

TiO₂ photocatalysis for the abatement of ubiquitous indoor pollutants: study of the simultaneous degradation of aldehydes

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ABSTRACT

In industrialized countries, people spend more than 20 hours a day indoors, being constantly exposed to several pollutants. Among the various pollutant molecules found in closed environments, aldehydes are the most prevalent and, specific attention is given to formaldehyde as a carcinogenic compound and as a ubiquitous substance, because of the large number of sources from which it is released. Photocatalysis was studied here in particular for the reduction of indoor air contaminants; specifically, we investigated the performances of three commercial powdered TiO₂, two nano-sized and one micro-sized, for the photodegradation of formaldehyde alone, and in a gaseous mixture of aldehydes, taking into consideration the most recent studies of indoor pollutants. The first purpose of this study was to prove the effectiveness of TiO₂ on formaldehyde, even when its particles are micro-sized; secondly, the study was directed to the photodegradation reactions of many aldehydes, with specific attention to the fact that they were degraded simultaneously, in a context much closer to reality, but still poorly studied. For this reason photodegradation was monitored by PTR-ToF-MS (Proton Transfer Reaction-Time of Flight-Mass Spectrometer), which is able to detect

several molecules without any difficulty or interference.

KEYWORDS: indoor air quality, organic pollutants, TiO₂ photocatalysis, simultaneous monitoring of organics, TiO₂ particles size, formaldehyde

INTRODUCTION

Contrary to what is generally assumed, air in several indoor environments is often more polluted than outdoor air. This is because of the many sources of indoor pollution, which include mold and pollen, tobacco smoke, household products and pesticides, and materials usually used in buildings such as formaldehyde and organic compounds in general [1]. Health effects from indoor air pollutants generally occur after long or repeated periods of exposure and they can be severely debilitating or fatal. There is still uncertainty about the level of concentrations that can produce specific health problems but it is accepted that even low concentrations of some pollutants that are ubiquitous can be very dangerous [2].

Volatile organic compounds (VOCs) include a variety of chemicals, which are often up to ten times higher indoors than outdoors, because they are released by a wide array of products of common use. Formaldehyde is one of the major ubiquitous pollutants [3]. Even if in small amounts, we are

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often exposed to formaldehyde that has off-gassed from composite wood products usually used in buildings, resins, disinfectants and fixatives, or in several common products in which it is used as a preservative [4]. Formaldehyde is very dangerous for human health, in particular after long exposure. IARC (International Agency for Research on Cancer) has classified formaldehyde as a human carcinogen (Group 1) [5]. The TLV (Threshold Limit Value) of formaldehyde is 0.1 mg/m^3 , equivalent to 80 ppb [5, 6, 7]. However, during the past few years formaldehyde levels have sharply increased in polluted urban areas and have reached the same dangerous levels both outdoor and indoor [5]. It is ubiquitous in many indoor environments with a concentration often between 10 ppb and 40 ppb with the highest values being registered in prefabricated houses and where chipboard furniture or carpets are used [8, 9, 10]. After Asia, European Union (EU) is the second largest formaldehyde producer, with 7 million tons per year [11]. Considering that in industrialized countries, the population spends more than 90% of their time in indoor locations, the quality of air inside homes, schools, offices and public buildings is an essential determinant of healthy life and the wellbeing of people [6, 9, 12].

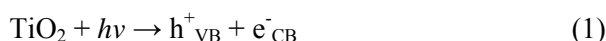
However, formaldehyde is not the only pollutant that affects the everyday locations. Most part of the chemical indoor pollutants are volatile organic compounds or aldehydes, of which formaldehyde, acetaldehyde, hexanal and acrolein are the most common and have been detected even in high concentrations.

Table 1 shows the average concentrations of aldehydes monitored in indoor environments, with a comparison with outdoors [6].

Formaldehyde abatement: a general overview

One of the reasons why formaldehyde draws attention is the lack of suitable methods for its removal. Two approaches are usually used to remove formaldehyde: the first one uses impregnated potassium permanganate or organic amines as adsorbents but they are effective only for short periods; the second one is based on chemical reactions or catalytic oxidations that have a great potential but can be very expensive because they require high temperatures or noble metals as catalysts [13]. These methods are rather difficult to use for the purification of indoor air. Several efforts have been made in the past few decades to develop fitting solutions for the abatement of organic compounds, and photocatalysis is one of the most promising methods to improve air quality, thanks to the features of some semiconductors, mainly TiO_2 , which are able to convert the polluting molecules to CO_2 or to less dangerous by-products when irradiated by a proper light source [14, 15].

Briefly, TiO_2 can be activated under ultraviolet (UV) light irradiation, with a wavelength ranging from 315 nm to 400 nm, and the direct consequence is the formation of electron-hole pairs on its surface. In particular, the so formed positively charged holes have a very high oxidation potential and they can easily react with water molecules producing hydroxyl ($\text{OH}\cdot$) radicals (reaction 1, 2, 3):



where e^-_{CB} is the electron in the conduction band, and h^+_{VB} is the positive hole in the valence band.

Table 1. Average indoor and outdoor concentrations of major aldehydes.

