Behaviour of TiO$_2$-SiMgOx hybrid composites on the solar photocatalytic degradation of polluted air

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Abstract

The photocatalytic performance of TiO$_2$-SiMgOx ceramic plates for trichloroethylene abatement in gas phase has been evaluated under sun irradiance conditions. A continuous flow Pyrex glass reactor fixed on the focus of a Compound Parabolic Collector has been used. The performance of the hybrid photocatalyst has been evaluated as the variation of the TCE conversion and reaction product formation with the solar irradiance at different total gas flow, TCE concentration, and water vapour content. SiMgOx not only provides adsorbent properties to the photocatalyst, but it also allows the effective use of the material during low solar irradiance conditions. The adsorption–desorption phenomena play a pivotal role in the behaviour of the system. Thus, TCE conversion curves present two different branches when the sun irradiance increases (sunrise) or decreases (sunset). CO$_2$, COCl$_2$ and DCAC were the most relevant product detected. Meanwhile CO$_2$ concentration was insensitive to the branch analysed, COCl$_2$ or DCAC were not indicating the ability of these compound to be adsorbed on the composite. An increase of the UV irradiation at total TCE conversion promotes the CO$_2$ selectivity. The excess of energy arriving to the reactor favours the direct reaction pathway to produce CO$_2$. The photonic efficiency, calculated as a function of the rate for CO$_2$ formation, decreases linearly with the solar irradiance up to around 2 mW cm^{-2}, where becomes independent. For decontamination systems high TCE conversion is pursuit and then high solar irradiance values are required, in spite of lower photonic efficiency values. The present photocatalyts configuration, with only 17 % of the reactor volume filled with the photoactive material, allows total TCE conversion for 150 ppm and 1 L min^{-1} in a wide sun irradiance window from 2-4 mW cm^{-2}. The incorporation of water vapour lead to an increase of the CO$_2$ selectivity keeping the TCE conversion around 90 %, although significant amounts of COCl$_2$ were observed.

Keywords: TiO$_2$-SiMgOx; sepiolite; hybrid photocatalysts; Trichloroethylene TCE; adsorption; VOC; compound parabolic collector CPC; sunlight irradiance; solar photocatalysis; ceramic plates.

1. Introduction

Heterogeneous photocatalysis is an efficient technology for the treatment of pollutants in air or water. It can operate under mild conditions, such us low concentration of pollutant and gas flow, without the use of additional chemicals. The possibility of using solar light as the excitation source increases the environmental value of this technology. Initial studies in this field reported the applicability of solar energy for photocatalytic applications in water [1,2, 3]. Thus, solar assisted photoreduction of CO_2 into formaldehyde and methanol was reported in 1981 [4]. Moreover, Ollis et al. showed the potential application of this technology for degradation of trichloroethylene (TCE) and chloroform in water [5].

There are numerous reactors available for the use of solar radiation [6] [7] [8] [9]. Among them, Compound Parabolic Collectors (CPC) have proved to be one of the best technological options for water decontamination and disinfection. For one sun concentration systems practically all the UV irradiation arriving to the aperture of the collector (both, direct and diffuse) is reflected to the reactor. Moreover, the use of non tracking systems results in low manufacturing and maintenance cost; Since the early works of Vidal et al. concerning the design and construction of CPC collectors [10,11] many studies have denoted the high performance of these systems in water applications [12, 13]. Nevertheless, studies about air treatment are scarce in open literature [14, 15, 16]. In spite of the higher reaction rates expected for gas phase applications compared to water medium, due to the lower competition of water molecules and pollutant for the same active sites, the easier interaction between O_2 and TiO_2, and the higher photonic efficiency than those obtained in water applications, only a few works are reported. A reactor based on a plate configuration was optimised by Leung et al. with parallel glass plates with TiO_2 prepared by sol-gel and tested with formaldehyde [14]. In a previous work we have analysed the feasibility of using this technology using a fix bed continuous reactor with TiO_2 immobilised on Rasching rings [17]. One limitation of these systems is the cyclic nature of the solar irradiance and then the efficiency is limited to a certain hours per day. A possible way to widen the operating window is the use of adsorbents.

The so-called hybrid photocatalysts have been recognized as ideal materials for the preparation of supported photocatalysts for industrial applications, due to the combination of adsorption and photocatalytic properties within the same material. Compared to traditional photocatalysts, in a hybrid composite the pollutant can be retained in the absorbent functionality and subsequently, diffuse to the photoactive sites. Moreover, the migration of non desirable reaction intermediates into the adsorbent could restore the active sites, prolonging the lifetime of the

photocatalyst. This interaction induces a synergism able to increase the photocatalytic efficiency [18,19].

Hybrid composites based on TiO_2-SiMgOx have been deeply characterised in previous articles and their photocatalytic performance evaluated for the photooxidation of trichoroethylene as a model VOC in gas phase [20] [21]. The effect of synthesis parameters, such as the temperature treatment and the catalyst configuration (incorporated vs. coated materials), on the textural and physicochemical properties was investigated. From these studies it was concluded that the so-called *incorporated materials* treated at 500ºC led to the optimum photocatalyst configuration. The "corncob like" structure of the silicate fibres decorated by TiO_2 nanoparticles allows the migration of non desirable reaction intermediates into the adsorbent promoting the TCE mineralization. Controlling the gap between the external surface of the TiO_2 layer, where the photocatalytic process occurs, and the adsorbent functionality, high selective photocatalysts can be designed.

In this work the performance of plate-shape TiO_2-SiMgOx hybrid composites ~~easily handle~~ has been analysed under sun irradiation conditions. We report results from a series of experiments recorded on a daily basis from June to October in Madrid, Spain. The evolution of the photocatalytic activity with UV irradiation in continuous mode has been recorded under different operating conditions i.e. total gas flow, VOC concentration and water vapour content. Different parameters such us the photonic efficiency, and the effect of the solar irradiance on the formation of reaction products have been further discussed.

2. Experimental section

The details related to the preparation of the photocatalyts are described elsewhere [20, 21]. Briefly, the plates were prepared by extrusion of ceramic dough consisting of $SiMgO_x$, TiO_2 and water. Once the plates were extruded they were dried at 25ºC for 168 hours, at 110ºC during 24 hours and finally thermally treated at 500ºC for 4 hours.

