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Influence of temperature on gas-phase photo-assisted mineralization of TCE using tubular and monolithic catalysts

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Abstract

The influence of temperature on the photocatalytic oxidation of a model volatile organic compound, trichloroethylene, in gas streams using UV–Vis radiation is analyzed. Two different photoreactors have been tested at different temperatures from 60°C to 250°C. A solar simulator consisting of a Xe lamp with filters to remove IR radiation was used as the source of illumination for the first monolithic photoreactor, but for the second, a tubular catalyst in a Pyrex tube is concentric to a fluorescent UV lamp. The experimental setup was prepared to discriminate the thermal effect from the purely photocatalytic process at wavelengths below 400 nm. From the results, it may be concluded that the oxidation mechanism has two different phases. The first phase of TCE oxidation, in which the active species are chlorine radicals, is not improved by an increase in temperature. The second phase, corresponding to dechlorination of first-phase by-products, seems to follow a thermal-catalytic mechanism. A good balance between temperature and residence time is necessary to obtain the best cost/benefit relationship.

Keywords: Photocatalysis; VOCs; Monolith; Tubular; Titania; Trichloroethylene

1. Introduction

Photocatalytic oxidation (PCO) has been receiving increasing attention for VOC abatement and air purification. Since early tests with TiO_2 for the degradation of toluene in air were published by Ibusuki and Takeuchi [1], fundamental studies and laboratory tests have evolved into such successful applications as indoor air purification and emission-abatement in gas streams [2,3].

Photoactivity tests have paid little attention until now to the influence of temperature on process conversion and mineralization efficiency. In the case of PCO applications in water, the narrow temperature range, which can be selected, can be a serious drawback, but in gas-phase applications, the operational range is wider. Catalytic oxidation with high yields is possible today at temperatures as low as 150°C. Therefore, maximum energetic optimization of PCO processes is necessary, since comparison with catalytic oxidation is unavoidable.

Changes in relative positions of the Fermi level of TiO_2 powders during photocatalysis at temperatures between 21°C and 75°C have been reported as relatively small (0.04 V), but at least favorable interfacial electron-transfer kinetics is observed when the temperature is increased [4]. Therefore, if semiconductor powders become available for processes under solar

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irradiation, where the accompanying thermal effect is not negligible, cooling of such devices would not be necessary [5].

Only a few examples in the literature discriminate the possible effect of temperature on the process. Fu et al. [6] determined a beneficial effect of increased temperature during degradation of benzene. However, from our experience with a similar low-quantum VOC, such as toluene, we concluded that the increment in conversion was basically motivated by thermal catalysis [7]. Only a 3–5% photo effect could be found under some conditions. At temperatures higher than 150°C, when strong mineralization is required, the photo-effect may be said to be negligible. A review by Nimlos et al. [8] shows BTEX compound reaction rates ten to one hundred times slower than for TCE. Therefore, the temperature effect would seem to be better discriminated by focusing on high-quantum compounds.

Kennedy et al. [9] claim photothermal synergism in high-quantum efficiency experiments with a compound (TCE) at temperatures of up to 250°C and TiO_2/Pt catalyst. According to their results, TCE photothermal degradation is more than merely the sum of photocatalytic and thermal tests. At higher temperatures (>250°C), the thermal activity of Pt swamps the photoactivity of the titania.

Taking into account the relevance of temperature in solar-driven applications, we have conducted specific tests with TCE to analyze its influence not only on substrate conversion, but also on mineralization.

2. Experimental

A stream of dry, CO_2-free air is delivered by mass-flow controllers (UNIT Instruments) from an air generator (Peak Scientific Gas Generator) at flow rates of 4–28 $l\,min^{-1}$. TCE is bubbled into the air stream and through the catalyst in the reactor. Heat-traced outlet gases are analyzed by on-line direct sampling with a GC with an FID and a TCD detector (Hewlett Packard 6890). Manually switched samples were adsorbed with Tenax, a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide, commonly used as an adsorbent for trapping volatile compounds from air for analysis for further GC/MS identification using a Perkin Elmer (Model ATD 400 with a MS HP 5971 MSD with HP 5890 GC) thermal desorption system. The experimental set-up and methodologies have been previously described by Sanchez et al. [10] and Blanco et al. [11]. A diagram of the experimental apparatus is depicted in Fig. 1.

