Synthesis of carbon monoliths with a tailored hierarchical pore structure for selective CO$_2$ capture

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ABSTRACT

Carbon monolithic adsorbents exhibiting a hierarchical pore structure are produced via a synthesis route based on the stabilization of liquid foams followed by a carbonization step. The macro-microporous structure is achieved by the incorporation of microporous, biomass-derived activated carbon particles in the liquid foam enclosed by a cationic surfactant as stabilizer. This method yields crack-free monoliths (solid foams) with a compressive strength of the order of 20 kPa. The microstructure and the textural properties of the final solid foams have been investigated by means of Scanning Electron Microscopy (SEM) and gas adsorption. The behavior as selective CO$_2$ adsorbents at 25 °C has been evaluated using breakthrough experiments under simulated post-combustion conditions (16% V/V CO$_2$/N$_2$), resulting in a selectivity factor of 13 over N$_2$. The hierarchical pore structure of the monoliths allows a rapid transport of the gas mixture through the macropores with no appreciable pressure drop, retaining more than 90 % of the adsorption capacity ($\sim$ 0.868 mmol/g) after several adsorption/desorption cycles. Moreover, the monolith has shown a CO$_2$ uptake capacity of 2.62 mmol/g under static condition at 1 bar and 25 °C. This study provides guidelines for the design of carbon-based foams decorated with carbon particles, which have morphological and textural properties that can be carefully selected for any gas-selective capture application.

1. Introduction

A concern for the emissions rise of greenhouse gases and their possible influence on global warming has led to an increase in research interest in several technologies with the capability of reducing the emissions of such gases or even removing them from the atmosphere. Of all greenhouse gases, the gas making the largest contribution from human activities is carbon dioxide (CO$_2$). Because of this, a significant amount of interest has been developed for the capture and the elimination of CO$_2$ from the atmosphere [1]. Post-combustion CO$_2$ capture at coal-powered power plants can be considered one of the most attractive short-term solutions to decrease CO$_2$ emissions, as the gaseous waste from these power plants has been found to account for up to 25% of the annual CO$_2$ released globally [1]. The state-of-the-art technology used for CO$_2$ sequestration involves aqueous amine solutions which chemically adsorb CO$_2$ [2,3]. Unfortunately, this technology results in an energy penalty of around 20–30% of the output of the power plant required to regenerate the absorption unit [4]. Moreover, there is an environmental issue related to the corrosive nature of the amine solutions.

Novel systems based on adsorption phenomena have been investigated to overcome these drawbacks. For instance, a pressure or vacuum swing adsorption (PSA/VSA) unit is a promising technology that consists of a column filled with a properly designed adsorbent material, through which the gas stream flows, selectively capturing the CO$_2$ until the adsorbent reaches saturation. The subsequent regeneration is achieved by applying a change in pressure, resulting in a much cleaner and more cost-effective technology than the aforementioned aqueous amine solutions. In this procedure, the performance of the adsorption unit is governed by: the adsorption capacity of the material; the selectivity for the desired compound; the mechanical and chemical stability of the material, especially in the presence of moisture; and its capability to be regenerated. There are a great number of candidates among adsorbents to be used for this process such as zeolites [5,6], mesoporous silica [7–9], metal organic frameworks (MOFs) [10–12], porous organic polymers [13] and activated carbon [14–17]. The latter has proven to be a low-cost alternative with highly tunable features, such as high surface area, high thermal and chemical stability [18–21]. Furthermore, the current challenges in PSA/VSA based carbon capture are to significantly increase the productivity while ensuring high purity

(95%) and recovery (90%) requirements. For instance, the selectivity in respect to other gases in the stream flow has to be very high. But at the same time, the CO$_2$-surface interaction has to be sufficiently weak to assure a fast regeneration of the carbon bed (i.e. high curvature of the CO$_2$ isotherm is detrimental) [22]. The largest disadvantage of activated carbon is that high-surface area carbon powder would produce a significant pressure drop in the gas stream if applied in columns [23]. Only a few previous attempts to produce high-surface area activated carbon monoliths have resulted in mechanically stable monoliths. For instance, Hao et al. [24] reported a carbon monolith prepared through a self-assembly of poly(benzoxazine-co-resol) followed by a carbonization process, which withstood a compressive stress of up to 15.6 MPa. A few years later, Hao et al. [25] reported a new type of hierarchically porous carbon monolith made from graphene oxide and asparagine which was able to withstand up to 28.9 MPa. Recently, Fernandez-Catalá et al. [26] reported the preparation of AC@MOF hybrids using a binderless activated carbon monolith from petroleum residue with a crushing strength of ca. 8 N. In any case, the mechanical resistance of the obtained monolith decreases with increasing surface area.