The photocatalytic experiments were conducted under sunlight irradiation conditions and in continuous flow using Pyrex glass tube reactors placed on the focal line of a CPC collector (latitude 40º27' N, longitude 3º44' W). The two CPCs were mounted on a fix platform tilted at 40º (local latitude) and oriented to the south A scheme of the experimental setup location is depicted in **Figure 1.** Two glass reactors (160 cm length, 32 mm external diameter, 29 mm inner diameter) were used. The photocatalyst was placed in one reactor where the photocatalytic process was monitored. The other reactor was empty to detect any contribution of the photolytic process. Rectangular ceramic plates of 2.9 x 2.5 x 0.2 cm (length x width x depth) were fixed with two Teflon grids in the centre of the reactor with an angle between plates of 45º to favour the diffusion of the pollutant into the active sites (Figure 1). The total photocatalysts volume was 35 cm^3 and only ¼ of the reactor length was used. From all the solar irradiation arriving to the collector, only the UV irradiance (required to activate TiO_2) was monitored, using a a UV sensor GaAsP photodiode with a spectral response range between 260-400 nm with a peak sensitivity wavelength at 370 nm (Hamamatsu). The relative humidity and the temperature were measured with a RH sensor (HIH-4000 series from Honeywell) and a T-type thermocouple placed inside the reactor. Trichloroethylene, supplied from a cylinder (Air Liquid) and compressed air, free of moisture and CO_2, were used to feed the reactor. The desired water vapour concentration was obtained by forcing an air stream to pass through a saturator vessel filled with water at controlled temperature.

The flow rate of each gas line was controlled by electronic MFC Brooker units and the evolution of the reactants and reaction products was monitored by a Fourier Transform Infrared (FTIR) Nicolet 5700 spectrometer, provided with a temperature controlled multiple reflection gas cell (2 m optical path). The temperature of the gas cell was set at 110ºC and the spectra were collected by accumulating 64 scans with a resolution of 2 cm^{-1}. The analysis of the reaction products was performed by following the evolution of the representative vibrational bands of the desired molecules at the following wavenmumber: TCE (965-903 cm^{-1}), CO_2 (2435-2233 cm^{-1}), $COCl_2$ (1873-1780 cm^{-1}), CO (2231-2027 cm^{-1}), HCl (2885-2662 cm^{-1}), DCAC-dichloroacetylchloride (1114-1037 cm^{-1}). The actual concentration of TCE, CO_2 and $COCl_2$ was evaluated against calibration mixtures provided by Air Liquid.

The experiments were conducted varying the total flow between 1 - 4 L min^{-1}, the TCE concentration between 130-400 ppm and the relative humidity between 0-80%.
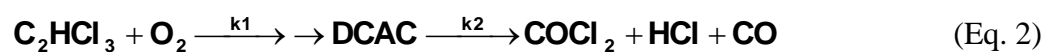
3. Results and discussion

The hybrid structured material selected for this study, with a TiO_2:SiMgOx ratio 1:1 was treated at 500ºC. Its surface area was 153 m^2 g^{-1} with a total pore volume of 0.62 cm^3 g^{-1} displaying a mesopore structure and mean pore size around 44 nm. The strong reduction of the photocatalytic activity observed for samples treated at higher temperature, was ascribed to features such us the severe loss of OH surface groups, the reduction of the surface area and the pore volume and the growth of TiO_2 anatase crystal size; nevertheless, it was observed that the presence of the silicate inhibited the transformation of TiO_2–anatase to rutile [20] [21]. On the other hand, the samples treated at lower temperature presented a poor mechanical resistance that made them non suitable for practical use.

A typical experimental procedure to evaluate the photocatalytic performance of this composite under sunlight irradiation conditions is represented in **Figure 2.** The evolution of the concentration of reactants and products with the temperature and the UV radiation and temperature was monitored during 28 hours; these parameters were monitored during all the period in order to detect adsorption or desorption processes assigned to the temperature increase by effect of the sunlight irradiation. For this set of experiments 150 ppm TCE and 1 L·min^{-1} were selected as a reference operating conditions. After the stabilization of the TCE concentration on the reactor overnight, the TCE concentration in by-pass was checked and then the gases were fed again into the reactor that contains the photocatalyst. From 2 mW cm^{-2} to 4 mW cm^{-2} solar irradiance, total TCE conversion was achieved during seven consecutive hours.

A moderate increase of the concentration of TCE was recorded during the dark period. Remarkably, the value of the concentration of the TCE recorded during the dark period was well below the initial TCE concentration. This is due to the adsorption capacity of the composite. After the dark period, the solar irradiance and temperature increased along with a strong TCE desorption process accompanied of its total photodegradation. Furthermore, it should be remarked that even at low UV irradiation conditions (*i.e.* 0.7 mW cm^{-2}) a TCE conversion value as high as 50 % can be attained.

CO_2 was the main reaction product detected under these experimental conditions. Even if the experiment was performed in the absence of water vapour, the main reaction is that shown in Eq. 1 with the hydroxyl groups present in the composite. The chlorine radicals produced during the reaction contribute to increase the reaction rate [22] [23]. This justifies the faster reaction rates as compared to other VOC molecules such as toluene and benzene or other chlorinated compounds

with less Cl atoms. Side reaction pathways also take place and the formation of $COCl_2$ and DCAC (Eq. 2) was observed, according to previous results [22] [24].

$$C_2HCl_3 + \frac{3}{2}O_2 + H_2O \rightarrow 2CO_2 + 3HCl \qquad (Eq.\ 1)$$

$$C_2HCl_3 + O_2 \xrightarrow{\ k1\ } \rightarrow DCAC \xrightarrow{\ k2\ } COCl_2 + HCl + CO \qquad (Eq.\ 2)$$

3.1 Effect of the UV irradiation on the photocatalytic activity

Temperature changes along the day may affect the adsorption-desorption properties of the photocatalysts. Therefore, the variation of the TCE conversion and reaction products formation was analyzed during increasing (sunrise) or decreasing (sunset) solar irradiance periods. Desorption processes are favoured with the increasing temperature, so they are expected to dominate during the sun rising period. The opposite is true during the sunset period.

The results obtained at 2.5 L min^{-1} for different TCE inlet concentrations are represented in **Figure 3**. Two well defined branches with different slopes were identified. When the irradiation rises, the TCE conversion progressively increased until a maximum was reached. Above this value the solar irradiance went down and the reaction rate decreased following a different trend. The changes of temperature along the day had an important influence on the adsorption-desorption phenomena. A maximum conversion near 80% for 150 ppm was obtained and progressively decreased with the TCE amount. In experiments performed with 1 L min^{-1} gas flow, total conversion were reached with TCE concentration values as high as 500 ppm at 3.4 mW cm^{-2} irradiance (see section 3.2).

