting as surface poisons have mainly been identified as carbonyls, carboxylic acids and cyclic ketones. Investigating the different products issued from the oxidation of a series of terpenes with atmospheric constituents, Calogirou *et al.* have observed pina ketone (6,6-dimethyl-bycyclo[3.1.1]heptan-2-one), pinon aldehyde (*cis*-3-acetyl-2,2-dimethyl-cyclo-butyl-ethanal) and limona ketone (4-acetyl-1-methylcyclohexene) as the main reaction products resulting respectively from β-pinene/OH, α-pinene/OH and limonene/OH oxidation.[24] The oxidative regeneration treatment with humid air and under UV-A illumination led to the photooxidation of the partially oxidized intermediates blocking the active sites of the TiO$_2$ surface, together with the corresponding formation of CO$_2$ (Fig. 4B). It should be noted that performing the photocatalytic tests and regenerating the deactivated TiO$_2$ did not result in any changes in the structural properties of the photocatalysts.

As the aim of the photooxidation of pinenes for industrial purposes is to maintain the longest duration at complete (100%) removal efficiency, the regeneration treatment has to be performed directly at the terpene breakthrough, *i.e.* after 120 min of time on stream, when the terpene removal decreased with time on stream. The cyclic procedure alternating a 100% removal efficiency step and a consecutive regeneration treatment is reported in Fig. 6, with the reactor working at the reference covering ratio (1.2 mg/cm^2). For this purpose and in order to shorten and optimize the regeneration duration, 8 W and 15 W-UVA regeneration procedures have been performed and compared, directly after 120 min of photocatalytic tests, corresponding to the beginning of the photocatalyst deactivation after total terpene removal.

It could be observed that increasing the UV-A lamp power from 8 to 15 W (Fig. 6A) yielded a more efficient regeneration procedure, because it allowed the full recovering of the terpene removal efficiency. However, 2 h of 15 W UV-A regeneration led to recover this total activity only for a few minutes, whereas increasing the regeneration duration to 3 h and 4 h resulted in maintaining this high efficiency for at least 60 minutes. Nevertheless, this procedure consisting of 120 minutes activity and 4 h 15 W UV-A regeneration is not valid for setting up activity/regeneration cycles using two photoreactors working alternatively for removing pinene and regenerating the photocatalyst: for this purpose, the regeneration duration should be similar to the duration at complete terpene removal. Targeting a high efficiency and continuous terpene elimination process would thus imply the use of three reactors with a 1/3 removal and 2/3 regeneration work-duration for each of them, the electrical power change being usually obtained by varying the lamp power input.

3.2.2. Direct photocatalytic experiment without any dark adsorption step.

Activity. In the absence of any dark pre-adsorption period, the reactant mixture was exclusively composed of β-pinene. The tests were performed at a temperature of 80 °C, under similar reaction conditions than when a first dark pre-adsorption period was observed (Fig. 7). At a 1.2 mg/cm^2 surface coverage, performing or not a dark adsorption step had no influence on
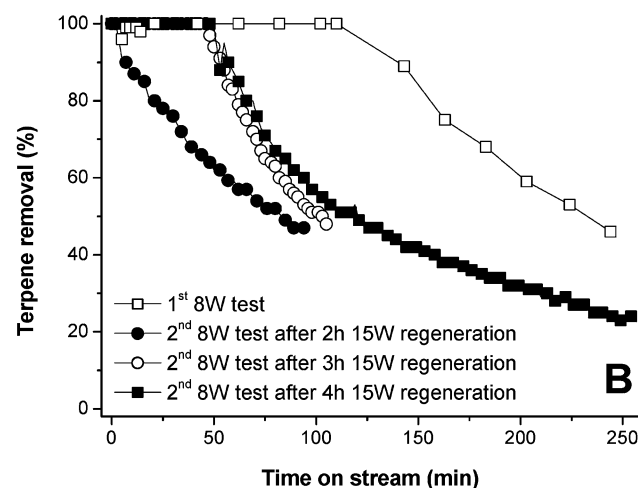
Fig. 7 Terpene removal with time on stream at 80 °C as a function of the TiO_2 reactor surface coverage in mg/cm^2, on UV100 TiO_2 without any prior dark adsorption. Inset: DCTR (in min) as a function of the reactor TiO_2 coverage in mg/cm^2.