Aldehyde	Average indoor concentration ($\mu\text{g/m}^3$)	Average outdoor concentration ($\mu\text{g/m}^3$)
Acetaldehyde	11.6	1.3
Acrolein	1.1	Not found
Formaldehyde	19.5	1.9
Hexanal	13.6	0.5

The key species for the oxidation reactions are the hydroxyl radicals that have an oxidation potential of 2.80 V and they quickly react with a wide range of organic compounds.

Indeed, TiO₂ is an effective photocatalyst for VOC abatement, particularly thanks to its high population of hydroxyl radicals [16, 17].

Another issue that directly concerns formaldehyde, is the methodology used to monitor or measure it [7]. The standard endorsed method is based on the sampling by 2,4-dinitrophenylhydrazine (DNPH) cartridges, which are analyzed, after desorption, by liquid chromatography. However, the sampling procedure requires at least 30 minutes and the complete analysis takes typically 30 h overall [18].

Generally, the concentrations of many organic compounds, including formaldehyde, can be monitored even by gas chromatography (GC); nevertheless, GC typically has a very low time resolution, and it is not always suitable for detecting several molecules simultaneously.

An interesting alternative is the proton-transfer-reaction mass spectrometry (PTR-MS) allowing the real time monitoring of most VOCs at very high sensitivity, typically in the sub-ppbv region. Being a direct-injection mass spectrometric method, it does not require any pre-treatment of the sample. In PTR-MS, firstly the hydronium ions are produced in a pure and intense hollow cathode source; then, they interact with the neutral molecules in a drift tube [19, 20]. Proton transfer reaction (PTR) takes place whenever the proton affinity of the analytes is higher than that of water. Product ions formed from PTR are then separated on the basis of their mass-to-charge (m/z) ratio in the Time of Flight (ToF) mass analyzer, which allows for both a relatively high mass resolution and the determination of the sum formula of the observed peaks [21]. Thanks to its high sensitivity (>200 cps/ppbv) and high mass resolution (up to 8000 $m/\Delta m$) [22], this instrument is able to detect most VOCs in real time [23, 24].

Specifically in photocatalysis, for studying the degradation pathways of various organic molecules or detecting by-products that are formed before the complete oxidation, a rapid and high-sensitivity method to simultaneously monitor different molecules is needed. This would allow the simultaneous

monitoring of several processes, such as the degradation of the pristine pollutant, the formation and subsequent degradation of by-products, and also to confirm the complete mineralization of the pristine molecule to CO₂ [25].

As already explained, in real conditions a TiO₂ photocatalyst will never be in contact just with a single molecule, but will be in contact with a wide range of organic compounds, typical of polluted indoor environments. Thus, taking advantage of the ability of PTR-MS instrument to simultaneously monitor several organic molecules [26, 27, 28], we tested all the commercial samples of TiO₂ on a gaseous mixture of aldehydes, including formaldehyde.

Further, the objectives of this study are a) to test the ability of different commercial samples of TiO₂ in degrading volatile organic compounds, in particular aldehydes, when they are present together as a mixture; b) to study the behavior of TiO₂ particles of different sizes, in particular in terms of performance, development of by-products and abatement; c) to evaluate PTR-MS as a tool both to investigate photocatalytic degradation reactions and to optimize TiO₂ photocatalysts in the reduction of indoor pollution.

MATERIALS AND METHODS

Chemicals

Formaldehyde was purchased from Sigma-Aldrich and it was diluted in water to obtain the required final concentration. The polymerization of the unstabilized aldehyde was avoided by lowering the concentration of the molecule by dilution.

A gas cylinder containing a gaseous mixture of aldehydes was purchased from Apel-Riemer Environmental Inc. Atmospheric Chemistry/Specialty gases. Standards were gravimetrically prepared in high-pressure aluminum cylinders that were cleaned and treated to eliminate contamination and ensure inertness.

Aldehydes contained in the mixture are listed in table 2.

TiO₂ samples

Three commercial samples of TiO₂ powders, two nano-sized and one micro-sized, (P25 by Degussa, PC105 by Cristal and 1077 by Kronos, respectively)

were selected for testing and comparison [29]. The reference target is the comparison between the different particle sizes. The main features of each sample are summarized and reported in table 3.

Photocatalytic system

Photocatalytic tests were performed in a PIREX glass reactor of 5 L volume. The detailed description of the setup is also reported elsewhere [30]. Formaldehyde or the gaseous mixture of aldehydes was loaded by means of LCU (Liquid Calibration Unit, IONICON Analytik GmbH, Austria) or GCU (Gas Calibration Unit, IONICON Analytik GmbH, Austria) in case of liquid or gaseous standards, respectively. TiO₂ samples were deposited on a glass support by dissolving the TiO₂ powder in

2-Propanol (Sigma-Aldrich, anhydrous, 99.5%) and then depositing the suspension on the glass using a Pasteur pipette. The TiO₂ glass sheet was placed at the bottom of the reactor.

Irradiation was obtained by a UV lamp (Jelosil – Model HG-500, 500 W, $\lambda = 315 \text{ nm} - 400 \text{ nm}$), placed at the required distance to get an irradiation power of 30 W/cm² (measured on the catalyst surface).

The reactor was simultaneously connected to the injection tool (LCU or GCU) and to the PTR-MS instrument. Figure 1 shows the system scheme.

