3D solid carbon foam-based photocatalytic materials for vapor phase flow-through structured photoreactors

Shabnam Hajiesmaili, Sébastien Josset, Dominique Bégin, Cuong Pham-Huu, Nicolas Keller, Valérie Keller*

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), European Laboratory for Catalysis and Surface Sciences (ELCASS), CNRS, Strasbourg University, 25 rue Becquerel, 67087 Strasbourg, France

A B S T R A C T

3D solid carbon foams were used as support for preparing photocatalytic materials working in a traversing-flow mode and designing efficient vapor phase flow-through structured photoreactors. The carbon foams were obtained by resin polymerization and pyrolysis treatments starting from a three-dimension structured reticulated polyurethane foam used as a pre-shaped precursor. The 3D solid carbon foam supported TiO$_2$ photocatalysts were characterized in terms of morphology, pressure drop, light transmission ability and static mixer role, and using the vapor phase methanol UV-A photocatalytic oxidation as target reaction. The foam-structured photoreactor benefits from a strong gain of exposed surface leading to an increased surface to reactor volume ratio with a large increase in the TiO$_2$ amount inside the reactor. Further, the improved air-to-surface contact probability ratio induced by the static mixer effect of the foam resulted in a high methanol conversion obtained at a given TiO$_2$ amount in the reactor. The potential of this 3D-structured photocatalytic material for flow-through photoreactors targeting real applications was also highlighted by induced ultra-low-pressure drops resulting from a high porosity and a large cell size morphology.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In parallel to the search for highly efficient photocatalytic materials, the design of high performance photocatalytic reactors remains an important obstacle in the development of photocatalytic processes meeting the requirements for industrial and commercial applications, for treating industrial effluents as well as for targeting a domestic use such as indoor air purification [1]. De Lasa et al. claimed that achieving a successful commercial implementation of the technology will require the optimization of the photoreactor geometry, the type of photocatalyst and the use of radiated energy [1].

Purifying indoor air as well as industrial gaseous effluents is a promising field of applications for photocatalysis, from both preventive and curative points of view. This concerns the treatment of large gas flows with low-pressure drops, and requires simultaneously a good photocatalyst irradiation and an efficient photocatalyst/reactant contact. This aspect remains highly challenging. Many photoreactor configurations are reviewed, including *e.g.* flat plate fluidized bed reactors [2], fluidized bed reactors [3], fixed layer photocatalytic reactors [4], packed-bed reactors [5],

TiO$_2$-coated monolith reactors [6], photoreactors with optical fiber bundles [7] and annular photocatalytic reactors [8]. The annular design is interesting for controlling volatile organic compound emissions in indoor air, since it benefits from a maximal direct irradiation issued from the lamp located inside the inner central tube of the reactor. However, this geometry suffers from a low area of photocatalyst per unit reactor volume, which is restrictive in terms of gas velocity, and only remains of interest for laboratory scale on-flow studies.

Novel designs of photocatalytic reactors are thus expected to be engineered. Studying the interaction between the light, the catalyst and the reactant gas flow, which needs a careful investigation of the UV source, as well as of the reactor configuration, the lamp location, the catalyst type, distribution and impregnation modes, is required [1]. Similarly to thermal catalysis, designing efficient processes should take into account the photocatalytic reactor engineering as a key-aspect.

Porous or multichannel materials, among which honeycomb-shaped monoliths were investigated from both modelling and experimental approaches, have gained interest with the need for a good contact between the air and the photocatalyst at a low-pressure drop [9,10]. Indeed, honeycombs are designed to process high flow rates at low-pressure drops and for positively increasing the surface area to reactor volume ratio and therefore the exposed photoactive surface. However, the monolith-based reactors also

suffer from poor irradiation distribution, due to the location of the irradiation source outside of the monolith and its resulting limited penetration depth within the monolith [11]. One should also note the use of porous pelletized C/TiO_2 microsphere composites for avoiding the drawback related to the use of TiO_2 nanopowder [12].

Recently, Furman et al. studied the influence of the geometry of a monolith (static mixer, crossed channels and star geometry) on the efficiency of photocatalysts for air cleaning [13]. They reported that the geometry has practically no influence on the external mass transfer rate, but influenced the photocatalytic kinetics, with a higher apparent kinetic constant shown by the static mixer geometry, as a result from a higher absorption of photons per unit area of support. Honeycomb-shaped monolith and optical fiber approaches were combined by incorporating optical fibers inside a ceramic monolith [14,15] and took advantages from the remote delivery of photons to the reactive sites of the catalysts.

Thermal catalysis recently showed the growing attention attracted by 3D solid foam structures for use as catalytic support for overcoming some of the drawbacks of 'conventional' packed beds. The high porosity structure (0.60–0.95) reduces the pressure drop along the catalyst bed even at high gaseous space velocity, together with suitable mass transfer properties [16]. Recently, bactericidal silver nanoparticles were anchored on a polyurethane foam, for reducing the *Escherichia coli* contamination in water and targeting low cost drinking water filter applications [17].