This led to estimate the VOC conversion before deactivation, at 48 $mg_{terpenes}/g_{TiO2}$, 52 $mg_{terpenes}/g_{TiO2}$, 40 $mg_{terpenes}/g_{TiO2}$ and 26 $mg_{terpenes}/g_{TiO2}$ for TiO_2 loadings of 1.2 mg/cm^2, 2.4 mg/cm^2, 4.7 mg/cm^2 and 14.3 mg/cm^2 respectively.

Compared to what was observed with a dark pre-adsorption period, similar surface functionalities were observed by DRIFT analyses on the used TiO_2 surface and selectivity into CO_2 close to 20% was obtained. Again, complete deactivation occurred for longer duration tests, although the duration necessary to reach a near-zero activity corresponding to a full deactivation of the catalyst, was strongly lengthened by increasing the TiO_2 amount. As previously suggested, the large amount of TiO_2 involved in the reactor wall coating and thus the too large thickness of the TiO_2 coating compared to the UV-A penetration depth, led to the consideration that the main part of the TiO_2 particles remained non-illuminated. The involvement of non-illuminated TiO_2 particles, located behind the UVA penetration depth, could also be put forward for possibly explaining such a great increase in efficiency with the increase in the TiO_2 coating depth. Further investigations are being conducted to provide more evidence on this point.

Deactivation/regeneration. Since the H_2O/air regenerative treatment was more efficient using a 15 W illumination rather than an 8 W one (Fig. 6), the regeneration treatment has been performed in a similar way to the previous section, but with a 15 W UV-A light. Fig. 8 shows the efficiency of this regenerative treatment over a fully deactivated photocatalyst obtained after an 8 W test using a 14.3 mg/cm^2 reactor coverage. An *on-stream* regeneration of 2 h led to recover an initial terpene removal close to 80% before deactivation, whereas a regeneration of 6 h allowed a complete terpene removal to be recovered for 6 h, and a regeneration of 12 h led to recover the full activity of the photocatalyst, with a similar duration for the initial 100% removal efficiency period for both fresh and regenerated photocatalyst, *i.e.* a DCTR of 9 h.

The increase in the reactor surface coverage resulted in a considerable increase in complete β-pinene elimination duration, and therefore the influence of this surface coverage on the
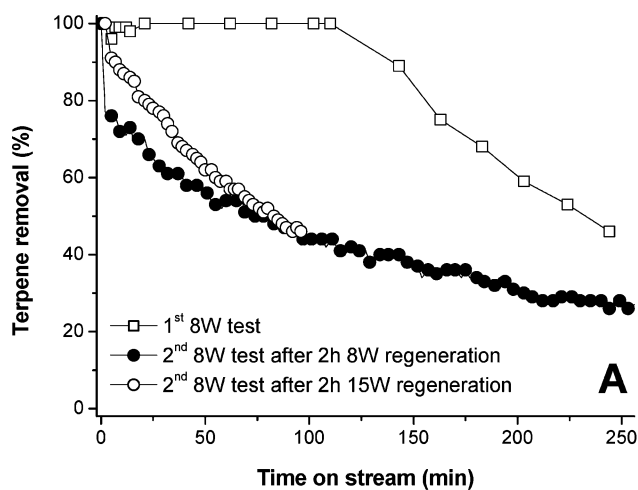

Fig. 6 (A) Influence of the light power during the 2 h UV-A regeneration. (B) Influence of the duration of the 15 W UV-A regeneration. In all cases, the regeneration treatments were started after the total terpene removal period (around 120 min).