In case of pure formaldehyde, tests were performed at both 500 ppb (0.5 ppm, corresponding to 0.6 mg/m³) and 5000 ppb (5 ppm, corresponding to 6 mg/m³). Working concentrations were consciously made higher in comparison with the normal average values in real environments; this way it is possible to study the degradation reaction of formaldehyde and the reaction by-products from a chemical and kinetic point of view. Secondly, it was possible to evaluate the real possibilities of the materials by working in border-line conditions, that is concentrations of the pollutant much higher than in reality. Indeed, the photocatalytic activity of the powder TiO₂ is usually higher than the activity of the ceramic materials on which it is applied. The mixture of aldehydes was used at the concentrations provided by the supplier and is listed in table 1.

After closing and loading the reactor, the initial concentrations of the volatile compounds were monitored by PTR-MS and, when a stable value was achieved, the photocatalytic reaction was initiated by switching on the UV lamp. Photocatalytic test duration was 30 min for each catalyst.

Table 2. List of aldehydes and their concentrations (ppb).

Aldehyde	Concentration (ppb)
Formaldehyde	1119 ± 5%
Acetaldehyde	1100 ± 5%
Acrolein	933 ± 5%
Propanal	986 ± 5%
Butanal	1023 ± 5%
Crotonaldehyde	1022 ± 5%
Pentanal	968 ± 5%
Hexanal	923 ± 5%
Heptanal	952 ± 5%
Octanal	965 ± 5%
Nonanal	721 ± 5%
Decanal	815 ± 5%

Table 3. Main features of the TiO₂ commercial samples.

Sample	Anatase:rutile	Average crystallite size (nm)	BET surface area (m ² g ⁻¹)	XPS	XPS OH/O _{tot}	Band gap (eV)
P25	75:25	26	50	Ti(IV)	0.14	3.21 (Lopez, R. and Gomez, R., 2011)
PC105	100	23	80	Ti(IV)	0.85	3.19
1077	100	130	12	Ti(IV)	0.32	3.15

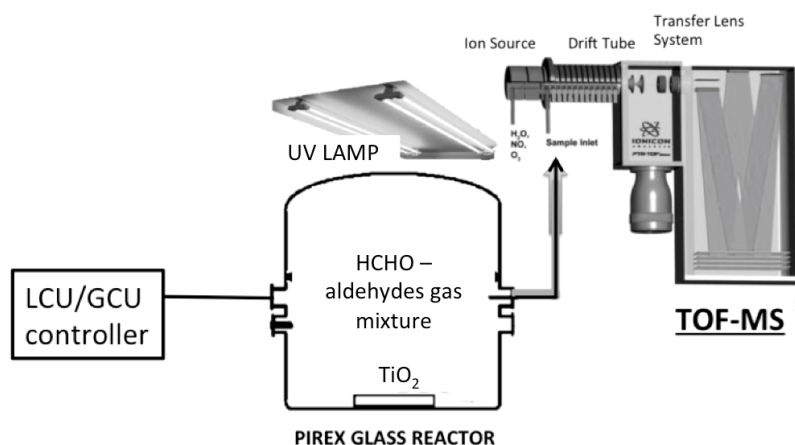


Figure 1. Photocatalytic system. The reactor, in the middle, is directly connected to LCU or GCU (to the left) and to PTR-MS (to the right). UV lamp was suspended above the reactor.

Proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS)

Proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS 8000, Ionicon Analytik, Innsbruck, Austria), in its standard configuration (V mode), was used as the online technique to monitor VOCs at the sub-ppbv level. Degradation of pristine molecules and the formation/degradation of main by-products were monitored as well.

The technique offers several advantages including (i) high time resolution, (ii) ability to simultaneously detect a large number of VOC compounds [20], (iii) high sensitivity (>200 cps/ppbv) and (iv) high mass resolution (up to 8000 m/ Δ m) [31].

The calibration of the instrument was automatically done by the acquisition program [32]. Precisely, the selective reagent ions (SRI) used as reference were H₃O⁺ (mass 21,022), NO⁺ (mass 29,997) and C₆H₅I⁺ (mass 203,943).

The measurement of volatile organic compounds in atmosphere using proton-transfer-reaction mass spectrometry has been reported in many publications. De Gouw *et al.* presented a review [25], with several references regarding aldehydes, ketones, alcohols and aromatics. In general, to assess the performance of each TiO₂ catalyst, we followed the overall proportion of degradation (based on the delta-concentration). Specifically, formaldehyde was detected using PTR-ToF-MS by monitoring the mass spectral signal of H·HCHO⁺ at m/z 31.0184 [23].

Sample characterization

XRD (X-Ray Diffractometry) spectra were obtained using a PW 3830/3020 X' Pert diffractometer from PANalytical with the Cu K α radiation ($k = 1.5406 \text{ \AA}$). High-resolution transmission electron microscopy (HR-TEM) imaging were performed by means of the JEOL 3010-UHR instrument (acceleration potential 300 kV; LaB6 filament). X-ray photoelectron spectra (XPS) were taken in an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al K α radiation (1486.6 eV), and the accuracy of the reported BE (Binding Energies) is estimated to be $\pm 0.2 \text{ eV}$.

RESULTS AND DISCUSSION

Characteristics of the TiO₂ commercial samples

The commercial samples here presented were already investigated and deeply characterized in many previous works [29, 30]; however the main and crucial structural features are reported here.