Catalysts based on mixtures of titania (anatase) and magnesium silicate as permanent inorganic binder were prepared by extrusion of ceramic pastes in two different shapes (monolith and tubular), following a method described elsewhere [7].

Titania-based catalyst doped with platinum (0.1 wt.%) were obtained by impregnation of monolithic support with hexachloroplatinic acid solution, following a method described elsewhere [12]. Square-cell monoliths, after having been dried at 383 K and treated at 773 K for 4 h in an air atmosphere, had a pitch of 3.4 mm, wall thickness of 0.9 mm and a geometric surface area of 865 $m^2\,m^{-3}$. Tubular catalysts, after treatment at 773 K for 4 h in air atmosphere, presented internal and external diameters of 42 mm and 48 mm, respectively.

Textural properties were analyzed by measurements of nitrogen adsorption isotherms (BET) and mercury intrusion porosimetry (MIP). Nitrogen adsorption isotherms were determined using Micromeritics ASAP 2300, and the surface areas were calculated using the BET method. Porosity was measured by MIP using CE Pascal instruments 140/240. UV–Vis diffuse reflectance spectra were obtained in a Shimadzu model 2100 UV–Vis spectrometer.

The two reactors, monolithic and tubular, tested at lab scale are shown in Figs. 2 and 3. Continuous-flow tests of several hours were conducted in both photoreactors, in an attempt to reproduce the operating parameters of a real solar system. The monolithic photoreactor consists of a windowed direct-absorption catalytic receiver similar to the volumetric receiver concept, which has had such successful results at solar test facilities. The stainless steel reactor has a 40 mm internal diameter and 200 mm length, with an effective aperture diameter of 4 cm, sealed by a Pyrex window (Fig. 2).

Monolithic catalysts have significant advantages in lowering pressure drop and improving both chemical and photon contact surfaces. This makes them especially useful for reactor designs with large treatment capacities. IR filters (UG11 of Schott trademark) are necessary to remove the visible and infrared spectrum bands in order to avoid overheating the catalyst sur-