The changes in the concentration of CO_2, $COCl_2$ and DCAC were also monitored (**Figure 4**). As expected, the concentration of these species increased with the solar irradiance. This trend was fulfilled for the three inlet concentration studied. The reaction rate results were similar in all cases suggesting that those experiments are recorded in the region limited by the number of active sites available. From that point, the slight decrease of the CO_2 concentration at 650 ppm lay within the experimental error. Whereas the concentration of CO_2 is independent of the branch analysed, the slight loop observed for the evolution of the DCAC and $COCl_2$, indicates that these compounds can be adsorbed or desorbed depending on the solar irradiance these compounds can be adsorbed or desorbed depending of the actual reactor temperature during the solar heating period.

3.2 Effect of TCE inlet concentration and solar irradiance

The photonic efficiency is usually calculated based on the removal rate of the pollutant. In this case, and because of the contribution of the adsorption-desorption phenomena in the overall process, it is

The results obtained for the three TCE inlet concentrations selected are represented in **Figure 5** .. The photonic efficiencies in air for the treatment of pollutants are higher than those found in water, where values do not exceed 1%. In the UV irradiation range studied, the photonic efficiency remains stable with both the solar irradiance and the TCE as it will be explain below. Consequently, and due to the high concentration of pollutant studied, the reaction rate is limited by the number of active sites available on the photocatalyst, as it was previously observed, and therefore independent of TCE concentration.

Taking into account that an important amount of TCE was adsorbed, CO_2 selectivity was estimated considering the main reaction products detected instead of the TCE eliminated, according to equation 3. Other minority products generated besides CO_2 and $COCl_2$, such as DCAC or CO, were not considered significant.

$$S_{CO_2} = \frac{CO_2}{CO_2 + COCl_2} \cdot 100 \tag{Eq.3}$$

The set of data obtained at a solar irradiance value of 2.6 mW cm^{-2} for the two gas flows and TCE concentration range studied are shown in **Figure 6.** As discussed above, total TCE conversion was achieved at 1 L min^{-1} and TCE concentration values between 100-450 ppm. A moderate activity loss is observed at higher flow rates. At equal TCE conversion, a higher TCE molar concentration implies a decreasing in the selectivity to CO_2, at expenses of a higher formation of $COCl_2$. This result was in fact previously observed at laboratory scale with the same photocatalyst operating with artificial UV irradiation [20]. The results suggest that at high TCE concentration the oxidation to $COCl_2$ is favoured through the formation of DCAC according to Ec. 2.

3.3 Effect of gas flow rate

A set of experiments recorded by modifying the total flow from 1 to 4 L min^{-1}, equivalent to a residence time between 0.53-2.1 s, calculated as the ratio between catalysts volume and the total flow feed into the reactor, was carried out in order to define the optimum operating conditions of the system. The variation of the TCE conversion and the concentration of the main reaction

products (CO_2, $COCl_2$ DCAC) as a function of the solar irradiance are represented in **Figure 7** and **8,** at sunset conditions. Total TCE conversion was achieved up to 2 L min^{-1} at UV irradiation values over 3 mW cm^{-2}. As expected higher conversion values were obtained at higher residence times, however the increment of the photocatalytic activity with irradiance becomes progressively attenuated with irradiance. At low UV irradiation 40 % of TCE was eliminated by adsorption, increasing the operating time of the photocatalytic system. Accordingly, the formation of reaction products is poor. For the lowest residence time studied an appreciable reduction of the photocatalytic performance was recorded; however even at these severe reaction conditions near 40 % of TCE was eliminated.

According to the literature, the concentration of CO_2 increases progressively with the solar irradiance, being attenuated at higher photonic flux. For the lowest residence time this curve can be reproduced assuming a dependence with irradiance of $I^{0.66}$, similar to those found for 2-propanol in the gas phase [25]. In this case, the rate of CO_2 formation did not reach a constant value and gradually increased due to the transformation of reaction intermediates into CO_2. At low residence time and solar irradiance, the variation of the photoactivity is almost linear, becoming independent above 3.0 mW cm^2 [26].

Concerning the formation of non desiderable products, two different situations were appreciated. At UV irradiation <1.5 mW cm^{-2} a linear relationship independent of the total flow was observed. At >1.5 mW cm^{-2} the slope of the curves changed. It is specially relevant the behaviour observed for the DCAC at the highest residence time. For this compound a curve with a maximum around 2 mW cm^{-2} was observed, coincident to the point in which total TCE conversion was attained. As it was explained before, TCE oxidation goes through the formation of DCAC in a first step that is further oxidised to $COCl_2$ (Eq. 2). The results obtained indicate the influence of the UV irradiation in the formation of reaction intermediates and therefore, in the product selectivity. When total TCE conversion is achieved the excess of energy arriving to the reactor promotes the direct reaction pathway to produce CO_2 (Eq. 1).

The variation of the photonic efficiency with the solar irradiance at difference total flows was estimated (supporting information). According to the literature, an exponential decay of this parameter was observed with the UV irradiation, becoming independent at high solar irradiance [25]. A soft increase of the photonic efficiency with the total flow was observed up to 3 L min^{-1} [15]. It is reported in the literature that the presence of a high amount of reactive molecules attenuated the recombination rate of the photo-produced charge carriers; however this may not be

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the scenario for this case. Experimental errors arising from the complex experimental setup may explain, at least partly, this behaviour. For the experiment performed at 4 L min^{-1} the photonic efficiency decayed becoming independent of the solar irradiance within the studied range. These results could be explained by the development of preferential flux lines in the reactor, with important mass transfer limitations hindering the adsorption of the reactive gas molecules onto the active sites. The results discussed above show that there is room to improve the performance of the photocatalyst by optimizing its distribution inside the reactor. Although the photonic efficiency decays with the solar irradiance, in the case of continuous reactors, the conversion must be maximized and then high irradiance is required to increase the degradation of the pollutant.

