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Enhancing the activation of silicon carbide tracer particles for PEPT applications using gas-phase deposition of alumina at room temperature and atmospheric pressure

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ABSTRACT

We have enhanced the radio-activation efficiency of SiC (silicon carbide) particles, which by nature have a poor affinity towards ^{18}F ions, to be employed as tracers in studies using PEPT (Positron Emission Particle Tracking). The resulting SiC–Al_2O_3 core–shell structure shows a good labelling efficiency, comparable to γ-Al_2O_3 tracer particles, which are commonly used in PEPT. The coating of the SiC particles was carried at 27 ± 3 °C and 1 bar in a fluidized bed reactor, using trimethylaluminium and water as precursors, by a gas phase technique similar to atomic layer deposition. The thickness of the alumina films, which ranged from 5 to 500 nm, was measured by elemental analysis and confirmed with FIB-TEM (focused ion beam – transmission electron microscope), obtaining consistent results from both techniques. By depositing such a thin film of alumina, properties that influence the hydrodynamic behaviour of the SiC particles, such as size, shape and density, are hardly altered, ensuring that the tracer particle shows the same flow behaviour as the other particles. The paper describes a general method to improve the activation efficiency of materials, which can be applied for the production of tracer particles for many other applications too.

1. Introduction

Positron Emission Particle Tracking (PEPT) is a powerful non-invasive technique to follow the motion of individual particles in industrial processes [1,2], which are opaque to other tracking methods [3–5]. The positron emitter most commonly used in such studies is ^{18}F, which has a half-life of 110 min. The level of radioactivity of the tracer will define the performance of the PEPT measurement, which depends on the intensity of the signal in the "positron camera" detectors to reconstruct the trajectory of the tracer in the three dimensions [6]. Using a tracer with low emission intensity results in poor resolution of the spatial location of the tracer [7–9].

In previous PEPT studies [10–12], tracers have been produced either by direct irradiation of the sample in a suitable cyclotron, converting oxygen in the sample directly to ^{18}F, or by irradiation of water, which is then exchanged with, or attached to, molecules on the surface of the tracer. The trajectory of the tracer is understood to be representative of the motion of all the particles in the system, which is only the case if the emitting particle is identical, from a granular-matter point of view, to the particles of interest. This can be readily achieved if the particles can adsorb the emitter. However, in some cases this does not occur. This work deals with the problem that appears when the particles do not adsorb the emitter. Then, one can take a different particle to be used as tracer, accepting the mismatch in some properties, or one can develop a particle that emits sufficiently and remains practically identical to the other particles. This paper explores this last option for silicon carbide (SiC) particles.

SiC particles are used as a heat transfer medium in fluidized beds to harvest solar energy in concentrated solar thermal plants [13,14]. The advantages of SiC in this application include high heat capacity, high sintering temperature, good availability and low cost. The favourable properties of fluidized beds regarding mixing and processability at large scale make them attractive in energy applications such as gasification and combustion of biomass, and chemical looping combustion [15–17]. In all these applications, ensuring and quantifying the good circulation of the particles is

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essential, and for this PEPT is a uniquely powerful technique. Unfortunately, SiC hardly adsorbs ^{18}F.

We demonstrate the production of a core–shell structure to be used as a PEPT tracer particle that better adsorbs the radioactive ions than the core itself. We used SiC as core material and deposited films of Al_2O_3 using a gas-phase coating technique, similar to atomic layer deposition (ALD), using trimethylaluminium (TMA) and water as precursors, at atmospheric pressure and room temperature [18]. Providing the native SiC particles with a thin coating that can be made radioactive is an attractive alternative to enhance the labelling efficiency of these particles, defined as the ratio of radioactivity absorbed by the SiC particles to the radioactivity of the water solution [19]. Historically aluminium oxide has proved to be a very successful material used for PEPT tracers due to its high affinity for ^{18}F ions [20].

The SiC particles used here, with an average particle size ($d_{3,2}$) of 68 μm and density of 3210 kg/m^3 (Appendix A), have the required thermal properties and fluidization behaviour (Geldart A type [21]). However, the inert surface of SiC particles causes poor adsorption of ^{18}F. Other particles with higher labelling performance, such as ion exchange resins or γ-Al_2O_3 particles [22], are effective as emitters, but their different density, size and shape make them poor tracers in this application because their trajectory is different from the SiC particles in the fluidized bed.

ALD is used to deposit inorganic compounds with accurate control based on a set of two reactions repeated a certain number of times [23,24]. ALD has been applied either to functionalize [25,26] or protect [27,28] the surface of flat substrates or powders. We used ALD to reproduce the affinity between ^{18}F ions and the surface of γ-Al_2O_3 particles [20,22]. Normally, ALD of alumina is performed at about 170 °C and absolute pressures of about 1 mbar to ensure the removal of the excess of precursors from the reactor, and obtain atomic growth of the films, i.e. between 0.1 and 0.2 nm per cycle [29–31]. We carried out the coating of SiC particles in a fluidized bed reactor [30,31] at 1 bar and 27 °C. At these conditions, the removal of the excess of precursors is diminished, and this excess can physisorb on the surface of the SiC particles [32], resulting in a CVD (chemical vapour deposition) type of reaction and thus, higher growth per cycle (GPC) of alumina [18,33].

