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Photocatalytic reaction intensification using monolithic supports designed by stereolithography

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ABSTRACT

An original photocatalytic reactor for the treatment of polluted air is designed. The titanium dioxide is supported on various supports that consist in photopolymers and are built using the stereolithography technique and placed in a glass tube illuminated from the outside, while the air containing the pollutant to be removed flows through the glass tube and the photocatalyst support. It is shown that the gas–solid mass transfer plays a role only at the very smallest gas velocities investigated. The global depollution kinetics are then determined for the different geometrical forms of the photocatalyst support and the efficiency of the forms compared.

1. Introduction

During the last two decades, the contamination of air and water by organic pollutants has been becoming a matter of concern of public safety, regarding their harmful effects on human health [1,2]. Intensive traffic [3] and industrial activities are on the origin of outdoors pollutions. While indoors, volatile organic compounds (VOCs) presence is due to the domestic materials and products [4]. Causing sometimes, even at low concentration, the appearance of so called “Sick Building Syndrome (SBS)” [5]. Remediation of such phenomena could be prevented when pollutant sources are inhibited, use of well stabilized materials and better recycling the interior air [6]. Processes of elimination by adsorption and incineration are also of great help [7,8].

Photocatalysis is one of the techniques which have been proposed for reduction of indoor air pollution, as it is an advanced oxidation process which has the advantage of degrading many volatile organic compounds into CO_2 and H_2O [9]. In this process, the catalyst, generally TiO_2, is activated by UV light (<400 nm) and becomes a “redox” system able to react with electron acceptors (O_2, VOCs) and electron donors (H_2O, VOCs). This process requires only standard room conditions (temperature and pressure) with an inexpensive, non-toxic, and stable catalyst showing high photocatalytic activity such as TiO_2 [10]. Furthermore, photocatalysis is well adapted to the treatment of low concentrations (0.1–0.5 g/m^3) at low flow rates.

Many photoreactors such as fluidized beds, packed beds, coated glass tubes [11] and others have been built and tested in order to improve their efficiency.

However, significant work still has to be done in the design of photoreactors so as to make them as efficient and compact as possible in order to install them in relatively inaccessible areas. This work intends to contribute to the intensification of such reactors through the choice of optimal photocatalyst support geometry.

In the present study, TiO_2 has been coated on monolithic supports with different geometries. The supports have been made by stereolithography [12]. The experiments have been carried out in a tubular reactor, in which the coated supports were introduced; the reactor was surrounded by fluorescent tubes emit at λ = 365 nm. An important parameter, which has been considered in this study, is the ratio of the surface of the support to the volume of occupied reactor S/V, which is of importance in the choice of the most appropriate support geometry. In an earlier work, the influence of geometry on the chemical rate has been investigated [13].

In addition, as the catalyst was immobilized on a support, mass transfer limitations could occur [14], so experiments have been carried out to quantify their influence on the photocatalytic activity of the coated supports.

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2. Experimental

2.1. Design and construction of the monolithic supports by stereolithography

Stereolithography is a rapid prototyping technique which enables the fabrication of physical 3D parts directly from 3D models designed by computer-aided design (in our case, CAD Top Solid' Design, Missler Software). Fig. 1 shows the process of stereolithography developed in our laboratory and the principle of building a part.

The software of the stereolithography machine (OptoVue) slices the 3-D CAD model into a series of thin horizontal layers (cross-sections) of typical thickness 100 μm.

An ultraviolet laser (355 nm of Nd:YAG laser) scans the top layer of the photopolymer in a vat, in relation to the build cross-section. The drawing speed of the laser beam is adjusted to 0.46 m/s according to the desired cure depth with an irradiation power of 0.80 W. The first cured layer adheres to a platform, then a fresh liquid resin is coated over the previously solidified layer and the process is repeated until the last layer of the part is built. The object on the platform is then withdrawn from the liquid resin and cleaned.

A post-treatment step is necessary to complete the polymerization of the object, by an exposure to an UV irradiator for a couple of hours. The total time of fabrication varies from a few hours to one day, which permits several geometries to be tested rapidly. This is an advantage when the goal is to optimize the geometry of the support [15].

Using this process, it is possible to build different supports with very complicated structures, which would not be possible using classic mechanical methods. Four geometries of the monolithic support have been designed (Fig. 2), all were made to fill the cylindrical tube of the reactor. The total surface, of each geometry, has been determined on the macroscopic scale from the CAD data.

