



Acetylene photocatalytic oxidation using continuous flow reactor: Gas phase and adsorbed phase investigation, assessment of the photocatalyst deactivation

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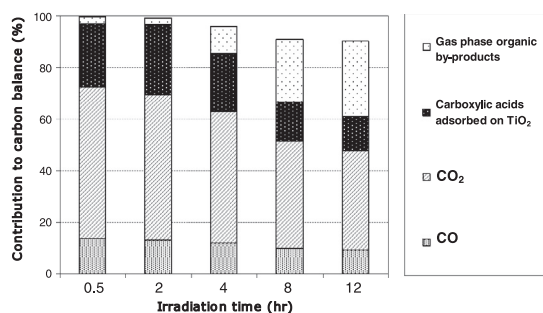
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HIGHLIGHTS

- Simultaneous characterisation of the gas phase and adsorbed phase by-products.
- Evidence of photocatalyst deactivation due to adsorbed carboxylic acids.
- Recovery of the oxidation efficiency using regeneration sequences.
- Long term efficiency using the cyclic treatment/regeneration approach.

GRAPHICAL ABSTRACT

Contributions of CO, CO₂, adsorbed carboxylic acids and identified gas phase organic intermediates to the carbon balance as a function of irradiation time during the photocatalytic dynamic flow treatment of acetylene.



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ABSTRACT

Acetylene, used as a model volatile organic compound (VOC), is submitted to photocatalytic oxidation. This study is based on the simultaneous characterisation of: (i) the gas phase at the reactor outlet; (ii) the adsorbed phase on the photocatalytic media. Experiments are performed in a continuous flow reactor, and analytical procedures have been developed to identify and quantify the gaseous and adsorbed side-products. The photocatalytic media consists in P25 Degussa TiO₂ nanoparticles deposited on glass fibres. First, the process efficiency is investigated through C₂H₂ conversion rate and mineralisation. The treatment performances tend to decrease with time regarding conversion and mineralisation. Then, the oxidation process is investigated through gaseous and adsorbed by-products. Three carboxylic acids have been quantified in the adsorbed phase during oxidative treatment; their temporal evolutions are determined. Their contribution to the carbon balance is discussed. It is evidenced that their adsorption on the photocatalytic media leads to a saturation of the surface. Formaldehyde, glyoxal and formic acid are quantified in the gas phase. Their cumulative temporal profiles and their contribution to the carbon balance confirm the hypothesis of a surface deactivation. The decrease of the process performances with time and the increase of gaseous by-products are correlated with the photocatalyst coverage by adsorbed acids. Carbon balances calculated for various treatment times, give an overview of the process evolution. The regeneration of the photocatalyst surface is possible under synthetic air; 80% of the adsorbed

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compounds are mineralised. The performances of a cyclic procedure (treatment/regeneration) are evaluated. This approach preserves the photocatalyst performances and ensures a mineralisation of 85% of the converted acetylene.

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1. Introduction

Heterogeneous photocatalysis performed on TiO_2 is extensively investigated and developed to remediate environmental pollution. After water purification [1], researches rapidly focused on photocatalytic oxidation of volatile organic compounds (VOCs) present in the air. The oxidation mechanisms of several types of VOCs have already been investigated. Linear or saturated volatile organic compounds, such as hexane [2], heptane [3], octane [4], and isobutane [5] can be removed from gas phase by heterogeneous photocatalysis. Oxygenated VOCs, such as alcohols [6,7], or ketones [8–10] can be degraded by UV activation on TiO_2 . Most of the alkenes have been studied too, and irradiated TiO_2 is able to lead towards a complete mineralisation of the initial pollutants, mainly under static batch reactor treatment. Simple molecules, such as ethylene [11] or 1-butene [12], as well as complex and halogenated molecules like trichloroethylene can be mineralised [13,14] under precise experimental conditions. In addition, UV-irradiated TiO_2 is able to mineralise organic pollutants containing a triple carbon–carbon bonding like acetylene [15]. Authors report that, under static conditions, the complete mineralisation of the alkyne can be achieved.