XRD patterns relative to the three selected samples is reported in figure 2; it is evident that anatase is the unique crystallographic phase present in both Kronos and PC105 powders; in the case of P25, instead, the 80:20 anatase/rutile phase composition ratio is confirmed.

TEM images, reported in figure 3 indicate that the 1077 sample exhibits an average crystallite size of 130 nm, whereas both P25 and PC105 powders possess comparable crystallite sizes, centered around 25 nm. These structural properties are reflected in

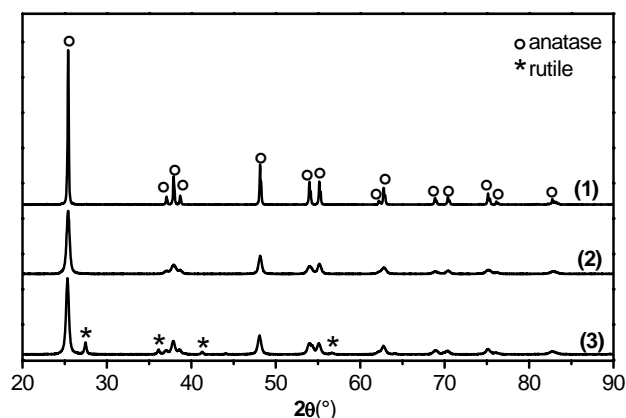


Figure 2. XRD Patterns of 1077 (1), PC105 (2) and P25 (3).

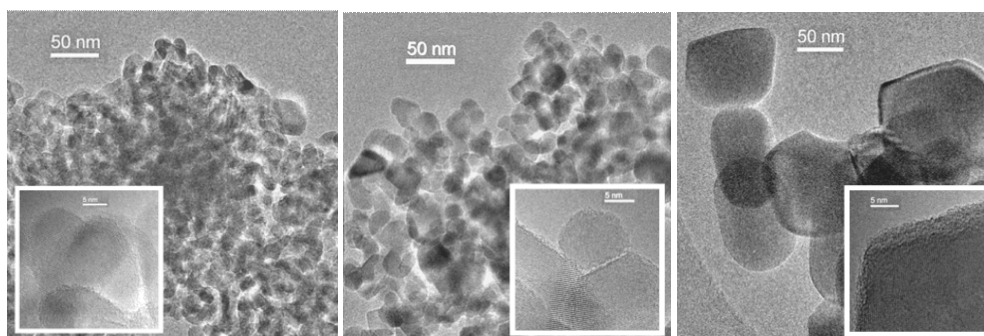


Figure 3. Left-hand image refers to PC105, middle image refers to P25 and right-hand image refers to 1077.

the BET (Brunauer–Emmett–Teller) surface area of the micro-sized sample (1077), which is much lower compared to the nano-sized ones (see table 3, second column). This feature is in total agreement with the indications obtained by means of XRD analysis, evidencing that the average particle dimensions are in the 120 nm - 200 nm range for the 1077 sample.

The $\text{OH}/\text{O}_{\text{tot}}$ surface ratio, reported in the sixth column of table 3, is a quantitative measure of the hydrophilicity/hydrophobicity of the TiO_2 surface, estimated using the XPS-determined surface OH atomic concentrations normalized by the total oxygen atomic concentrations (O_{tot}) [33]. The calculation of the $\text{OH}/\text{O}_{\text{tot}}$ surface ratio was performed starting from the XPS spectra, as reported in figure 4.

The hydrophilicity/hydrophobicity character of the surface of the photocatalysts plays a crucial role in determining the adsorption step and

thereby the photocatalytic activity in the degradation of pollutants. PC105 exhibits the highest concentration of OH that represents 85% of the oxygen at the surface as previously mentioned.

Formaldehyde photolysis

The first investigation on the formaldehyde photolysis reaction was performed simultaneously with the evaluation of the relative humidity (RH) inside the reactor [34]. The dual-axis graph (Figure 5) reports the formaldehyde concentration (ppbv) on the left axis, while the relative humidity (RH%) value is reported on the right. Both variables were monitored over time.

At the beginning of each test, the reactor was loaded with a continuous and controlled flow of gaseous formaldehyde up to the set concentration. Because of the presence of the UV lamp, the control of temperature was crucial: after 30 minutes the

temperature increased by 2 degrees and then remains unchanged for the whole duration of the reaction. Figure 5 shows the contribution of the formaldehyde photolysis, which can be considered null.

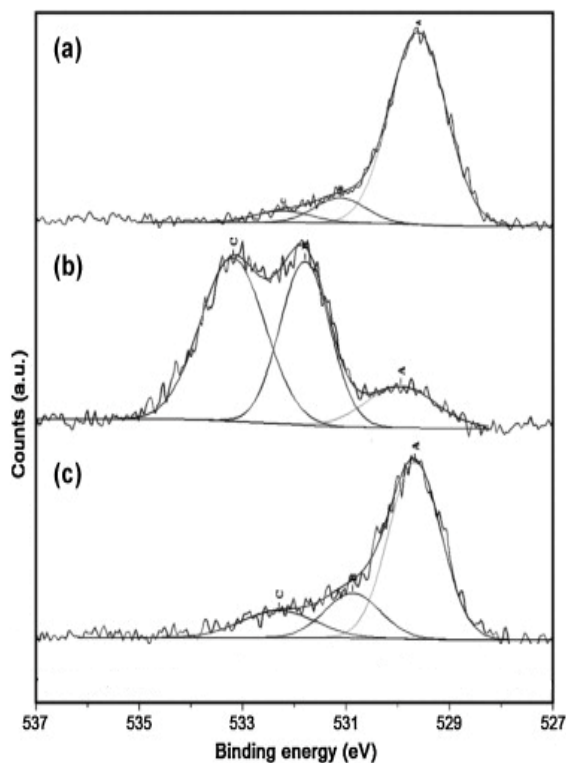


Figure 4. O1s XPS spectra for (a) P25; (b) PC105 and (c) 1077.