2.1.1. Geometry 1: Static mixer (Fig. 2a)

The shape of this support might be able to break the flow and to improve mass transfer. It was worthwhile then to consider this geometry in our study. The total surface area of the support was 79 cm^2.

2.1.2. Geometry 2: Double spiral (Fig. 2b)

This shape looks like a spiral. It has the same dimensions as the static mixer but its arrangement in space provides a higher surface area, i.e. 115 cm^2 for the same length, which represents an increase of 45% compared to the static mixer.

2.1.3. Geometry 3: Quadruple spiral (Fig. 2c)

The third shape is basically the same as the double spiral; both are generated by rotation and translation of a diameter (*Double spiral)* or crossed diameters (Quadruple spiral) of the cylinder. The difference is a larger total surface of 145 cm^2.

2.1.4. Geometry 4: Crossed channels (Fig. 2d)

The crossed channels shape is a porous structure (external porosity $\varepsilon = 0.7$) composed of vertical and horizontal crossed channels, which has a total surface of 185 cm^2. The vertical channels allow the circulation of the gas flow whereas the horizontal channels allow the light to reach practically all the support surface.

2.2. Impregnation of the supports

The supports are coated several times by pouring a suspension of TiO_2 Degussa P25 (6 g/L) with a 2 mL syringe. The pH of the suspension in our preparation conditions was 3, which is an optimal pH value to obtain a well-dispersed suspension and small particle size and consequently a larger surface area [16]. The supports are then fixed to a motor and kept continuously in rotation during the impregnation.

After each deposition, the supports are dried with a hot air flow at 50 °C for 30 min, and finally, when the expected mass of TiO_2 is reached, the supports are maintained under the drying flow for a longer time, so as to eliminate all traces of water from the catalyst surface.

In order to compare the influence of the different support geometries on photocatalytic activity, the supports were coated with a thick deposit of titanium dioxide, sufficient for total absorption of the light so that the activity would not depend on the mass of TiO_2. In a previous study [17], the influence of the amount of TiO_2 deposit on the light absorption had been investigated, and the absorption was found to vary with the deposit thickness following

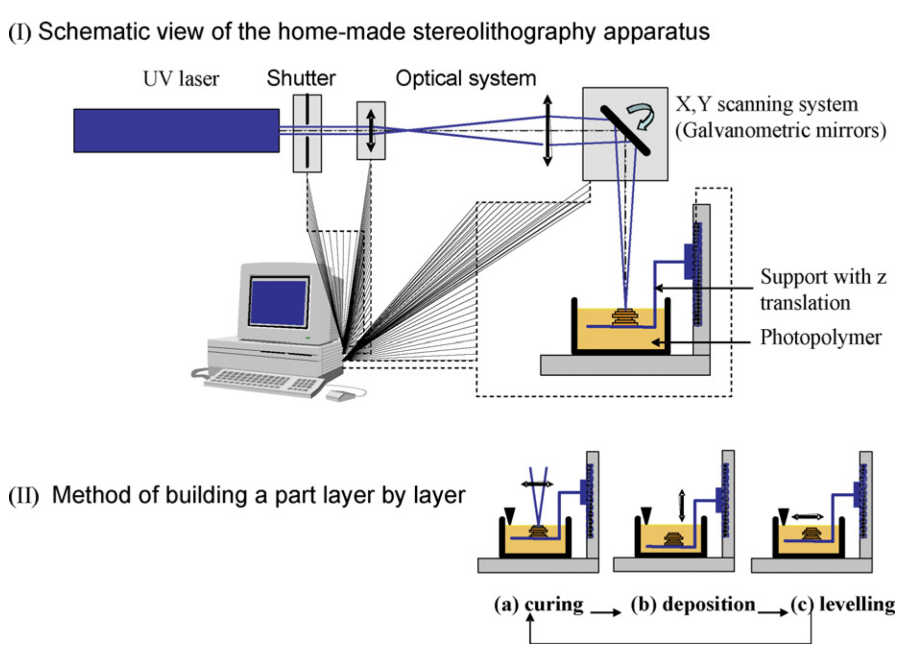

Fig. 1. Principle of the stereolithography process; (I) schematic view of the home-made stereolithography apparatus; (II) details of the manufacture of a part layer by layer: (a) curing of the upper layer by scanning with the laser beam; (b) deposition of a new layer by plunging the support into the vat; (c) levelling of the fresh new layer.