Photocatalytic NO$_x$ removal with TiO$_2$-impregnated 3D-printed PET supports
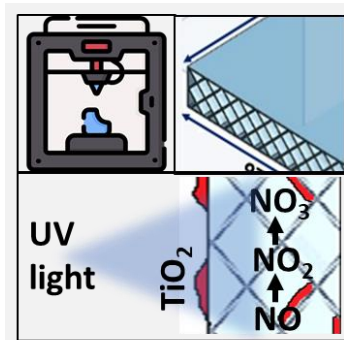
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In this work, the photocatalytic removal of NO$_x$ with 3D-printed supports was studied. The technology consisted of a continuous gas flow phase reactor containing a 3D printed PET support impregnated with TiO$_2$ as photocatalyst. The 3D impregnated supports were characterized by diffuse reflectance spectrometry and SEM/EDS. The effect of several key-factors on the removal capacity were studied: type of PET filament (native, BPET vs glycol-modified, PETG), type of TiO$_2$ (P-25 vs Hombikat UV-100), UV-light source (LED vs tubular lamps) and number of deposited TiO$_2$ layers. The highest NO and NO$_x$ removal were achieved by only one layer of Hombikat UV-100 over PETG supports, irradiating from both sides of the flat reactor with two sets of black light lamps. This work demonstrate that 3D printing is a reliable and powerful technique for fabrication of photocatalytic reactive supports.

Introduction

3D printing, together with computer aided design (CAD), is a powerful tool for the construction of precise geometrically controlled reactors with complex internal structures such as channels of well-defined dimensions [1]. These manufacturing systems involve short production times that can speed up the thinking-designing-production cycle of reactors.

It is well documented that NO$_x$, preponderant species in photochemical smog formation, can be efficiently transformed to nitrates retained in the surface of TiO$_2$ [2].

The aim of this work was to demonstrate the reliability of 3D printing to build-up an efficient heterogeneous photocatalytic TiO$_2$ impregnated gas-phase reactor by exploring the effect of reactor's construction and operation key factors on the NO removal efficiency.

Material and Methods

PET monoliths of 97 mm × 80 mm × 15 mm with transversal square section channels were printed, using a Chimak León 2020 3D printer. Two types of PET filaments were used: native (BPET) and glycol-modified (PETG). Each printed piece was impregnated with TiO$_2$ by immersion in a 20% suspension of the photocatalyst (Hombikat UV-100 and Degussa P-25) at pH = 2,5 continuously ultrasonicated. After 10 min they were pulled out and dried overnight at 50 °C.

Flat test pieces of BPET were also printed and covered with TiO$_2$. These pieces were analyzed by SEM (Quanta Fei 200) and UV-vis-NIR diffuse reflectance spectrometry (Shimadzu 3600+).

NO$_x$ removal experiments were undertaken in a PTFE flat continuous flow gas phase reactor with Pyrex glass tops sealing one TiO$_2$-impregnated support inside. A gaseous 40 ppm NO stream, generated by online mixing of a 1000 ppm NO stream with compressed air, was introduced in the reactor and irradiated by UV light for 3 hours. The UV light sources used were a Thorlabs 525 mA UV LED lamp light and two sets of three Yarlux T5 8 W black light lamps. In each experiment the concentration of NO, NO$_2$ and NO$_x$, were continuously monitored by using a Teledyne T-200 M NO$_x$ analyzer.

The removal efficiency (R^X) of NO, NO$_2$ and NO$_x$ was calculated in mol of each species per gram of TiO$_2$ by integration of the time resolved NO, NO$_2$ or NO$_x$ concentration profiles during the experiments as follows:

$$R^X = \frac{Q}{m \times \phi} \times \int_{t_0}^{t_f} [X] \times dt$$

were R^X is the removal efficiency of X = NO, NO$_2$ or NO$_X$ (μmol X/g TiO$_2$), m is the mass of photocatalyst in the supports (g), Q is the volumetric flow rate (L/min), ϕ is the ideal molar volume (L/mol) and [X] is the concentration of X in ppmv.

Results and Discussion

SEM images of the impregnated supports show that the filament surface is covered by the TiO$_2$ nanoparticles in irregular micro-aggregates that are more concentrated around filament irregularities as valleys or pits. UV-vis-NIR TiO$_2$@PET spectra showed a clear increase in the absorbance around 380 nm with respect to the original PET filament, clearly denoting the photocatalytic potential of the impregnated supports.