To further accelerate the growth of the alumina films, we treated two samples with oxygen plasma prior to coating to increase the initial surface density of hydroxyl groups, crucial to initiate the deposition of alumina (reaction A). The surface of SiC is formed by carbon- and silicon-terminated groups. While carbon-terminated groups are stable and rather inert, silicon-terminated groups are prone to oxidation [34,35], providing the SiC surface with hydroxyl groups. By using stronger oxidising media, such as oxygen plasma, we can increase the initial density of hydroxyl groups on the surface [36,37], enhancing the deposition of alumina during the first cycles, achieving higher GPC. Nevertheless, having relatively high GPC is a good compromise between depositing thick films of Al_2O_3 in a fast way, improving the activation with ^{18}F, and preserving the particle properties relevant for the hydrodynamic behaviour of the particles, i.e. size, shape and density.

This experimental paper describes a generic method –using gas phase deposition of alumina– for making tracer particles that closely resemble the original particles. The resulting alumina films are very thin compared to the size of the original particles, and therefore have a negligible influence on properties such as size, shape and density. We demonstrate this with the specific example of the improved labelling efficiency of SiC particles towards ^{18}F ions. For that, we coated five samples of SiC with different thicknesses of Al_2O_3 films, using two deposition temperatures, and surface pre-functionalizing treatment in two of the experiments. After the coating, we radio-activated the five samples with ^{18}F ions, and compared the activity with the uncoated SiC and γ-Al_2O_3 particles. We demonstrate the use of an activated SiC-Al_2O_3 core–shell particle as a tracer in a PEPT experiment on fluidizing SiC particles. Using this novel tracer, more accurate studies on the hydrodynamic behaviour of SiC particles can be performed, increasing knowledge of their behaviour in industrial applications such as direct solar harvesting.

2. Experimental

Al_2O_3 films were deposited in a purpose-built fluidized bed reactor consisting of a glass column of 26 mm in diameter and 500 mm in length. Two stainless-steel distributor plates with pore size of 37 μm, placed at the bottom and top of the column, are used to obtain a homogeneous distribution of the gas inside the column and to prevent particles from leaving the reactor. The reactor and the rest of the setup have been described in detail previously [18,38]. We use TMA and water as precursors to deposit Al_2O_3 films according to the reaction mechanism (A) and (B). In an ALD process, the surface species in reactions (A) and (B), respectively OH^* and $CH_3{}^*$, determine the completion of the reactions, and once they are depleted, the reactions end. That confers the self-terminating feature to the ALD process, which ensures atomic growth of the aluminium oxide film. N_2 is pulsed into the reactor in between the reactions for purging purposes. This cycle of reactions can be repeated to grow thicker coatings of aluminium oxide.

(A) $SiC{-}OH^* + Al(CH_3)_3 \rightarrow SiC{-}O{-}Al(CH_3)_2{}^* + CH_4$

(B) $SiC{-}O{-}Al(CH_3)_2{}^* + 2\ H_2O \rightarrow SiC{-}O{-}Al{-}(OH)_2{}^* + 2\ CH_4$

We calculated the dosing time for TMA based on the maximum amount of TMA molecules that can be accommodated on the surface of the particles [23], considering the steric hindrance between the methyl groups of the TMA, and 0.12 nm as the ligand radius for a TMA molecule [39]. We measured with BET (Brunauer–Emmett–Teller) a specific surface area of 0.12 m^2/g for the SiC particles, and calculated the total particle surface area inside the column for the 8.00 g of powder loaded in the column in each experiment. A N_2 flow of 0.8 L/min, which corresponds to a superficial gas velocity of 2.5 cm/s, was applied to fluidize the powder. To calculate the amount of TMA we dose to the column, we assumed that at the bubbler temperature of 30 °C, TMA is found as dimers [40,41] and that the components follow the ideal gas law. We estimated, using the model proposed by Mayer et al. [42], a saturation of the N_2 bubbles with TMA of about 50%. With these assumptions, we calculated a dosing time of 2.6 seconds for TMA and 2.0 s for water to obtain saturation of the particles with the precursors (Appendix B). In order to ensure a faster growth of the alumina films, and therefore, have a higher improvement in the radio-activation of the SiC particles, we overdosed both precursors to the reactor by a factor of about 120 more than the calculated times. With this, we established the dosing times for the sequence of TMA–N_2–H_2O–N_2, in 5–10–4–10 min in all the coating experiments.

We considered that at ambient conditions, the large amount of excess molecules of precursor introduced in each cycle will accumulate on the surface of the particles, resulting in a parasitic-CVD type of growth and thicker films [18]. In addition, we pre-functionalised two samples with oxygen plasma before the coating to obtain a higher GPC. For that, SiC was uniformly spread over a glass Petri dish and introduced into a Harrick Plasma PDC-002 plasma cleaner device for 1 min; the pressure of the chamber was kept at 6 mbar. Immediately after exposing the SiC to the