Photocatalytic reduction curves of formaldehyde: the effect of the starting concentration

All samples were able to reach satisfactory values of formaldehyde conversion in the case of starting concentration of 500 ppbv (Figure 6); overall, the morphological differences between the three TiO₂ catalysts do not affect the abatement of the pollutant. However, minimal differences found in the specific formaldehyde degradation values show that the results are consistent with the respective values of surface area. 1077 sample, with a lower surface area due to its higher particle dimension, leads to a higher final value of formaldehyde concentration. Indeed, the degradation percentage achieved with the micrometric sample is around 80%, with P25 is 89%, and with PC105, it is higher than 90%. Thus, from a general point of view, all catalysts were effective. Moreover, the slight differences in the final result reflect the peculiar characteristics of each sample.

In the case of higher formaldehyde concentration, morphological differences mainly affected the final result, as is evident from the kinetics shown in figure 7 that shows a lower conversion value attained by the micrometric sample. Indeed, in the case of high formaldehyde concentrations, a higher surface area is crucial to have much more available active sites onto which the pollutant can adsorb. The adsorption onto the TiO₂ surface is the first step to start the photodegradation reaction. Furthermore, aldehydes are polar compounds that exhibit the

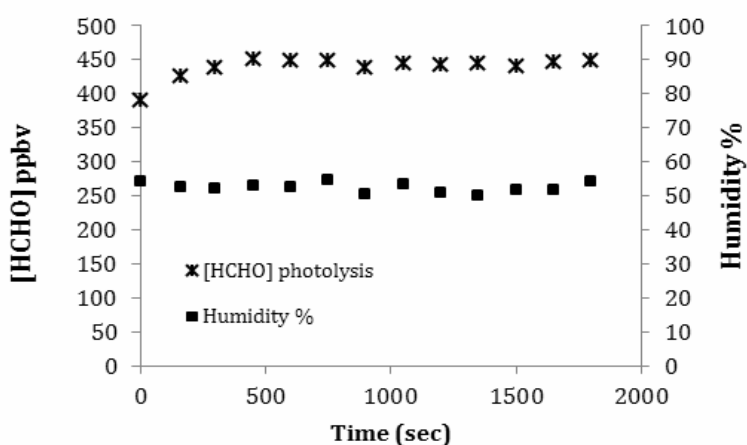


Figure 5. Left-axis reports formaldehyde concentration - black crosses refer to formaldehyde concentration (ppbv) values over time. Right-axis reports the relative humidity % - black squares refer to RH% values measured at regular time ranges during the entire photolysis run.

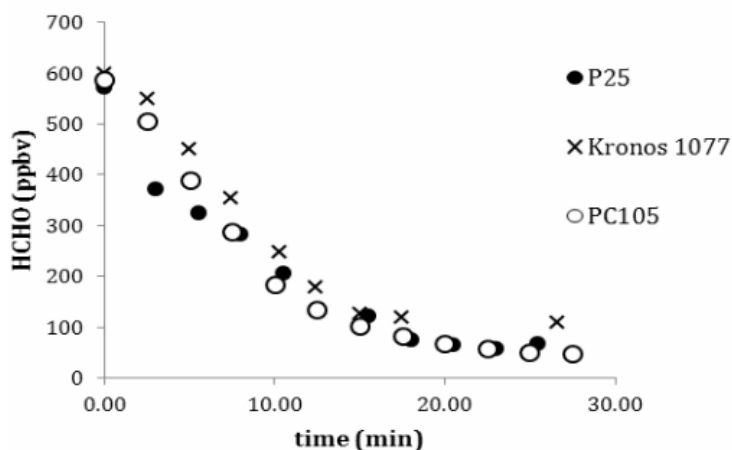


Figure 6. HCHO (ppbv) trend over time using the three different commercial TiO₂ samples—starting concentration set at 500 ppbv: a) P25 (black dots); b) 1077 (crosses) and c) PC105 (empty dots).