However, most of the experiments are performed using batch reactors, meaning that the same volume of gas is submitted to the photocatalytic treatment during several hours, or, until the complete mineralisation of the initial pollutants. Thus, considering this type of process, the contact time between the photocatalyst and the compounds to be treated is not a limiting parameter. As assessed by Mills and Le Hunte [16], batch irradiation systems are perfectly suitable for kinetic investigations of the photocatalytic reactions, however, photocatalytic treatments performed on real effluents have to be investigated under flowing conditions which is the best approach to mimic real air treatment systems [17]. Therefore, the contact time between TiO_2 and the VOCs is typically lower than 1 s. As recently reported by Destailats et al. [18], typical values of realistic residence time of VOC in the vicinity of the photocatalyst on a single pass range from 30 to 160 ms, depending on the photocatalytic media geometry and experimental conditions. Consequently, the experimental setup used in this study is a continuous flow reactor which aims at making closer fundamental laboratory experiments to typical treatment conditions.

Under flowing conditions, several authors have highlighted the fact that a complete purification of the air stream by photocatalytic systems is hardly achieved [19,20]. The removal of the initial pollutant may be incomplete, depending on the contact time between VOCs to be treated and the photocatalyst. Destailats et al. [18] underlined the fact that an extended reaction time window, at a lower recirculation rate, allowed for a more complete oxidation reaction. As a result, various by-products can be released downstream the purification systems depending on the process parameters. From an indoor air quality point of view the performances of VOC photocatalytic treatment cannot only be evaluated through the abatement of primary pollutants. The innocuity of the treatment must be addressed through the side products characterisation in the gas phase. This point is taken into account in this work.

Moreover, the performances of continuous flow systems could vary along the system lifetimes, although often reported, mechanisms involved in the photocatalyst activity loss are poorly investigated. The poisoning of the photocatalyst surface by less reactive species is frequently raised as a hypothesis to explain the decrease

of the oxidation process efficiency with time, even using static or batch reactor. Aromatic compounds are considered as the main species leading to the photocatalyst deactivation [21] especially in the presence of multi-VOC effluents. The stability and the planar adsorption mode of aromatic ring on TiO_2 are suggested by authors as the main reasons for deactivation. In parallel, carboxylic acids are frequently pointed out by authors as the species responsible for photocatalyst surface deactivation [22–24] too. The hypothesis of surface deactivation by adsorbed carboxylic acids is praised on by the study of McGill and Idriss [25] who evidenced that the heat of adsorption of formic and acetic acids on TiO_2 ranges from 100 to 150 kJ/mol depending on the surface coverage. However, the quantitative characterisation of the species adsorbed on the photocatalyst surface during the treatment, especially under flowing conditions, remains poorly investigated. Consequently, the investigation of adsorbed carboxylic acids on the photocatalyst surface, carried out in this work, represent a very original approach. In the context of photocatalysis, the side product characterisation is generally limited to the gas phase characterisation, whereas it should also include the adsorbed phase compounds. Indeed, adsorbed species may have a stronger impact on long term oxidation processes than gas phase species since photocatalysis is a heterogeneous process.

The objectives of this paper are: (i) to identify and quantify the reaction intermediates and by-products formed by the photocatalytic process in the gas phase and the adsorbed phase under flowing conditions; (ii) to determine the contribution of the various species into the carbon balance as a function of treatment time; finally (iii) to investigate the deactivation of a photocatalytic continuous flow reactor and to correlate this aging with the nature of the reaction intermediates and by-products (iv) to assess the interest of a cyclic treatment/regeneration approach on a photocatalytic continuous flow treatment.

2. Experimental

2.1. Reactor setup

The general scheme of the experimental setup is reported in Fig. 1. The photocatalytic reactor consists in a quartz tube. Dimensions are: 1.45 cm inner diameter with 0.15 cm thickness. The photocatalytic material is placed inside the reactor, wrapping the inner wall of the tube (10 cm long). Irradiation is performed from the outer part of the Quartz tube by two 24 W PL-L24W/10/4P Philips UV lamps. The emission spectrum of the lamps is centred at 365 nm. The UV photonic flux on the photocatalyst surface ranges from 8 to 10 mW/cm^2 . The temperature inside the reactor during the experiments ranges from 20 to 23 °C.

Gases used for experiments are all provided by Air Liquide. Gas flows are controlled by electronic Brooks mass-flow controllers. The main stream consists in synthetic dry air, flowing through the reactor at 450 mL/min. Acetylene used for experiments is provided by calibrated gas cylinders containing 1000 ppm of C_2H_2 diluted into N_2 . Less than 1 ppm of water and 1 ppm of organic impurities are certified in the gas cylinders. The total and constant gas flow through the reactor is 500 mL/min (450 mL/min synthetic air + 50 mL/min N_2 + C_2H_2). The reactor inlet concentration of acetylene is 100 ppm for all the experiments. The gas residence time into the photocatalytic zone of the tubular reactor is 2.0 s.

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