Important differences between the reactor configuration used in previous studies [17], where TiO_2 was immobilised into glass support, and the present configuration are to be highlighted. In the former, a compact fix bed reactor filled with Rasching rings was selected; this type of configuration shows high pressure drop and gas turbulence. In the configuration reported in this work, and in order to irradiate the maximum surface of the opaque plates, only 17% of the reactor volume was filled; thus, an important fraction of the reactor body was empty leading to a low pressure drop The contact between the gas and the photocatalyst is, therefore, not as good as in the former case and flow preferential lines can be developed along the reactor. Another important difference between both configurations is that in this case both photocatalytic and adsorption process occurs simultaneously on the hybrid photocatalyst, being negligible in the first case due to the low TiO_2 loading. In fact, this work demonstrates that these aspects play a key role when materials with a high surface area and porosity are selected for the abatement of pollutant both in air or in aqueous phase.

3.4 Influence of water vapour concentration

Finally, the influence of the water vapour concentration in the TCE conversion and the CO_2 selectivity was analysed (**Figure 9)**. The TCE conversion was slightly modified up to 20 % R.H and then sharply decreased due to the competitive adsorption of the water molecules and TCE for the same active sites. It is reported in the literature that the addition of low water vapour content reduced the $COCl_2$ formation [27][28]. Our results show that only a slight increase on the CO_2 selectivity was attained with a 20% R.H. maintaining the TCE conversion; although an important fraction of $COCl_2$ was detected. These results are in line with those obtained by Lo et al. [29]. These author also detected important quantities of $COCl_2$ at high relative humidity conditions. The overlapping between $COCl_2$ and H_2O signals in the region of the spectra analysed, could be the

responsible of a wrong analysis of the results. Besides, at high water vapour content the water signal overlaps with those of CO, DCAC, and CO_2. For the correct analysis of the data a proper water signal subtraction is required. Other alternatives, such as the increase of the residence times, or the use of caustic scrubbers [30], should be employed to improve the selectivity to CO_2 and reduce the formation of non desirable reaction products.

Conclusions

The combination of TiO_2 and SiMgOx in porous ceramic plates, working under sunlight irradiation conditions using a CPC collector, has been proven as an effective technology for treating large gas volumes with high concentration of pollutant in continuous mode, using a removable energy source. These systems are easily handled, indispensable for industrial applications. The combination of an adsorbent and a photocatalyst in the same composite widens the operating conditions window of the system. At low irradiation conditions, the adsorbent part of the composite dominates the process retaining the largest amount of the TCE fed into the reactor. Under UV irradiation conditions, the photocatalytic function works restoring the adsorbent capacity, promoting the elimination of the VOC molecule and reaction intermediates. An important influence of the UV irradiation on the CO_2 selectivity at total TCE conversion was observed, indicating that at these conditions the excess of photons favours the direct reaction pathway to produce CO_2. Even if only 17 % of the reactor volume was used, excellent results were obtained. The modification of the total flow from 1 to 4 $L \cdot min^{-1}$, keeping constant the TCE concentration at 150 ppm, indicated that the photocatalyst was able to treat up to 1.0 $L \cdot min^{-1}$ ~~from 12:00 h to 19:00 h (Madrid, Spain)~~ equivalent to at solar irradiance values above 2.0 mW cm^{-2} using 35 cm^3 of photocatalyst volume with conversion closed to 100%.