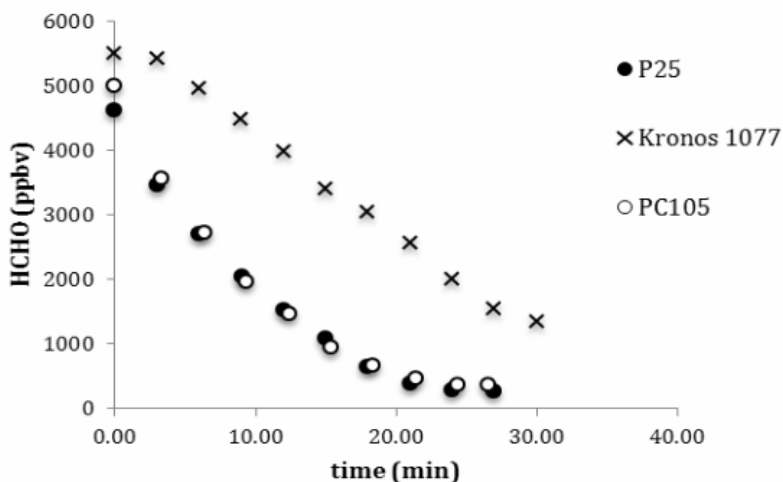


Figure 7. HCHO (ppbv) trend over time using the three different commercial TiO₂ samples—starting concentration set at 5000 ppbv: a) P25 (black dots); b) 1077 (crosses); c) PC105 (empty dots).

classical dipole-dipole interactions; therefore, their adsorption onto TiO₂ may be rather affected by the distribution of the $\cdot\text{OH}$ groups on TiO₂ surface. These two aspects (i.e. surface area and $\cdot\text{OH}$ distribution) together are helpful in explaining the results even better. In fact, despite the very high concentration of formaldehyde, and its much lower surface area (see table 3, fourth column), 1077 is able to reach a rather good value of formaldehyde degradation (>70% in 30 min). The OH/O_{tot} ratio calculated by XPS (see table 3, sixth column) shows that 1077 has a higher amount of free OH in relation to total oxygen, which is exactly twice that of P25.

As the speed of a photocatalytic reaction depends on known parameters, such as catalyst surface area and particle dimensions, crystallographic phases and distribution of the OH free radical species on the surface, the results are consistent with the main features of the powders. Both P25 and PC105 systems reach the best results in lesser time when compared to the micrometer 1077 sample; however, even the micro-sized powder showed good results even at a higher concentration of formaldehyde, obviously with slower speeds.

The Langmuir-Hinshelwood (LH) kinetic model can be used to analyze the reaction rates [35] and

the generation of the final products is assumed to be a first order reaction. This kinetic model provides that the rate of a heterogeneous reaction is controlled by the reaction of the adsorbed molecules, and that all adsorption and desorption pressures are in equilibrium. Langmuir–Hinshelwood kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes [35]. The Langmuir–Hinshelwood expression that explains the kinetics of heterogeneous catalytic systems is given in eq. 1.

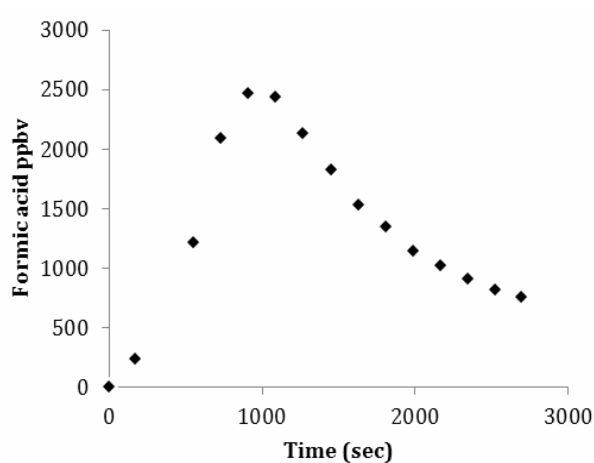


Figure 8. Formic acid formation and degradation over time in presence of micrometric TiO₂ (1077) with a starting formaldehyde concentration of 5000 ppbv.

$$r = -dC/dt = k_r KC / 1 + KC' \quad \text{Eq. (1)}$$

where r represents the rate of reaction that changes with time.

Eq. 2 gives the initial rate of reaction as a function of C_0 :

$$r_0 = k_r KC_0 / 1 + KC_0' \quad \text{Eq. (2)}$$

Most of the researchers have approximated eq. (1) to first order kinetics for the condition $KC < 1$ [36, 37]. We calculated the kinetic constants ($k \text{ h}^{-1}$) starting from the data collected in formaldehyde photodegradation over time using P25, PC105 and 1077, obtaining the following values: 4.5427 h^{-1} , 6.5115 h^{-1} and 2.7298 h^{-1} , respectively. The obtained data are in perfect agreement with the final degradation results.

By-products

Working at rather high concentrations of formaldehyde allows to easily follow the possible formation of by-products and their relative degradation.

Formic acid is the main by-product of formaldehyde degradation pathway. Due to the higher speed of analysis of the PTR-ToF-MS instrument, it was possible to obtain the complete trend of the formation and degradation of this molecule (Figure 8) [38].