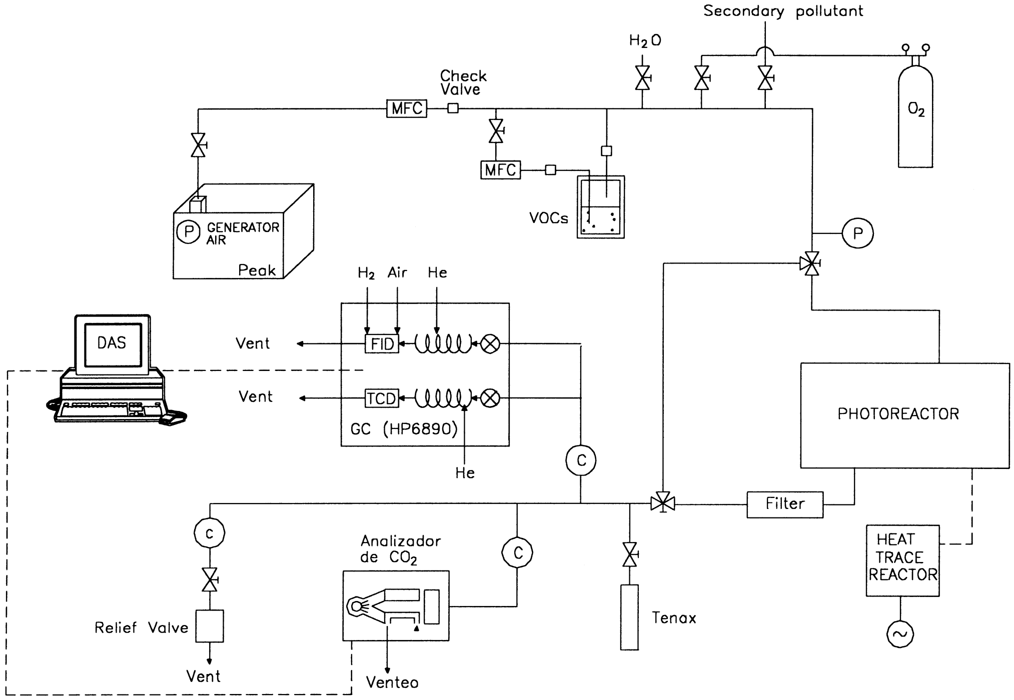

Fig. 1. Diagram of experimental system.

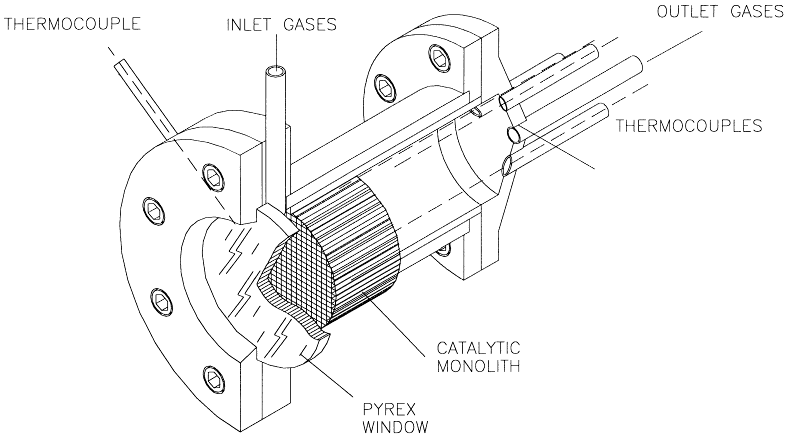

Fig. 2. Layered view of monolithic photoreactor.

face, and to distinguish between thermocatalytic and photocatalytic efficiencies. Since only UV photons finally enter the reactor, reaction temperature has to be reached by electrical pre-heating. With this configuration, photon flux rate and temperatures could be separated in every experiment. In addition, no thermal gradients are produced on the surface of the catalyst.

The tubular photoreactor consists of a Pyrex tube containing a tubular matrix of TiO_2-based catalyst concentric to an UV lamp (UVA-340 Q-Panel-40 W). The stream of gas flows between the inner wall of the catalyst, which is a mass mixture of $MgSiO_3/TiO_2$,

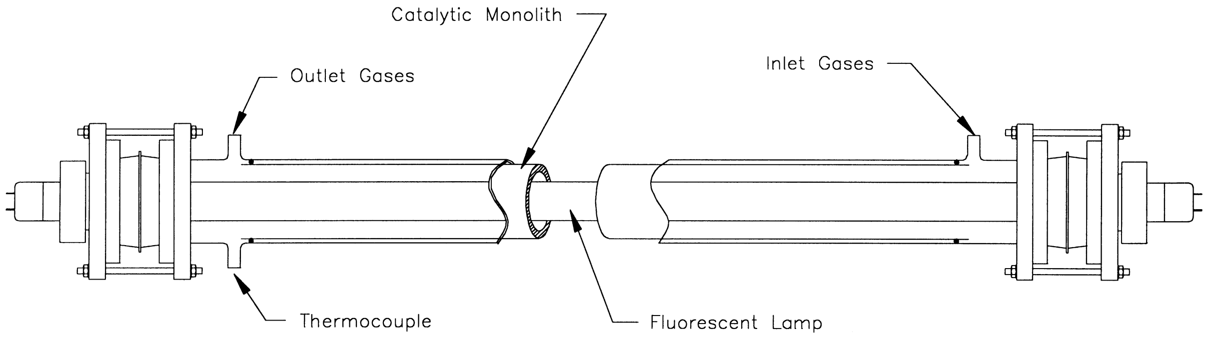

Fig. 3. Schematics diagram of the tubular photoreactor.

and the surface of the UV lamp (Fig. 3). The UV lamp irradiance is similar to the solar spectrum up to the 340 nm maximum of the lamp. A heat-trace box that controls process temperature encloses the photoreactor. Two thermocouples located at the inlet and outlet give the reaction temperature of gases in contact with the catalyst surface.