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Figures

Figure 1. Experimental reactor setup used for the photocatalytic test and front view of the photocatalyst plates distribution inside the reactor
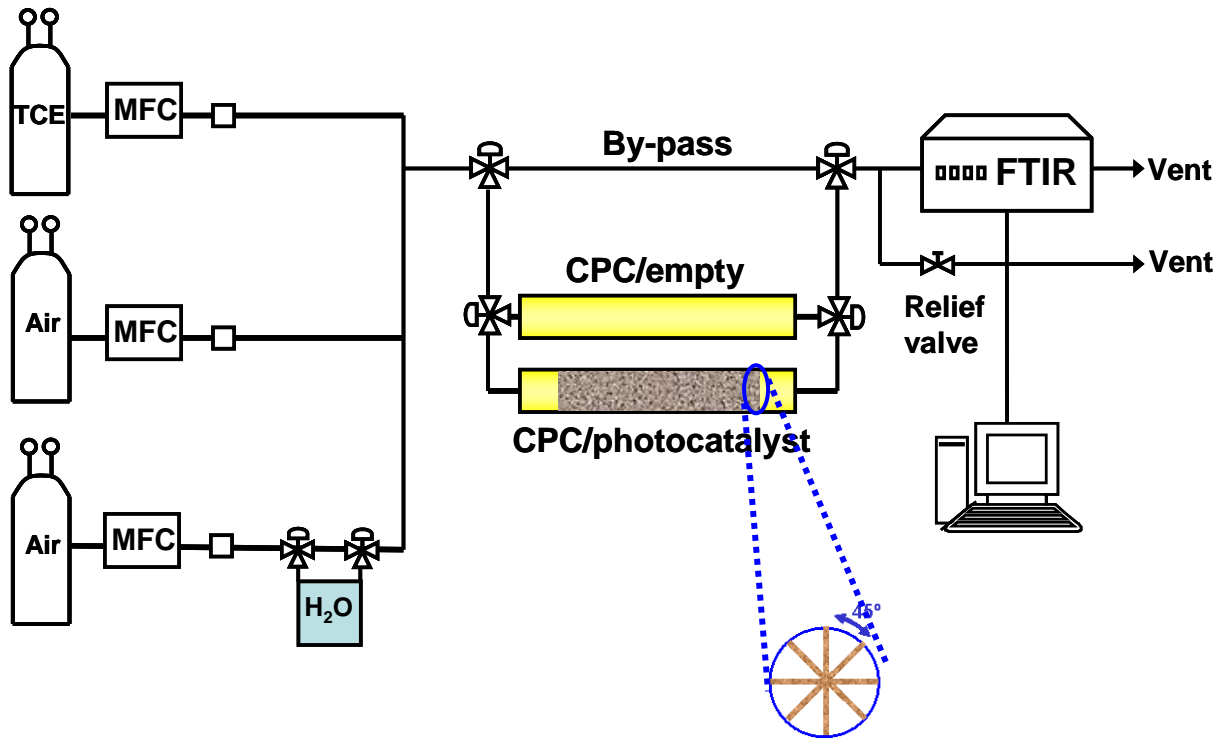
Figure 2. a) Variation of the TCE concentration and CO_2, $COCl_2$ formation, b) temperature and UV irradiation during a day-night cycle for the TiO_2-SiMgOx hybrid composite. Total gas flow = 1 L min^{-1}, [TCE] = 150 ppm, air =gas balance.
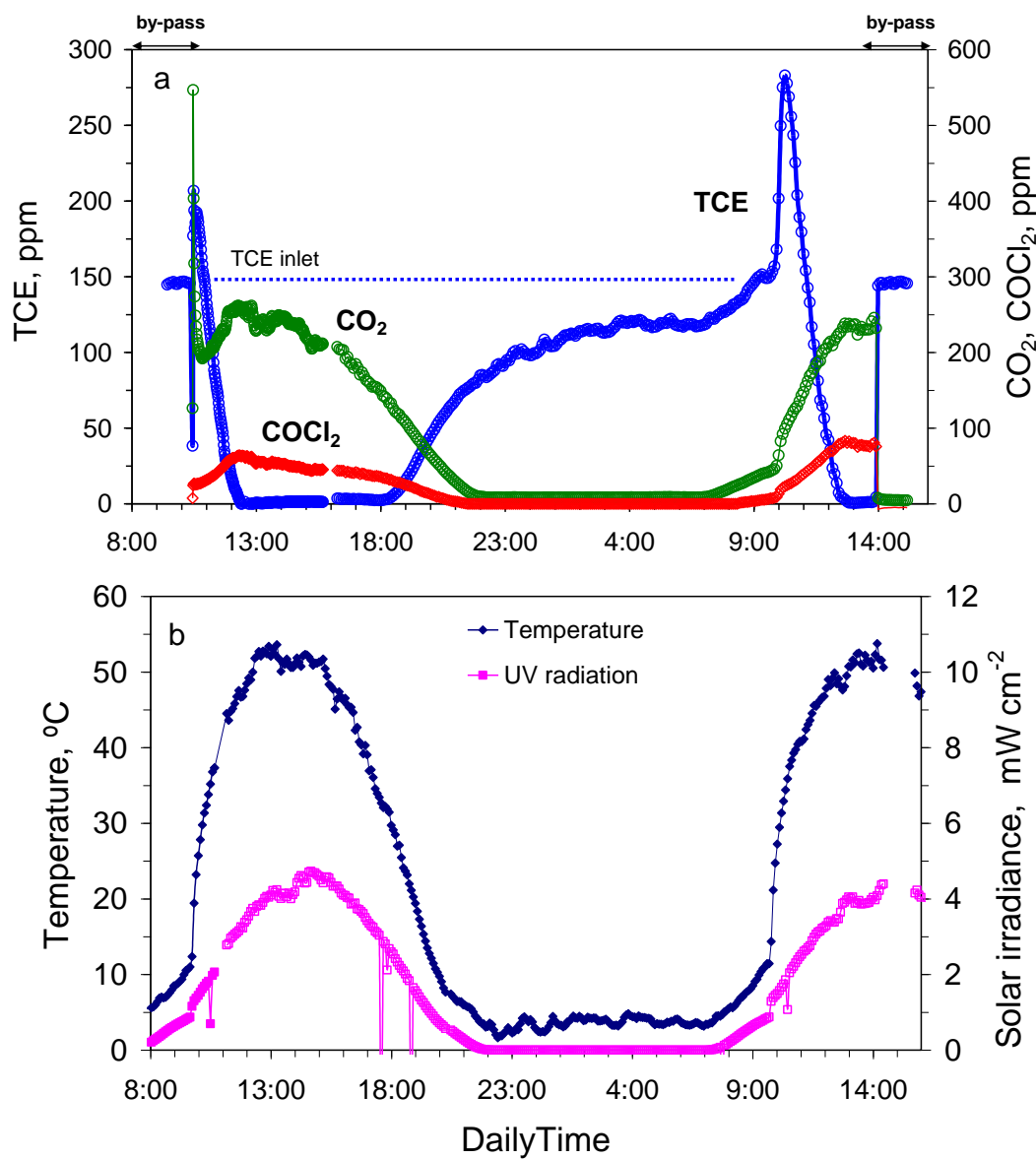
Figure 3. Variation of the TCE conversion when the UV irradiation rises ($\rightarrow$ morning) and falls ($\leftarrow$ afternoon) at different inlet TCE concentration: (O) 150 ppm, ($\square$) 300 ppm ($\triangle$) 650 ppm. Total gas flow: 2.5 L min^{-1}.