For reasons of brevity and because results were very similar, we report only the formic acid

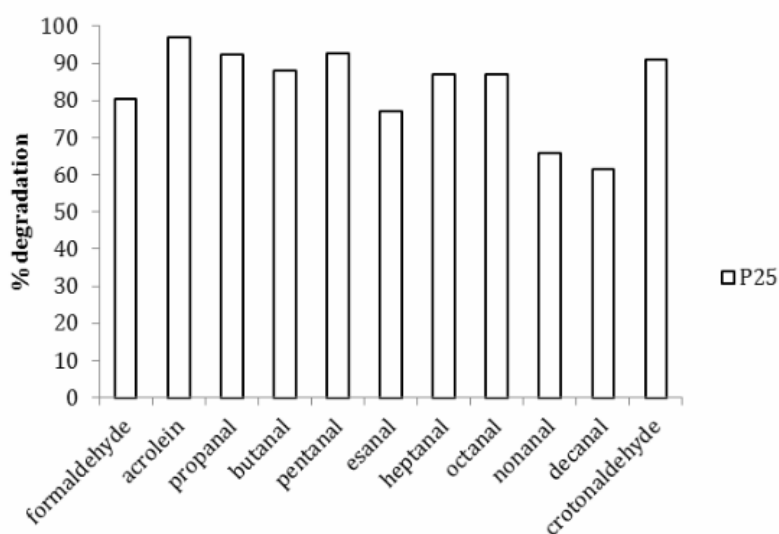


Figure 9. P25: % degradation value of each aldehyde after 30 min of UV irradiation.

kinetic using 1077 as catalyst. The micrometric catalyst showed a good activity and the complete degradation of formaldehyde was confirmed. Overall, formaldehyde can be completely oxidized to CO₂ by means of TiO₂ photocatalysis. The complete degradation pathway, including by-products, can be tracked easily with PTR-MS.

Photocatalytic reduction curves of gaseous mixture of aldehydes

P25 by Degussa, the nanometric commercial sample, was able to photodegrade all the aldehydes, reaching conversion percentages higher than 60% (see figure 9); also, the majority of the aldehydes degraded more than 80%.

Even more interesting is proving that the results obtained using micro-1077 are comparable. This means that 1077 is able to reach very good results even if strongly stressed as in this case with a mixture of organic pollutants.

By changing the catalyst, it was possible to note some difference in trends in the degradation of the aldehydes. Specifically, in the case of PC105 (Figure 10) and 1077 samples (Figure 11), the trends of some aldehydes are different; in particular, some molecules were formed in the first part of the kinetic and then degraded. The relative trends are reported in figure 12 and figure 13.

In the case of PC105, which differs from P25 mainly in particle size and crystallographic TiO₂ phases [29], the formaldehyde photodegradation reaction led to the increase in butanal, propanal and hexanal concentrations; in the case of Kronos 1077, instead, the formaldehyde photodegradation reaction led to the formation of butanal first, but subsequently the majority of the pollutant molecules was degraded in 30 minutes.

Overall, butanal is the aldehyde that is formed using both PC105 and 1077, while it is degraded using P25; PC105 is the sample that leads to an increase in the concentrations of the majority of the aldehydes.

The degradation pathways of different aldehydes can be explained taking into consideration the different features of the various TiO₂ powders, i.e. the dimension of particles, the crystallographic phase composition and the abundance of OH radicals on the TiO₂ surface. P25 and PC105 both consist of nanometric particles, but i) their crystallographic phase compositions are different (anatase only in case of PC105, and a mixture of anatase and rutile in case of P25), ii) the OH radical population on the two TiO₂ samples' surface is different. The OH free radicals on the catalyst surface are the key species that control the adsorption of

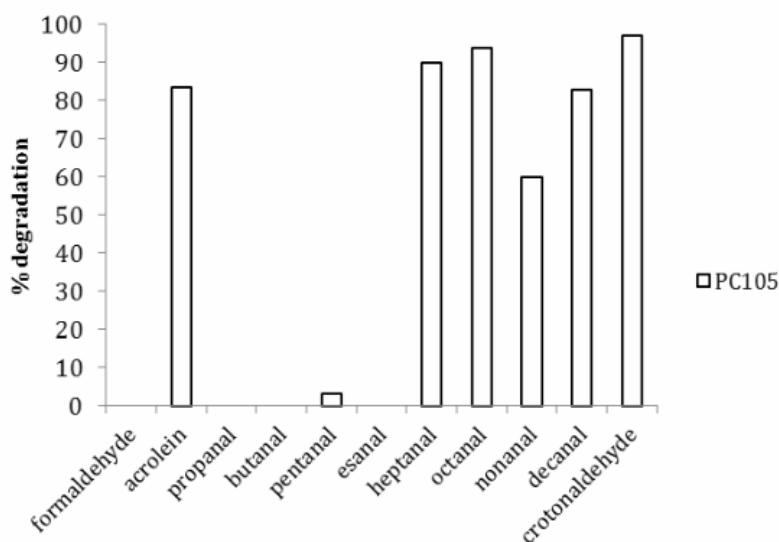


Figure 10. PC105: % degradation value of each aldehyde after 30 min of UV irradiation (the missing columns indicate aldehydes that are formed as by-products).

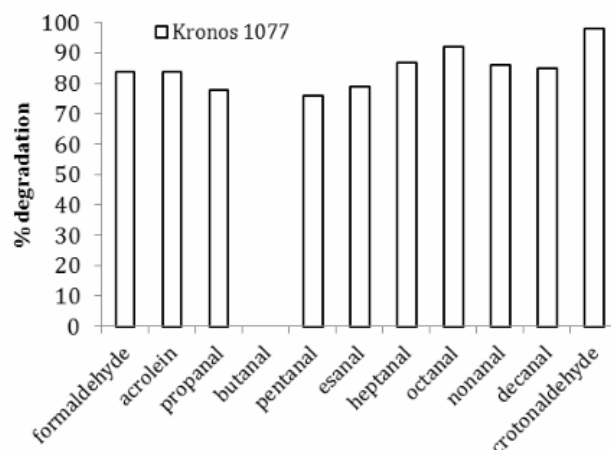


Figure 11. 1077: % degradation value of each aldehyde after 30 min of UV irradiation (the missing columns indicate aldehydes that are formed as by-products).