Parameters and results of the two types of photobreak reactors are compared in Table 1. Residence time and linear velocity are higher in the tubular reactor than in the monolithic reactor. The tubular photoreactor was used for mineralization tests because of its significant advantages in residence time operating range, better distribution of photon radiation and temperature control.

3. Results and discussion

3.1. Characterization studies of monolithic and tubular catalysts

The addition of natural magnesium silicates as inorganic binder to precursor paste ceramics of the catalysts give place to increase in the mechanical properties and the stability of titania-based catalyst to anatase form [12], thereby improving the rheological properties of the ceramic pastes. Moreover, this material affects the textural properties of the titania catalysts, thereby improving the adsorption capacity.

The results of BET and of mercury intrusion measurements on the monolithic and tubular catalysts are given in Table 2. It can be noted that both catalysts present a bimodal pore size distribution in the range of meso- and macropores, which represents an optimum ratio between accessibility and adsorption properties. Moreover, as concluded in a previous work [7], these catalysts can be considered as fibrous silicate structures covered by titania (anatase), where, in the case of Pt/TiO_2-based monoliths, platinum clusters were selectively impregnated on the TiO_2 particles in such a way that the distribution of this element in the catalyst was optimized.

To analyze the effect of platinum doping on the light absorption properties, UV–Vis spectra of the two studied catalysts, based on TiO_2 and Pt/TiO_2, respectively, are given in Fig. 4. It is observed from the diffuse reflectance spectra that titania monolithic catalysts doped with platinum increase the adsorption capacity of the catalyst in the 300–400 nm range.

3.2. Degradation of TCE at different temperatures

First tests with TCE at different temperatures were conducted in the monolithic photoreactor. Two important drawbacks had to be overcome to obtain reliable results from temperature tests. The first is the axial temperature gradients. With the full lamp spectrum, and no filtering, the best operating conditions were obtained after defocusing the lamp by taking the reactor out of the focal point. Even under these circumstances, we could detect thermal gradients of more than 300°C up to 10 cm long in the monoliths channels. Results of experiments conducted with different lengths of catalyst have demonstrated exponential distribution of photons at the channel entrance [12]. In this study, for homogenous photon distribution, a monolith length of 1 cm has been used.

A second drawback of the monolithic photoreactor for temperature tests was the difficulty in determining

Table 1
Comparative parameters of the two alternatives for TiO_2 photocatalytic detoxification of gaseous streams

Reaction parameters	Tubular reactor	Monolithic reactor
Temperature (°C)	60°C and 100°C	80–200°C
TCE concentration (ppm_v)	30–184	400
Incident photonic intensity (Einstein m^{-2} s^{-1})	9,97E-05	4,23E-03
Residence time (s)	0,023–1.48	0,42
Area velocity ($m\,h^{-1}$)	4,6–303,2	5,3
Conversion of TCE (%)	7,5–98,0	2,0–99.9
Mineralization (%)	0–79,88 (60°C and 100°C)	47% (80°C)
Linear velocity ($cm\,s^{-1}$)	27,2–132,8	2,38
Flow rates ($l\,min^{-1}$)	4–28	1,1
Type of catalyst	Titania-based	Titania and Pt/TiO_2-based
Irradiated area (cm^2)	39,6–530,3	4,86

Table 2
Textural properties of studied catalysts

Catalyst	Total pore volume ($cm^3\,g^{-1}$)	Mean pore diameter		BET area ($m^2\,g^{-1}$)
		d_M (nm)	dm (nm)	
Monolithic Pt/TiO_2-based	0.45	65.0	12.3	143
Tubular TiO_2-based	0.69	60.8	20.0	146