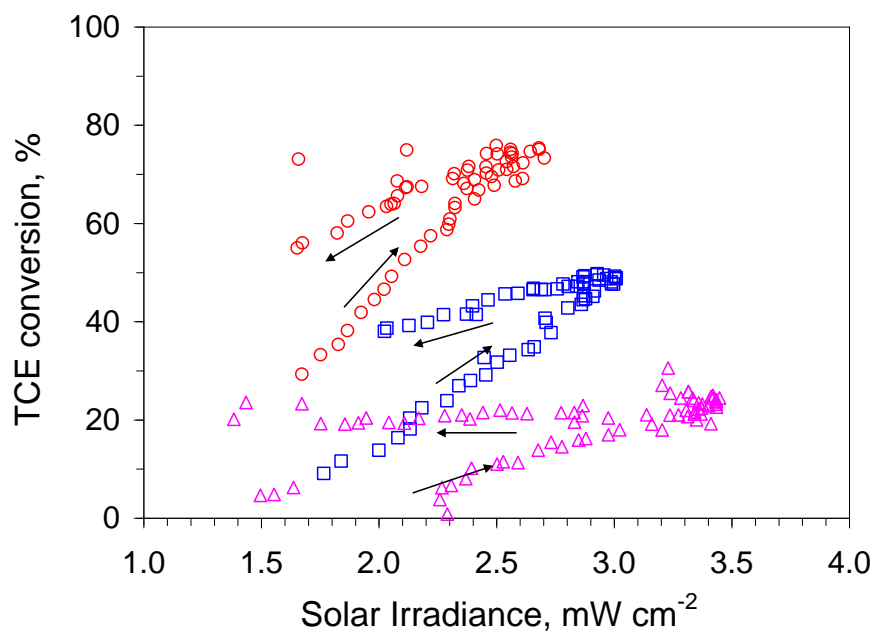
Figure 4. Evolution of the CO_2, $COCl_2$ and DCAC amounts with UV irradiation for 2.5 L min^{-1}: (O) 150 ppm, (□) 300 ppm, (△) 650 ppm.
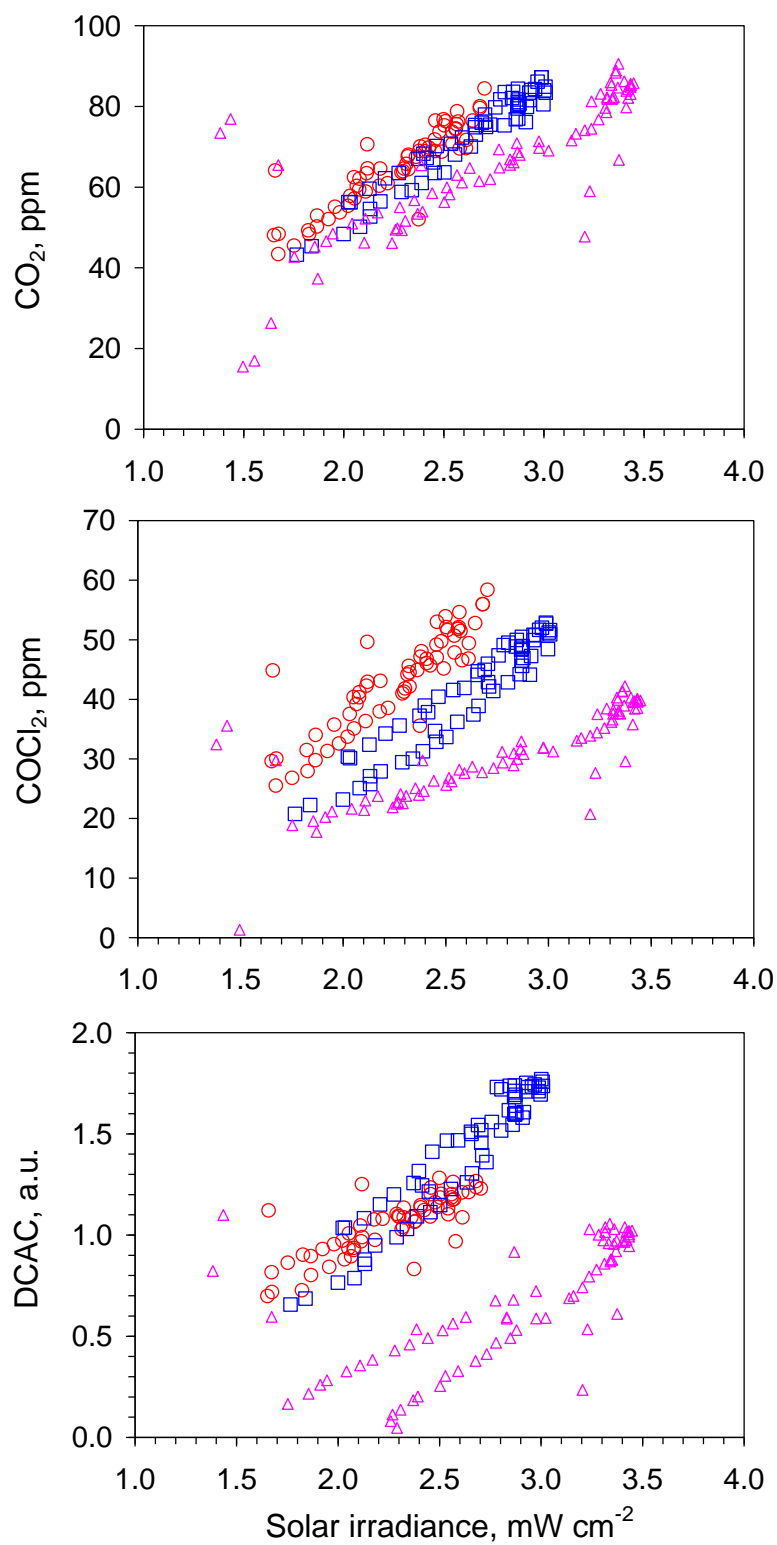
Figure 5. Photonic efficiency, based on the CO_2 production rate, with UV irradiation respect to CO_2 formation rate at different TCE concentration: (O) 150 ppm, (□) 300 ppm (△) 650 ppm. Total gas flow: 2.5 L min^{-1}.
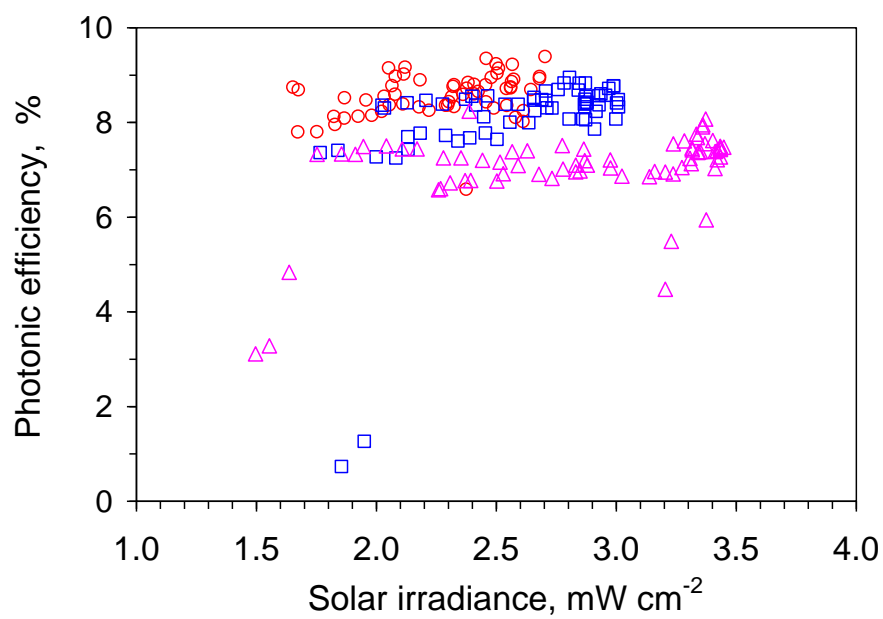
Figure 6. Variation of TCE conversion (close symbols) and CO_2 selectivity (open symbols) with TCE concentration at 2.6 mW cm^{-2} UV irradiation at sunset conditions for: (●, ○) 1 L min^{-1}, (■,□) 2.5 L min^{-1}.