In a typical time resolved concentration profile, NO and NO$_x$ concentrations rapidly decreases in the first 5 min after turning on the UV-light source with the gradually increase during the rest of the experiment. This concentration "valley" (see Figure 1) can be ascribed to a first reaction pathway involving adsorbed surface water as an electron acceptor. Then, after surface water consumption, only O$_2$ can act as electron acceptor with reduced efficiency. Additionally, the TiO$_2$@PET supports show a reactivity reduction over time because the generated nitrates can be strongly adsorbed to the TiO$_2$ surface poisoning the photocatalyst. However, the supports

recovered their reactivity after addition of a new TiO_2 layer over the poisoned one: R^{NO} and R^{NOx} went from 51.36 ± 9.06 and 38.75 ± 5.65 μmol/g TiO_2 respectively, to 43.64 ± 15.77 and 40.91 ± 14.13 μmol/g TiO_2, respectively.
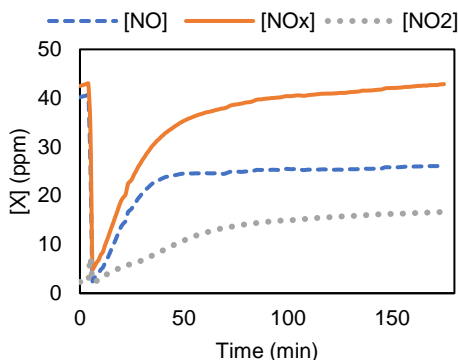

Figure 1. NO, NO_2 and NO_x time resolved concentration profiles with a PETG support with 1 layer of UV-100 irradiated by two sets of black light lamps.

Increasing the number of TiO_2 layers from 1 to 3 resulted counterproductive: for instance, R^{NOx} was reduced by 23% and 30%, when using 2 and 3 layers, respectively. This could be explained by the fact that part of the new TiO_2 aggregates in subsequent layers could cover the pre-existing TiO_2 particles reducing performance of the photocatalyst per mass of photocatalyst. Following experiments were performed with only one TiO_2 layer.

PETG showed lower UV-light absorption efficiency than BPET: 99.9% of the UV intensity is absorbed by a BPET monolith against a 90.4% for a PETG made monolith. This resulted in 2.5 times higher R^{NOx} for PTEG compared with the BPET monoliths.

Pollutant removal was showed to be strongly dependent on the irradiation strategy over a PETG monolith with 1 layer of P-25. Using the two black light lamps arrangements, each one irradiating from one side of the flat reactor, increased R^{NOx} around 300% in comparison to the values obtained with one UV LED light. Both UV-light set-ups present similar irradiance at the surface of the sealing glass windows of the reactor: 3775 µW/cm^2 for both sets of black tubes together and 3300 µW/cm^2 for the LED lamp. Therefore, the main factor that explains the increase in the removal efficiency is a better illumination of the inner structure of the monoliths when they are irradiated from both sides.

Finally, supports impregnated with UV-100 doubled R^{NOx} and quadrupled R^{NO} compared with the ones impregnated with P-25 (Figure 2). This remarkable increase in NO_x removal might be related not only to the UV-100 greater specific surface compared to P-25, but also with the higher amount of surface-retained water [3] that acts as the main electron acceptor in the first minutes of the process. We hypothesize that the rapid conversion of NO to adsorbed NO_3^- promptly saturates the catalyst sites needed for NO_2 to NO_3^- oxidation and this intermediate species escapes from the surface.
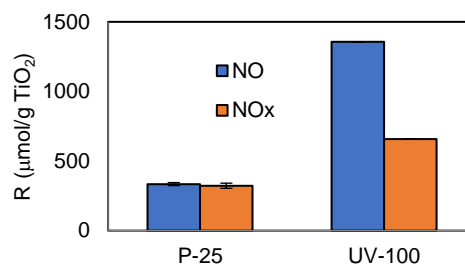

Figure 2. R^{NO} and R^{NOx} for PETG supports impregnated with 1 layer of P-25 or UV-100 irradiated by two sets of black light lamps.

Conclusions

NO_x removal via heterogeneous photocatalysis was successfully achieved using impregnated TiO_2 on 3D printed PET monoliths. The rational approach of our experiments allows us to reach the best conditions for the highest NO_x removal: 3D-printed PETG supports impregnated with only one layer of Hombikat UV-100 and irradiated from both sides with two sets of black light lamps. These results demonstrate the strength and simplicity of 3D printed supports as a potential tool to be used in the photocatalytic removal of gaseous pollutants.

References

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