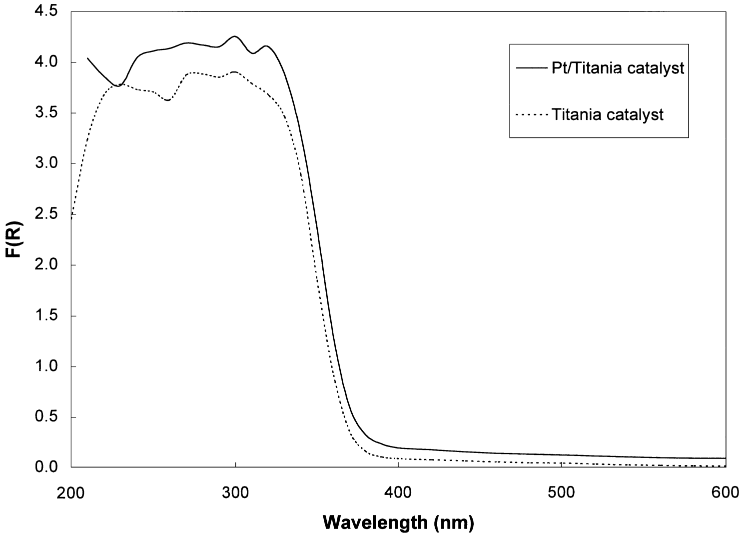

Fig. 4. UV–Vis diffuse reflectance spectra of the catalysts.

the effective temperature of the reaction, since temperatures of bulk gas and catalyst walls diverged widely (radial gradients). Filtering visible and IR photons generated by the Xe lamp could solve these problems. The temperature of the reaction was controlled by external heat tracing on the reactor jacket. Therefore, the experiments were planned in such a way that temperature distribution along the channel was kept almost flat, and electrical heating also controlled the feed gas temperature at the inlet to assure that thermal-catalytic and photothermal tests were carried out in analogous conditions.

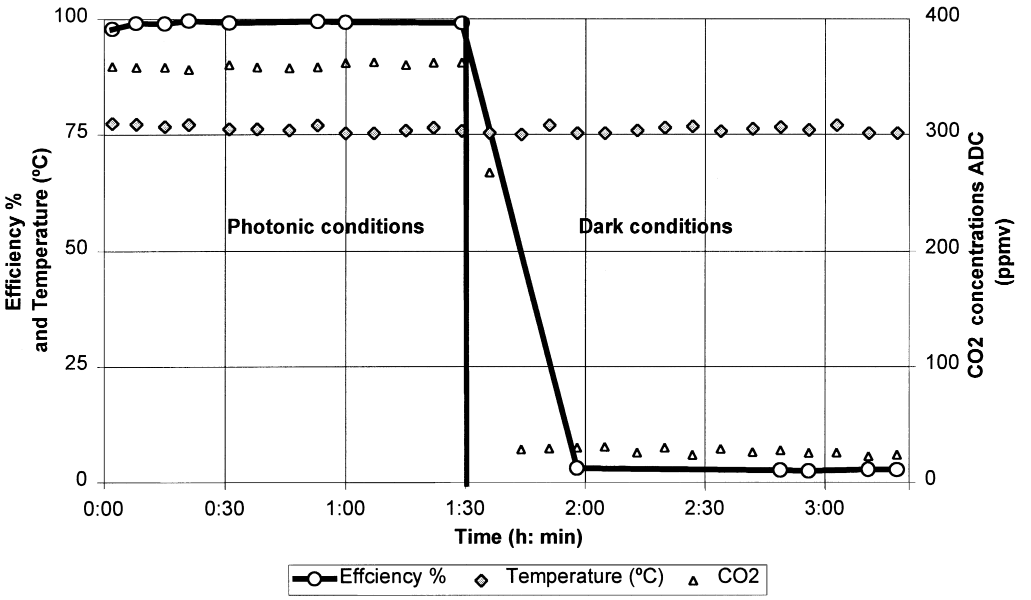

Fig. 5. Photocatalytic and thermocatalytic efficiencies and CO_2 formation at 80°C in photonic and dark conditions.

