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Effect of the morphology and pore structure of porous building materials on photocatalytic oxidation of air pollutants

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ABSTRACT

This study focuses on the effect of the morphology and the pore structure of two different porous substrates, namely wood-wool cement board (WWCB) and autoclaved aerated concrete (AAC), on the air pollutant removal efficiency by photocatalytic oxidation (PCO). Their rough surface and porous structure make them appealing choices for nitric oxide (NO) de-pollution, under indoor conditions. In-depth material characterization of the two substrates is realized in order to understand the effect of the porosity, roughness and surface area on the PCO efficiency, at different air flow rates. PCO assessment shows that both activated substrates can degrade up to 99% of NO. The morphology and pore structure analyses of the two substrates reveal that a high effective area and roughness increases the PCO efficiency and an open pore structure allows a better air flow, avoiding NO_2 release.

1. Introduction

For decades, researchers have shown that indoor air quality (IAQ) has a direct impact on human health [1]. It has been demonstrated that many hazardous substances such as combustion gases, volatile organic compounds (VOC) and respirable suspended particulates (e.g. $PM_{2.5}$, PM_{10}) are emitted from cooking, paints and resins, printers, cleaning agents, cigarette smoke or building materials [2]. With the increasing concerns about the IAQ, different methods have been developed to control and reduce the indoor pollution. Photocatalytic oxidation (PCO) of pollutants is a very promising technology which brings several advantages compared to more traditional methods like filtration [3]. First, it can degrade a wide range of pollutants such as nitrogen oxides (NO_x), sulfur oxides (SO_x) and VOC without being selective [4–6]. Furthermore, this technology has been widely studied for the past years, showing positive results under both indoor and outdoor conditions [7,8]. Finally, PCO is a cost-effective process, as currently, titanium dioxide (TiO_2) is the most used photocatalyst due to its relatively low price and wide availability [7]. It has been used for a wide range of applications such as air purification or water treatment due to its high chemical stability and low toxicity [9–11]. TiO_2 is a large bandgap semiconductor with two conventional phases, rutile and more notably anatase, with a bandgap of 3.2 eV, allowing high PCO activity under UV light [12]. However, the activity of TiO_2 under visible light is limited. Doping of TiO_2 with metal (Cu, Fe, Zn) and non-metal elements (B, C, N, O, F) decreases the band gap down to 2.1–2.6 eV, increasing its PCO activity under visible light irradiation [13,14]. Different coating methods have been developed in order to provide a homogeneous dispersion of the catalyst at the substrate's surface. Dip-coating, spin-coating and spray coating have been extensively used in many types of materials [15–18]. In addition to the photocatalyst, a number of external parameters may also influence the PCO efficiency. Previous studies have reported the effect of the pollutants concentration, relative humidity or light intensity as important factors to take into account under indoor conditions [4,19–22].

Besides, the photocatalyst substrate itself can have a significant impact on the PCO efficiency. Concrete, glass or polymers have been coated and studied under indoor conditions and they all showed very different air pollutant removal efficiencies [23–25]. However, not many studies provide information about the actual influence of the morphology of the materials' substrate on the PCO efficiency [26,27]. These studies mostly focused on the general macrostructure of the substrates, where it has only been shown that porous materials are good candidates due to their high surface area available for the photo-catalytic coating [28–30]. The roughness of the surface has also been reported as an important factor during the PCO process but no investigations about the link between pore structure and PCO efficiency have been performed yet [31]. In this study, two porous materials with different morphologies are chosen in order to provide a comparative study:

The first one, wood-wool cement board (WWCB; Fig. 1A), is a composite material made of ordinary Portland cement (OPC) and wood wool, usually spruce strands [32,33]. The processed composite has a

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(A) (B)

Fig. 1. Picture of the two substrates. A: WWCB and B: AAC.

low density, high porosity, and shows great physical and thermal properties for various indoor applications as acoustic and thermal insulation [34–37]. The presence of wood fibers provides a heterogeneous open structure and high surface area, created by the macro porosity formed by the twine of those wood elements within the board volume [38]. These properties underline the good potential of this material as photocatalyst substrate, so far never reported in the literature.

The second one, autoclaved aerated concrete (AAC; Fig. 1B) is categorized as a lightweight concrete and is usually applied as partition wall element or supporting structure, as it ensures high thermal performances. Due to the presence of unconnected pores, these materials features are related to its closed-pore structure, created by the air voids entrapped in the cement matrix [39,40]. Moreover, the presence of the foaming agent results in a high superficial roughness, where "roughness" stands for the average depth of the pores characterizing the material substrate. Unlike WWCB, the application of AAC as a substrate for photocatalytic purposes has been investigated successfully [41,42]. Thanks to their good thermal and acoustical properties, these two substrates can be used for various PCO indoor applications, such as activated ceiling tiles or self-cleaning walls.