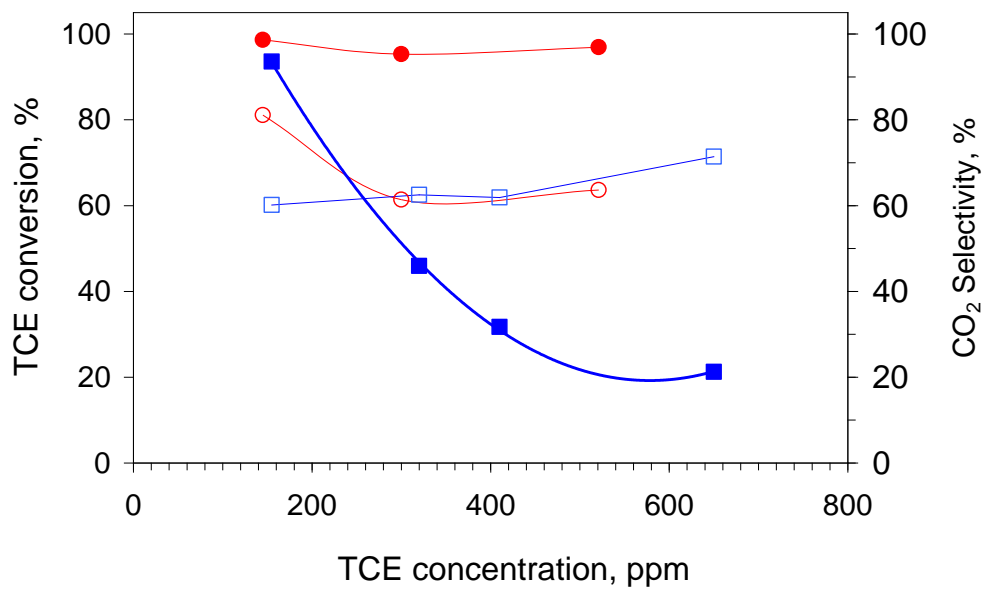
Figure 7. Variation of the TCE conversion with the UV irradiation for different total flows at sunset conditions: 1 L min^{-1} (○), 2 L min^{-1} (□), 2.5 L min^{-1} (◇) and 4 L min^{-1} (△). [TCE]$_{inlet}$= 150 ppm.
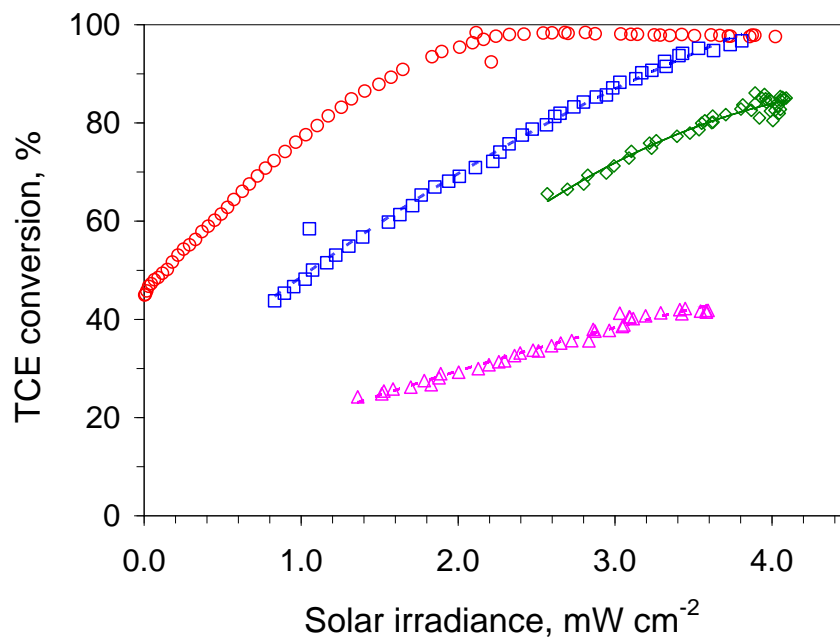
Figure 8. Variation of the main reaction products detected in the reactor outlet as a function of the UV irradiation at sunset conditions for different total gas flow: 1 L min^{-1} (○), 2 Lmin^{-1} (□), 2.5 Lmin^{-1} (◇) and 4 L min^{-1} (△). [TCE]$_{inlet}$= 150 ppm.
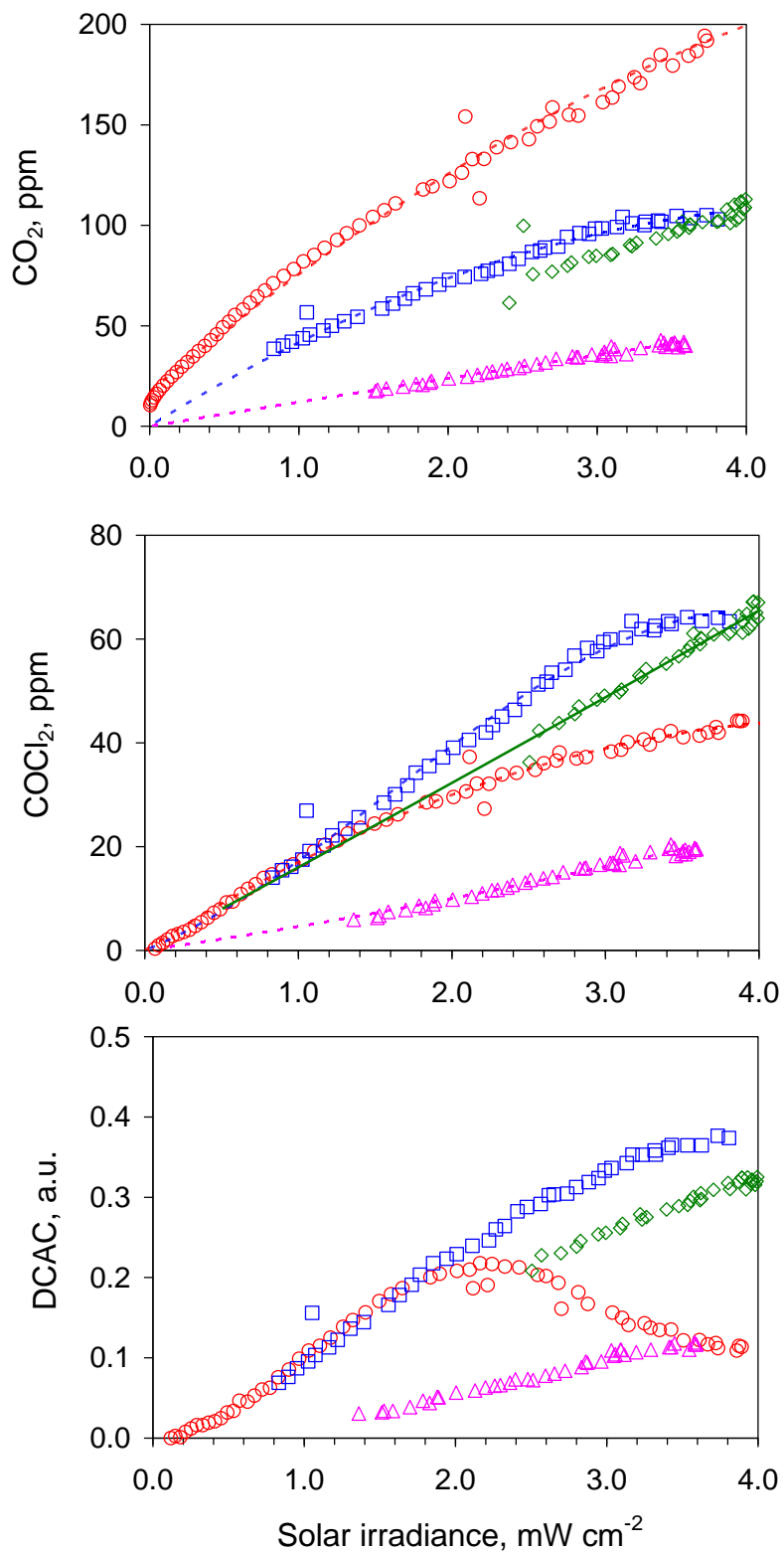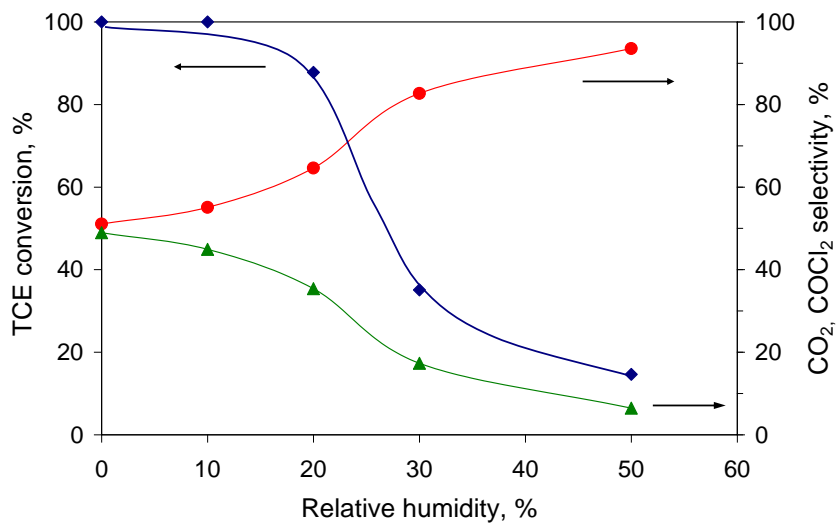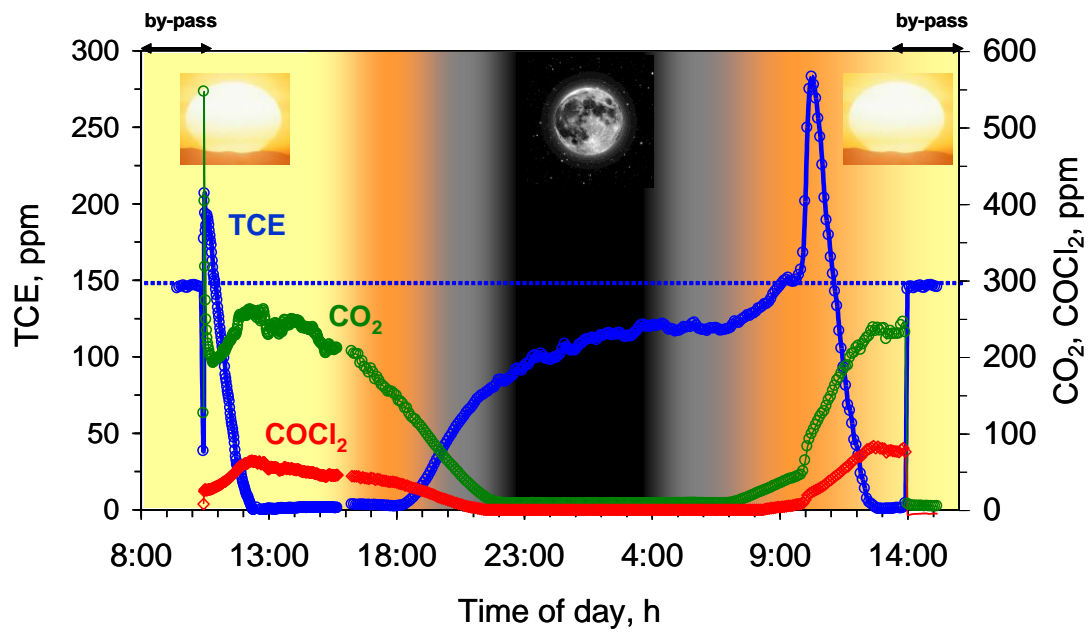
Figure 9. Effect of water vapour content on the TCE conversion ($\blacklozenge$) and selectivity to CO_2 ($\bullet$) and $COCl_2$ ($\blacktriangle$). Operating conditions: UV irradiance: 2.6 mW cm^{-2}, [TCE]$_{inlet}$ = 150 ppm, total gas flow 1L min^{-1}, RH: 0-50 %.

Research highlights

The photocatalytic performance of TiO_2-SiMgOx hydrid composites is evaluated for the degradation of tricholoethylene in gas phase under sun irradiation conditions, with a CPC reactor.

A combination of the adsorbent and the photocatalyst widen the time operating window of the system to low irradiance conditions.

The bifunctional system is able to treat up to 1 L min^{-1} in continuous mode with total trichloroethylene degradation for 2-4 mW cm^{-2} solar irradiance.

Supplementary Material