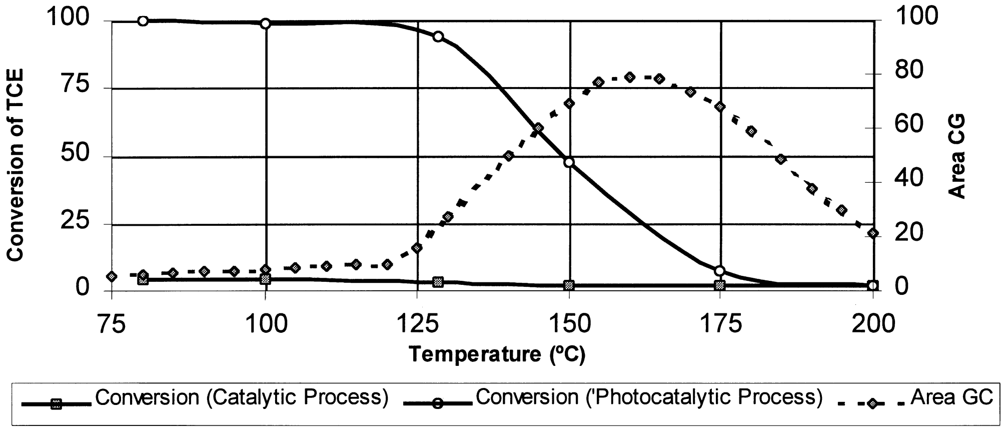

Fig. 6. Conversion of TCE between 80°C and 200°C in photocatalytic and thermocatalytic process using a platinum/titania catalyst (0.1 wt.%) in comparison with the desorption curve of TCE, expressed as uncalibrated chromatographic area. Reaction parameters: (TCE)o = 400 ppm TCE, residence time = 0.42 s, linear velocity = 2.38 cm s^{-1}, irradiated area of catalyst = 4.86 cm^2, area velocity = 5.3 m h^{-1} and incident photonic intensity + = 4.23 × 10^{-3} Einstein m^{-2} s^{-1}.

Fig. 5 shows pure photon degradation of TCE (400 ppm) at 80°C. TCE conversion is almost complete during illumination time. CO_2 formation is detected at this temperature, but figures reveal about 47% mineralization. What is clear is the drastic change in CO_2 formation and TCE degradation when illumination is cut off, even when the temperature of the inlet gas is electrically increased and remained with the external heating jacket up to 110°C. Under the same illuminating conditions, temperatures range from 80°C to 200°C, as shown in Fig. 6. TCE degradation remains constant up to 125°C, at which temperature

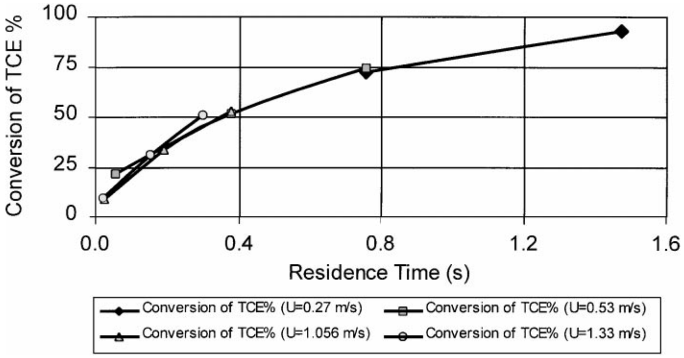

Fig. 7. Conversion of TCE vs. residence time for four linear velocities (0.27, 0.53, 1.06 and 1.33 m s^{-1}) and three catalyst areas (39.6, 269.0 and 530.2 cm^2). Temperature = 100°C.

the process becomes less efficient, so that at 150°C, efficiency is less than 50%, and at 180°C, it is almost negligible. Such a drastic decrease is perfectly understandable when compared with desorption temperature programme curves of TCE. The same figure includes desorption tests performed by gradual heating of TCE, previously adsorbed. In order to distinguish between TCE conversion and adsorption, all photocatalytic runs were started after catalysts were completely saturated of TCE, it is so when the inlet and outlet TCE concentration is the same.