Despite their comparable physical properties (i.e. porosity and density), the two substrates feature very different types of pore structure. The WWCB is characterized by an open structure, which allows the air flow to pass through the matrix due to the high presence of the macroporosity. On the other hand, AAC presents a closed structure, mainly based on smaller pores, minimally connected with each other, which prevents the air flow from passing through. The presence of similar physical features of the two substrates (i.e. surface area and porosity) aims to limit the influencing variables on the PCO activity and provide a more reliable comparison among the two type of structure.

The aim of this study is to investigate the effect of the morphology of WWCB and AAC on the photocatalytic oxidation of NO under indoor conditions. Different methods have been used to study the composite structure and morphology of the two substrates, by characterizing their type of porosity, roughness and specific area and their influence on the PCO efficiency. The PCO efficiency of coated WWCB and AAC is evaluated, following the ISO 22197-1 standard, with NO selected as the target pollutant. Computational fluid dynamics (CFD) simulation is realized to study the pollutant flow across the substrate and how it influences the photocatalytic oxidation of pollutants.

2. Experimental

2.1. Materials

For the WWCB manufacture, Norway spruce strands are provided by Knauf Insulation (the Netherlands) and mixed with a mineral binder consisting of 36.63% limestone and 63.37% CEM I 52.5 R white, provided by ENCI (The Netherlands). AAC substrates are manufactured by using lime, calcium hydroxide, CEM I 52.5 R (provided by ENCI, the Netherlands), fine quartz powder, calcium sulfate and metallic Al. The recipe applied is provided by HESS AAC Systems (The Netherlands) and all the materials fulfill the recommended requirements for AAC production. KRONOclean KC 7404 is provided by Kronos International. It consists of an aqueous suspension of carbon-doped TiO_2 with a concentration of 40% (m/m). Its properties are the following: pH of 7–8 (at 20 °C), flash point > 90 °C, density of 1.35–1.55 g cm^{-3} (at 20 °C) and dynamic viscosity < 800 mPa s.

2.2. Methods

2.2.1. Substrate manufacture

WWCB substrates are manufactured by using Norway spruce strands of 1.5 mm. The dry wood has been pre-soaked with water, in order to reduce the strands brittleness as well as to provide water for the binder reaction. The dry cement is sprinkled on the wet spruce and mixed, for achieving a homogeneous binder coating. The water to binder mass ratio applied is 1, while both the wood to binder mass ratio and the wood to water mass ratio are 0.75. Then the mixture is transferred to a mold of 20 × 15 cm^2, the boards are pressed for 24 h and then cured under ambient condition, covered with a plastic sheet for 10 days. Samples are dried overnight in the oven at 50 °C prior to PCO assessment.

The AAC substrate has been produced by mixing fine quartz and portlandite powder in preheated water (45 °C) in a mixer (Swinko EZR 22R, R/L with a 4 bladed propeller mixing rod). Once a homogeneous paste is acquired, lime is added, followed by cement and anhydrite (after 30 s). Finally, metallic Al powder, premixed with 100 mL of water, is added. The casted samples are de-moulded after 12 h and hydrothermally cured (autoclave: Maschinenbau Scholz GmbH&Co., KG/steam generator: WIMA ED36) for 8 h following this procedure: 1.5 h heating, 5 h plateau at 190 °C and 11 bar, 1.5 h cooling. All the samples are cut to fit the PCO reactor dimensions (20 × 10 × 1.5 cm^3).

2.2.2. Photocatalyst coating

To ensure a homogenous dispersion of the C-TiO_2 at the samples surface, 400 ± 15 mg of KC7404 is diluted in 10 mL of water. The coating is then deposited on the surface of each substrate by spray coating at a rate of 10 mL/min, resulting in 2 mg/cm^2 of C-TiO_2 at their surface. Samples are then dried at 40 °C for 24 h in order to remove the residual moisture.

2.2.3. Particle size distribution and zeta-potential

The particle size distribution (PSD) and the zeta potential (ζ-potential) of the suspension are measured by a Malvern Zetasizer Nano ZS. Pure and diluted KC 7404 C-TiO_2 suspension are evaluated in the 50 μL polystyrene cells. Each measurement is performed 3 times at 25 °C according to the operating instructions.

2.2.4. Digital microscopy

3D surface profiles of WWCB and AAC are acquired by using a VHX 5000 series Keyence digital microscope. Samples are cut into three parts with an area of 40 × 40 mm^2, where the surface area is measured. Therefore, the value measured is the total surface per 1600 mm^2. For each material, a cross section profile drawn on the substrate surface is measured by averaging an area of 10 mm^2 on the top of the substrate, by sectioning the surface at 0.5 mm^2 intervals. In order to get an overall profile, the average of three horizontal and three vertical cross section profiles are considered to calculate the board roughness.

2.2.5. Scanning electron microscopy (SEM)

SEM analyses are performed by using a Phenom ProX scanning electron microscope to observe the surface and microstructure of samples. Micrographs are recorded by using back scattering electrons detector at 15 kV with a spot size of 4.