the duration of the initial 100% pinene removal plateau, with a similar *on-flow* behaviour being observed, *i.e.* a DCTR of 120 min followed by a similar deactivation step. The similar results obtained at the 1.2 mg/cm^2 surface coverage reference, with and without a dark pre-adsorption period, confirmed that the pinene removal did not occur just by physical adsorption, in agreement to the low *on-stream* adsorption capacity shown by TiO_2 towards pinenes. By contrast, increasing the TiO_2 surface coverage from 1.2 to 14.3 mg/cm^2 yielded a considerable increase in the duration of complete β-pinene removal. Indeed, the duration of the initial 100% removal plateau reached 5 h and 9 h when increasing the surface coverage to 4.7 mg/cm^2 and 14.3 mg/cm^2 respectively, before deactivation occurred. The longer DCTR obtained without any dark adsorption period, *i.e.* with no pre-isomerization of the β-pinene, could be attributed by assuming a higher photocatalytic reactivity of the inlet β-pinene molecule compared to that of the isomers such as limonene, camphene and α-pinene formed on the non-illuminated particles.
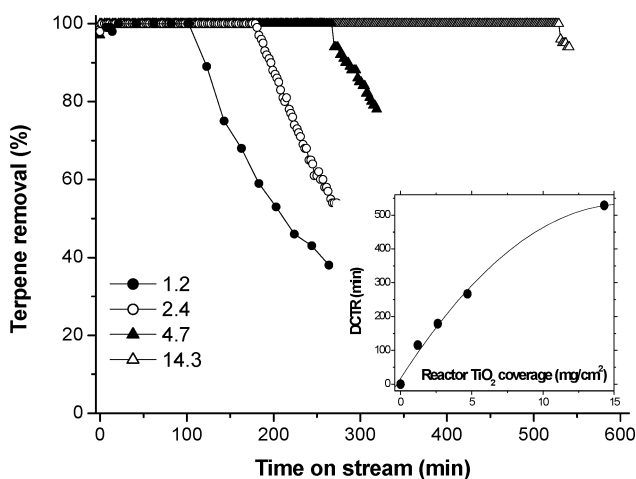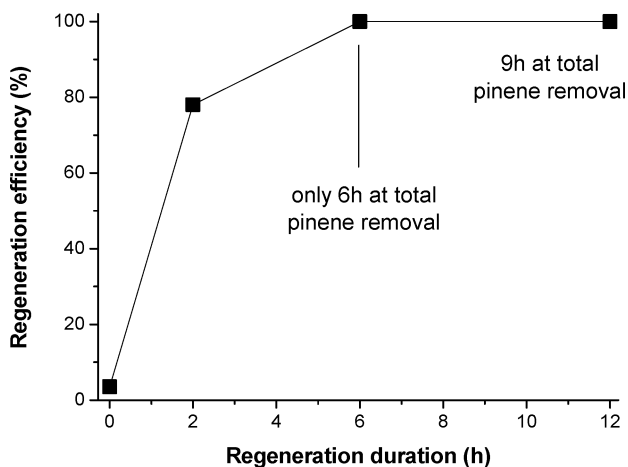
Fig. 8 Regeneration efficiency (in %) as a function of the duration of the 15 W UV-A regeneration at 80 °C performed after the complete deactivation of the photocatalyst during an 8 W test with a coverage of 14.3 mg/cm².

regeneration procedure efficiency was studied. Only 15 W regeneration procedures were investigated as it has been shown previously that they are most efficient than 8 W UV-A regenerations. Fig. 9 shows the influence of the TiO_2 coverage on the efficiency of the regenerative treatments for similar alternative testing/regeneration durations. The 15 W UV-A regeneration treatments were performed on used catalysts at the beginning of the deactivation breakdown, *i.e.* when the catalyst did not show a total terpene removal under 8 W UV-A illumination (at 3 h, 5 h and 9 h for the 2.4 mg/cm², 4.7 mg/cm² and 14.3 mg/cm² reactor coverage respectively). In order to investigate the possibility of designing an alternative activity/regeneration cyclic process, the regeneration treatments were performed for durations similar to
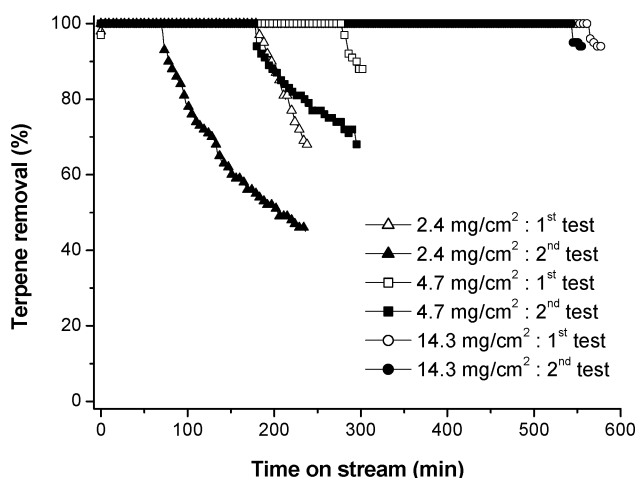