The relevant role of photons in stimulating TCE degradation, and the importance of temperatures being below 125°C open an interesting window for photocatalytic oxidation versus conventional catalysis in this application. Over the whole temperature range analyzed, no degradation by thermal catalysis without illumination could be detected. Since analysis of the monolithic photoreactor was restricted due to the influence of residence time and the estimation of photoefficiency (due to the complex distribution of photons inside the channels), we decided to complete a more detailed analysis of temperature influence and mineralization using a tubular photoreactor.

3.3. *TCE conversion and mineralization*

A tubular photoreactor, as described in Fig. 3, was used to analyze the influence of temperature not only on TCE degradation but also on CO_2 formation. A coaxial cylindrical catalyst was more feasible for estimating illuminated surface and more flexible for increasing residence times and Re numbers. Residence times could be shifted from 0.02 s up to 1.48 s, as can be seen in Fig. 7, by changing the catalyst tube length. For 30 mm of catalyst length, with a residence time of 0.023 s, the reactor photon efficiency is 97.4%, conversion of TCE 9% and mineralization 0% (Figs. 7 and 8). For 402 mm of catalyst length, with a residence time of 0.76 s, the conversion is 74%, the mineralization is 63% (referred to converted TCE), but the reactor photon efficiency is 20.4%.

From the work summarized in Figs. 7 and 8, the best conversion and mineralization are obtained at residence time of 1.48 s and a catalyst area of 530 cm^2 at linear velocities of 0.27 m s^{-1}. Nevertheless, this 0.27 m s^{-1} represents a worse mass-transfer process compared with the other ones tested, as can be seen clearly in the differences obtained for the same residence time at different linear velocities shown in Fig. 8. Residence time, thus, seems to be essential for improving CO_2 yield.

The influence of temperature on conversion and mineralization of TCE is shown versus residence time for two temperatures, 60°C and 100°C, in Fig. 9. The mineralization percentage is referred to the TCE converted. At 60°C, residence time of 1 s is long enough to achieve almost 100% TCE conversion. Conversion at 60°C (98%) is much better than at 100°C (72%). On the contrary, mineralization is more complete at 100°C. But the overall influence of temperature on mineralization is not very significant, since at 60°C absolute mineralization — total mineralization related to the initial concentration of TCE — is 32%, and at 100°C it is 38% (an increment of 6%). Lower temperatures increase substrate degradation, but decrease

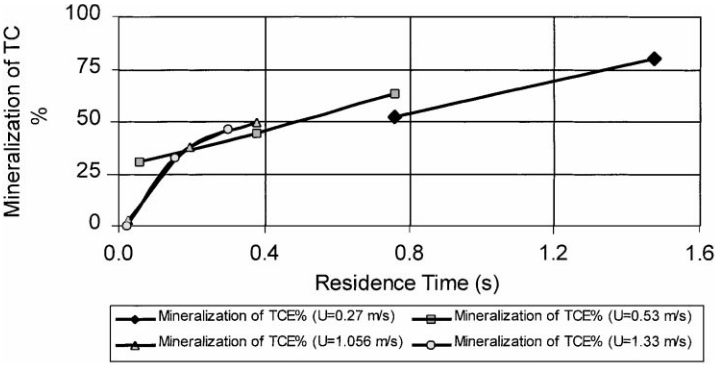

Fig. 8. Mineralization of TCE referred to TCE converted vs. residence time for three linear velocities (0.53, 1.06 and 1.33 m s^{-1}) and three catalyst areas (39.6, 269.0 and 530.2 cm^2). Temperature = 100°C.