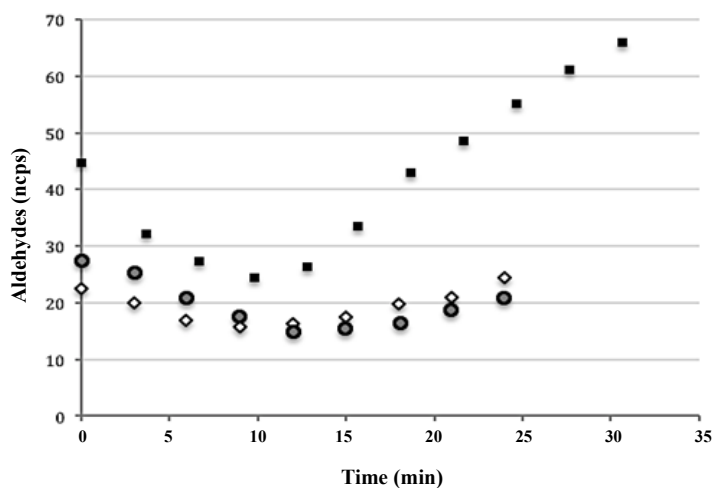


Figure 12. Trends of the concentrations of some aldehydes, monitored with PTR-ToF-MS instrument during the kinetic using PC105 – a) propanal (white rhombus); b) butanal (black squares); c) hexanal (grey dots).

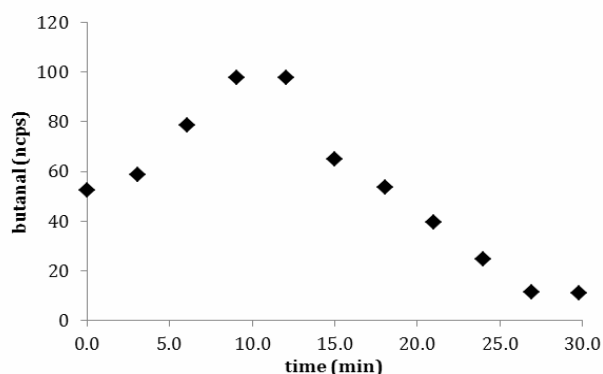


Figure 13. Butanal trend for the kinetic performed with Kronos 1077.

organic molecules onto the TiO₂ surface. Adsorption of the pollutants is closely related to the degradation reaction pathways. A huge number of active sites lead to better adsorption. However we also have to consider the interaction force between the organic species and the OH radicals. Indeed, in the case of PC105, the higher adsorption led to the formation of many aldehydes in the form of by-products, which limits the adsorption of other molecules, slowing down the overall degradation process. Thus, the final result is worse than that obtained using 1077, despite its lower surface area.

CONCLUSION

This work reports the results of photocatalytic tests performed using commercial TiO₂ powders, which mainly differ in their particle sizes. The aim of this study is to demonstrate the possibility of using photocatalysis as a way to improve the air quality of the indoor environments, in particular against molecules that are ubiquitous and very dangerous for human health, such as formaldehyde. Moreover, due to the technological advantages of the PTR-ToF-MS technique, for the first time TiO₂ was tested not just on a single molecule, but on a mixture of different volatile organic compounds.

This approach is particularly interesting for many different reasons, among which are: a) in a real environment, TiO₂ is never in contact with just a single molecule, because indoors are full of different unhealthy organic molecules as well-detailed in the literature; b) the behavior of each TiO₂ powder may be different when more than one molecule is present, as the simultaneous presence of different molecules, pristine or produced during the degradation reaction, leads to possible molecular interactions.

Therefore, this work demonstrates the possibility to efficiently monitor the photodegradation of formaldehyde and exemplifies how the PTR-ToF-MS technique allows both studying and monitoring various photocatalytic reactions, with more than one starting pollutant and with several by-products.

After showing that all the commercial TiO₂ samples are efficient in the photocatalytic formaldehyde abatement, tests on the gaseous mixture of aldehydes give clear information on the potential application of TiO₂ in the reduction of indoor pollutants.

From the point of view of the semiconductor, the use of TiO₂ photocatalysts, even in the form of micro-sized particles, seems very promising; formaldehyde is removed rapidly and efficiently even if the initial concentration is far above the values expected in any practical application. Moreover, when formaldehyde is degraded alone, TiO₂ particle dimensions dominate the process, as a higher specific surface area leads to better photocatalytic results. However, when a mixture

of pollutants is present, we observe that 1077 sample, even if micrometric and with a much lower specific surface area, is the only one that leads to a linear degradation of all the organic molecules present in the gaseous mixture.

To conclude, we showed that the different morphological features of the commercial TiO₂ samples affect the reaction kinetic; in this case, a lower surface area with a good distribution of active sites leads to more linear abatement of pollutants.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria, educational grants, participation in speakers' bureaus, membership, employment, consultancies, stock ownership, or other equity interest, and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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