Fig. 9 Influence of the TiO_2 reactor coverage on the efficiency of the 15 W UV-A regenerative treatments, performed after 8 W UV-A photocatalytic tests. Targeting the design of an alternative removal/regeneration procedure, the regeneration treatement was started exactly when the catalyst did not show a total terpene removal (after 3 h, 5 h and 9 h of testing for a reactor coverage of 2.4 mg/cm², 4.7 mg/cm² and 14.3 mg/cm² respectively). The 15 W UV-A regeneration was then carried out for similar durations, *i.e.* 3 h, 5 h and 9 h for a reactor coverage of 2.4 mg/cm², 4.7 mg/cm² and 14.3 mg/cm² respectively) and the 2nd 8 W UV-A photocatalytic test was further performed.

those of the corresponding photocatalytic removal tests. It was worth noting that performing the 15 W regeneration for a similar duration than that of the total removal plateau shown by the first test, did not allow the full activity to be recovered, independently of the TiO_2 coverage. Indeed, the duration of the complete pinene removal plateau obtained over the UV-A regenerated catalyst was shortened compared to that obtained over the fresh catalytic coating. However, the observed shortening was less pronounced when increasing the TiO_2 surface coverage from 2.4 mg/cm² to 14.3 mg/cm² coating, and thus increasing the depth of the TiO_2 coating. This was in agreement with the involvement of non-illuminated TiO_2 particles within the overall process, even if they could not be directly involved in the photocatalytic reactions. More characterization details on both used and regenerated photocatalyst will be presented elsewhere to provide more insight on the involvement of non-illuminated TiO_2 particles.

It should be noted that working with a surface coverage of 14.3 mg/cm² in a usual annular seep-flow photoreactor resulted in the low mechanical stability shown by the TiO_2 coatings inside the reactor, obviously not appropriate to design useful photoreactors. Therefore, there is the need for developing new photocatalytic substrates and/or new anchorage processes to further improve the mechanical stability of TiO_2 coatings at high loading.[25]

4. Conclusion

This article reports on the first use of UV-A photocatalysis for removing terpenes from flowing air at temperatures ranging from 20 °C to 80 °C. Performing the photocatalytic tests at elevated temperatures required taking into account the thermal catalytic isomerization occurring on TiO_2 surfaces. The *on-stream* behaviour showed an initial plateau with total terpene removal, followed by a progressive deactivation, associated to the surface poisoning by partially oxidized intermediates. Effective UV-A mediated oxidative regenerative treatment was performed through humid air flow, with the photooxidation of the reaction intermediate organic poisons and the corresponding formation of CO_2. We tried to evidence that reaction/regeneration cycles could be put forward to hold a continuous high efficiency pinene removal. The use of thick TiO_2 coating obtained by increasing the TiO_2 surface density from usual values (close to 1 mg/cm²) up to 14.3 mg/cm² resulted in an unexpected *on-flow* removal behaviour, notably by strongly limiting the *on-stream* deactivation. Depending on the way of testing, terpene removal before deactivation occurred was evaluated up to 52 mg of terpenes per g of TiO_2. Due to the very high terpene concentration in the inlet flow, at a gram scale per m³ of air, this weight percentage could not reach high values. The involvement in the terpene removal process, of non-illuminated TiO_2 particles located deep inside the TiO_2 coating has been advanced in order to explain both the large increase in the terpene removal efficiency and the reduced deactivation when increasing the thickness of the TiO_2 coating highly above the usual UV-A penetration depth. Further investigations are ongoing to explain in more detail the observed behaviour linked with the role of non-illuminated TiO_2 particles and the impact of the thermal isomerization, for alternatively pointing out the possible

dependence of the photocatalytic activity with the nature of the terpene isomers. However, using so large TiO$_2$ amounts led to seep-flow annular reactors with low mechanical stability, and therefore the design of new substrates and/or the use of new physico-chemical anchorage methods will be required for improving the mechanical stability of the TiO$_2$ coating.

Acknowledgements

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