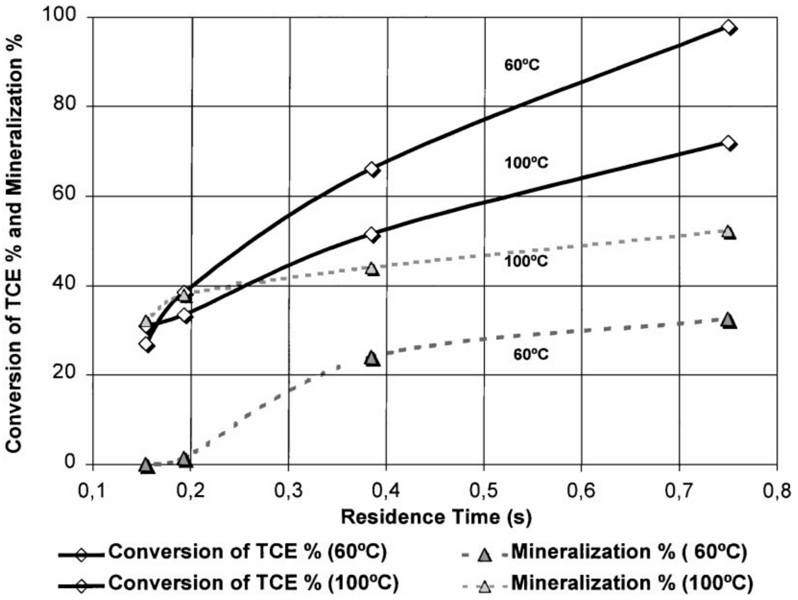

Fig. 9. Tubular photoreactor. Conversion of TCE and mineralization % at 60°C and 100°C as a function of the residence time. Linear velocity = 53.1–132.8 cm s^{-1}, $(TCE)_o = 100$ ppm$_v$, Photonic intensity = 9.97 E-05 Einstein m^{-2} s^{-1}, irradiated area of catalyst = 265 cm^2. (Mineralization percentage is related to TCE converted).

percentage of conversion to CO_2, and as a general result, absolute values of mineralization remain relatively constant.

The reason why higher temperatures are beneficial for the dechlorination of by-products is a matter of utmost interest. In a previous work, chloroform and pentachloroethane were identified as the main by-products [13]. In some situations (very low residence times and highly concentrated analytical samples), traces of phosgene and dichloroacetyl chloride could also be identified. The mechanism has been described by chlorine radicals as the active species initiating the process. The mechanism and by-products are similar to those presented by Nimlos et al. [14] and Hung and Mariñas [15]. The high quantum efficiencies obtained during this step of TCE degradation (100%) contrast with the relatively low efficiencies of CO_2 production. Since the photon process is clearly an heterogeneous reaction, the negative influence of temperature is perfectly understandable. Adsorption of substrate becomes worse and temperature has no relevance for the photocatalytic step based on activation of the semiconductor and generation of chlorine radicals. On the contrary, the second step, where dechlorination of by-products should take place, performs in a more complex way, adsorption seems to be less relevant and increased temperature becomes beneficial. This is a key point that requires study in the near future to clarify an appropriate mechanism.

4. Conclusions

Gas-phase photocatalytic oxidation of TCE by illuminating a semiconductor, such us TiO_2, is a process with high photon efficiencies.

The process presents a complex response to temperature changes. Mineralization to CO_2 of the TCE converted is significantly improved by increasing temperature, but, on the contrary, TCE degradation decreases very quickly at temperatures above 125°C. Adsorption/desorption limitation during the photocatalytic oxidation of TCE at temperatures above 125°C are definitively identified as a key point for monoliths based on TiO_2 + Sepiolite.

The increase of the catalyst length and residence time to a few seconds will finally permit complete conversion and mineralization of TCE. It seems necessary to establish in the near future a good balance between cost and benefit.

Physical–chemical limitations of the mineralization process should be well understood as a must to develop this technology. This forces a greater knowledge of events not only at semiconductor surface, but also during non-illumination steps once the by-products escape from the catalyst/gas interface.

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