Kinetic analysis of isopropanol and acetone mixture oxidation by photocatalytic paint

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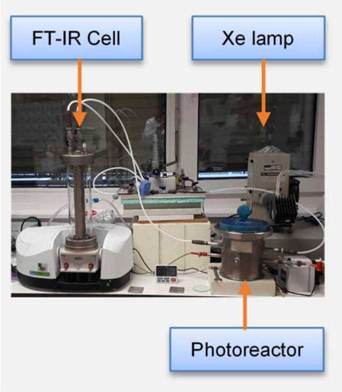

The activity of a photocatalytic paint was evaluated through the degradation of volatile organic compounds mixture in order to achieve the optimization of the air purification system and to approximate to a more realistic situation where airborne contaminants coexist. Isopropanol was primarily used, which is an organic compound that, upon irradiation in contact with a photocatalytic material, oxidizes into acetone. The effect of the environmental conditions, such as relative humidity and irradiance, on the isopropanol oxidation was studied. Additionally, the photocatalytic oxidation of a mixture of isopropanol and acetone was evaluated. A kinetic study of the isopropanol oxidation in the above described system was performed as a first approach to identify synergism or competition between both contaminants .

Introduction

Heterogeneous photocatalysis is an eco-friendly and sustainable technology that addresses environmental remediation and energy production issues. One of its applications is the formulation of building materials containing photocatalysts, in particular TiO_2, offering surfaces with self-cleaning, antimicrobial and air depolluting properties [1].

One of the most commonly used construction materials is the plastic paint, which serves both an aesthetic and protective function for walls. Photocatalytic paints have been developed with inorganic binders or polymeric binders, and their air purification efficiency has been evaluated for the degradation of several model air pollutants. However, these materials have not been applied under more realistic indoor and outdoor environmental conditions considering the coexistence of different pollutants in air. Even more, just few works have evaluated the photocatalytic elimination of mixtures of airborne contaminants [2].

In this work, a photocatalytic paint was evaluated for the degradation of a mixture of isopropanol and acetone. The reaction of the contaminants mixture is analysed as well as the optimal conditions to carry out the air purification process.

Material and Methods

The tested paint consisted in a mixture of water (30% w/w), polymeric resin (33.4% w/w) and dispersive agent (0.6% w/w), while the dispersed solids were the extender ($CaCO_3$, 18% w/w) and carbon doped TiO_2 KRONOClean 7000 (18% w/w).

The employed experimental device (shown in the Graphical Illustration). consists of a cylindrical reactor (1.4 L volume) covered by a quartz glass window, connected through Teflon tubes to a FT-IR spectrometer cell (Perkin-Elmer Spectrum BX, USA) The light source is a 300 W Xe lamp. The infrared part of the spectrum was blocked by an appropriate water filter. Photocatalytic sample was prepared in the form of a thin layer (86 mg of paint) on a 6 cm diameter borosilicate glass plate. The distance between the plate and the Xe lamp was 6 cm. This arrangement resulted in a radiation flux ($q_{w,UV}$) of approximately 18 mW cm^{-2} in the UV range. With the use of neutral filters the radiation flux was reduced to 12.6 and 5.1 mW cm^{-2}. The relative humidity (RH) was kept constant during the reaction by passing air through molecular sieves until a predefined value (between 75 and 30 %). Temperature and relative humidity were measured using a thermohygrometer, which was placed inside the reactor. Each experiment was conducted by injecting liquid isopropanol, acetone, or a mixture of them, which evaporates inside the reaction system (e.g. 8 μL of isopropanol corresponds to 711 ppm in the gas phase, and 8 μL of acetone to 735 ppm). The lamp was turned on after a certain period of time to allow the adsorption equilibrium of the contaminants on the photocatalytic material. The degradation of isopropanol and formation / degradation of acetone were monitored with the calculated area of their characteristic peaks at 951 and 1207 cm^{-1}, respectively, in the IR spectra measured by the FT-IR spectrometer.

The photocatalytic activity of the samples was initially evaluated with the degradation rate constant of isopropanol, adjusted with an exponential function obtained from the resolution of the perfect mixing mass balance in the reaction system and considering a first-order kinetics with respect to the concentration of isopropanol [3]:

$$C_{Iso} = C_{iso,0} \exp\left(-kt\right) \qquad (1)$$

Where C_{iso} is the concentration of isopropanol at a given irradiation time t, $C_{iso,0}$ is the initial concentration of isopropanol prior to irradiation, and k is the first-order degradation constant.

Results and Discussion

The isopropanol was oxidized into acetone and then into several further degradation products. At room temperature the photocatalytic oxidation of isopropanol to acetone is fast, whereas the subsequent oxidation of acetone to CO_2 and H_2O is slower [3].

In Figure 1, the evolution of isopropanol and acetone over time is shown, under conditions of RH equal to 32%, radiation flux of 18 mW cm^{-2}, and injecting a volume of 4 µL of liquid isopropanol and 4 µL of liquid acetone into the reaction space. Upon the contaminants injection, they rapidly volatilize increasing their concentrations in the gas phase. When irradiation begins, the concentration of isopropanol decreases, while acetone is formed (instead of to be degraded), increasing its concentration at a slower rate than the rate of isopropanol degradation (indicating that the photocatalytic degradation of acetone is slow, as previously stated).

Tables 1 summarizes degradation kinetic constants of isopropanol obtained by performing a non-linear regression of the experimental results using Eq. (1) for the different applied operating conditions.

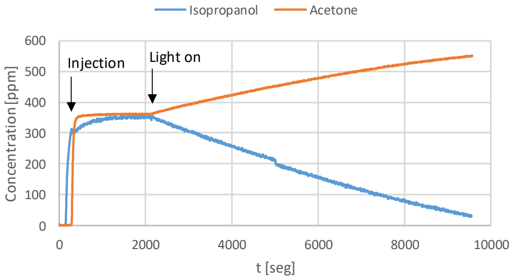

Figure 1. Contaminants evolution during the photoreaction. HR= 32%, q_w=18 mW cm^{-2}, V_{iso}=4 µL, V_{acet}=4 µL

It is observed that as the relative humidity increases, the degradation of isopropanol decreases due to a competitive effect between water and the contaminants for the active sites on the photocatalyst. On the other hand, as the radiation flux decreases, and thus the number of photons available, the degradation constant of isopropanol also decreases. When different ratios of initial concentrations of isopropanol and acetone were evaluated, an increase in the degradation constant of isopropanol was observed as its initial concentration decreased, and the concentration of acetone increased, demonstrating a synergistic phenomenon between both contaminants. On the other hand, when the degradation of acetone alone was tested, its degradation constant was an order of magnitude lower than the isopropanol one for the same reaction conditions.

Table 1. Operating conditions and estimated isopropanol kinetic constants employing photocatalytic paint.

V isopropanol [µL]	V acetone [µL]	HR [%]	$q_{w,UV}$ [mW/cm^{-2}]	k [s^{-1}] x 10^4	R^2
8	0	30.4	18.17	1.05	0.99
8	0	50.3	17.04	0.95	0.99
8	0	75.5	17.04	0.55	0.98
8	0	32.6	12.61	0.61	0.99
8	0	32.0	5.12	0.17	0.99
6	2	32.3	17.8	1.80	0.96
4	4	32.2	18.7	2.32	0.98
2	6	31.2	17.8	6.84	0.99
0	8	32.6	18.7	0.20 (acetone)	0.99

Conclusions

The presence of acetone influences positively on the photocatalytic oxidation of isopropanol, although its degradation is significantly slower than the isopropanol one.

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