Open cell titania foams were obtained by calcining polyacrylamide gels containing titanyl sulfate and urea [18]. The decomposition of the inclusions resulted in the foaming of the polymer body with and an open cellular structure consisting of anatase nanoparticles was obtained after combustion of residual organic components. Activated by UV-A light, the titania foams showed a gas phase acetaldehyde conversion rate about four times greater than that obtained on the TiO_2 P25 reference, whereas a decomposition rate about 2.5 times greater than that shown by fluffy commercial TiO_2 P25 or ST-01 was obtained for the aqueous phase methylblue dye decomposition test reaction. The enhanced performances were attributed to the high accessibility for the target molecules and to the high transparency to UV due to an open cellular structure with wide channels and thin walls. One can cite the interesting design of monolithic TiO_2 macrocellular foams obtained by integrative chemistry combining soft chemistry and soft matter [19,20]. Targeting the liquid phase photocatalytic oxidation of 1,8-diazabicyclo[5.4.0]undec-7-ene in water, Ochuma et al. reported the improved performances of a TiO_2-coated alumina reticulated foam monolith at 15 pores per linear inch, casted inside an annular photoreactor when compared to a slurry reactor [21]. Previous works showed that a 3D-structured reticulated polyurethane foam could be used as support for TiO_2 particles for designing an efficient single-pass air decontamination process within simple tubular reactors working in a traversing-flow mode, targeting *Legionella pneumophila* bacteria as model tool for airborne microorganisms [22].

Depending on the applications, low cost and easy-of-use polyurethane foams, suffer from a low thermal and chemical stability. Increasing the temperature and using aggressive media (*e.g.* for regenerating deactivated catalysts, either thermally or by soda-based washing, or for treating aggressive fluids) would irreversibly damage the foam. There is thus the need for overcoming such drawbacks, and extending flow-through photoreactors from alveolar polyurethane foams to suitable similar foams meeting such restrictive requirements. This article reports on the use of reticulated carbon foam supported TiO_2 photocatalysts, characterized in terms of morphology, pressure drop, light transmission ability, static mixer role and activity under UV-A illumination, by using the gaseous methanol oxidation as target reaction. The photocatalytic degradation of methanol is widely studied, first because methanol remains a valuable pollutant to select since it forms only a small number of partially oxidized intermediate products that are not significantly affecting the methanol removal rates [23–25]. Further methanol vapors are released by industrial processes [26] and methanol belongs to the list of priority pollutants and air toxics published by the US Environmental Protection Agency [27]. Its photocatalytic degradation was assumed to follow the Langmuir–Hinshelwood's model [13,28].

2. Experimental

2.1. Preparation of the carbon foam-based photocatalysts

The synthesis method used to prepare the three-dimensional carbon foam is a shape memory synthesis using polyurethane foam as pre-shaped alveolar precursor, derived from that developed few years ago to get β-SiC solid alveolar foams for catalytic and filtration applications [29]. The carbon foam material is obtained through a three step procedure, consisting in (i) the impregnation of the pre-shaped precursor polyurethane foam with a formo-phenolic resin followed by an overnight drying at ambient temperature, (ii) a polymerization step at 150 °C for 2 h, both steps being performed at the SICAT company, and (iii) a final pyrolysis at 700 °C for 2 h under argon flow, with a heating rate of 2 °C/min for obtaining the carbon foam.

The shape of the starting polyurethane foam can be manufactured for being adjusted to the photoreactor geometry and size. The pore structure of the commercially available polyurethane foam, shown in Fig. 1, evidenced a high degree of interconnectivity through the entire matrix of the foam. The most characteristic parameters are reported in Table 1, and concerned the cell size (Φ), the window size or pore diameter (a) which can be correlated in the literature with the pore density (the number of pores per linear inch, ppi), and the struts diameter (ds). The pre-shaped precursor polyurethane foams with 4520 μm and 2040 μm mean cell diameters were provided by Recticell (with 95–97% open porosity).

The deposition of the TiO_2 P25-Degussa catalyst on the three-dimensional carbon foam was performed by immerging the carbon foam support into a TiO_2-containing water/ethanol (1:1) suspension and further drying the sample at ambient temperature. The TiO_2-containing ethanolic aqueous suspension was kept under stirring for 30 min before turning off the stirring for immerging the foam. The impregnation process was triplicated. The TiO_2 concentration within the impregnation solution was ranged from 30 to 150 g/L depending on the targeted TiO_2 amount to deposit. The carbon foam coated TiO_2 material was weighted after a final drying at 100 °C to determine the TiO_2 loading.

2.2. Characterization techniques

Structural characterization was done by powder X-ray diffraction (XRD) measurement, carried out in a θ/θ mode with a D8 Advance Bruker diffractometer using a CuK$_\alpha$ radiation source. Information on the morphology was provided by scanning electron microscopy (SEM), carried out on a JSM6700F JEOL microscope. Experimental pressure drop (ΔP) across each sample was measured in a differential *on-flow* device, the gas velocity being measured with Testo 435-1 anemometer equipped with hot wire probe (0–20 m/s). Hot wire probe, due to its small diameter, was chosen to limit the gas flow perturbation. Pressure drop was measured with differential pressure sensor (Keller Druckmesstechnik PD-41, 0–200 mbar), on 0.1 m long materials varying the gas velocity in the 0–8 m/s range.