It is important to note that, in the area of ceramics, numerous techniques have been developed for the production of macroporous systems, the most common being reactive infiltration [27–30]. This technique has not been adapted to the manufacture of carbon foams, however it has been successfully applied to the synthesis of metallic foams [31]. In recent years, a new method, based on the solidification of particle-stabilized liquid foams, was developed for ceramic foams [32,33]. This approach has been successfully adapted to the production of macroporous carbon foams, using carbonaceous particulates, such as carbon black or carbon soot [34,35] as foam stabilizer. The carbon porous materials obtained exhibited a highly ordered macroporous system with a cell structure interconnected by struts. According to the method proposed in these studies, liquid foams stabilized by carbon colloidal particles are used as a template for a gel-casting process. The polymeric porous material obtained, also called "green body", is further treated at high temperature to eliminate the organic components and obtain porous carbon materials. A key aspect of this method is that the formulation of the initial liquid foam determines the structural and mechanical features of the final porous materials. By associating surfactant to solid nanoparticles it is possible to tune their degree of hydrophobicity, which consequently affects their affinity with the water-air interface and, therefore its effectiveness as foam stabilizer. Thus, the physico-chemical characterization of the precursor dispersions by determining the interfacial and bulk properties, is a fundamental step to monitor and select the right degree of the particle amphiphilicity. For example, it has been shown that after associating appropriate surfactants to carbon particles in the dispersion, it is possible to improve the mechanical strength and increase the specific surface area of the final porous materials.

In the present work, we apply this technique by using *ad hoc* produced microporous activated carbon powders as stabilizers of the precursor liquid foams. By using microporous particles, we obtained mechanically stable carbon monoliths with hierarchical micro/macro pore structures. The textural and structural properties of the monoliths were evaluated and the performance of the monoliths for CO$_2$ adsorption under both static and dynamic conditions were tested.

2. Experimental

2.1. Materials

Activated carbon particles were produced in-house from milled coconut shell through a physical activation process using CO$_2$ as activating agent [35–37]. Two particle size fractions were selected through sieving for this purpose, a fine fraction (20–50 μm) and a coarse fraction (50-100 μm). After sieving, the milled coconut shell was washed using a 1 M HCl solution and rinsed with distilled water. Both fractions were

carbonized at 800 °C for 1 h with a heating rate of 1 °C/min. Afterwards, the obtained carbon particles were activated using CO$_2$ at 950 °C for 6 h with a heating rate of 10 °C/min. The obtained activated carbon particles were characterized using gas adsorption (N$_2$ and CO$_2$) and scanning electron microscopy (SEM).

The cationic surfactant used to stabilize the liquid foams, hexadecyltrimethylammonium-bromide (CTAB); the gel-casting agents, Polyvinyl alcohol (PVA), the cross-linker 2,5-dimethoxy-2,5-dihydrofuran (DHF) and Nitric acid (HNO$_3$), were supplied by Sigma-Aldrich (Germany). The water employed for the preparation of the dispersions was obtained by using a multi-cartridge system (Millipore, Elix plus Milli-Q), providing a resistivity greater than 18 MΩ·m and surface tension of 72.5 mN/m without any appreciable kinetics over several hours.

2.2. Procedure

2.2.1. Carbon particles and carbon monoliths characterization

The textural properties of the activated carbon particles and the carbon monoliths produced were evaluated using physical adsorption (N$_2$ adsorption at -196 °C and CO$_2$ adsorption at 0 °C). Measurements were performed up to 1 bar in an in-house-built, fully-automated manometric equipment designed and constructed by the Advanced Materials Group, now commercialized as N2Gsorb-6 (Gas to Materials Technologies; www.g2mtech.com). Before any adsorption measurements, samples were degassed at 250 °C for 4 h. The surface area was calculated using the Brunauer-Emmet-Teller theory applied to the N$_2$ adsorption data (S$_{BET}$). The narrow micropore volume (V$_{DR,CO2}$) and the micropore volume (V$_{DR,N2}$) were calculated by applying the Dubinin-Radushkevich equation to the CO$_2$ and N$_2$ adsorption isotherms, respectively. Adsorption measurements were performed using whole monolithic specimens. The structure of the monoliths was evaluated using scanning electron microscopy (SEM).

2.2.2. Particle dispersion preparation

Activated carbon particles dispersions were prepared by stepwise addition of the aqueous phase (CTAB solution) upon continuous stirring. To ensure full dispersion of the particles, suspensions were put under sonication for 1 h and they were kept under stirring overnight. Afterwards, a 3.9 wt.% PVA solution was added gradually to the mixture. To avoid particle agglomeration, dispersions were stirred overnight.

2.2.3. Interfacial and bulk characterization of particle dispersions

The surface tension of the dispersions, γ, was measured by the drop shape tensiometry technique [38]. This method is based on the acquisition of the drop/bubble shape under gravity effect. The surface tension is determined by fitting the theoretical profile of an axis-symmetric drop calculated through the Laplace equation to each experimentally acquired drop profile. The instrument used in this work (PAT-1, Sinterface, Germany) allows the surface tension versus time, with an accuracy of 0.1 mN/m, to be measured using a pendant drop formed at the tip of a small Teflon capillary of a few millimeters in diameter. The instrument allowed the drop/bubble surface area during the surface tension measurement to be automatically controlled by means of a precision syringe pump. In this study, the drop surface area was maintained at a constant value of 30 mm^2 while the surface tension was acquired over time until the achievement of the equilibrium value. All the measurements were performed at 25 °C.

The size distribution and the surface charge of the AC particles in the water dispersions were obtained by Dynamic Light Scattering (DLS) and zeta-potential measurements, respectively, using a Zetasizer device (Nano ZS, Malvern Instruments, United Kingdom). In DLS measurements, the intensity correlation function of the dispersions was obtained using the red line (λ = 632 nm) of a He-Ne laser at a fixed temperature of 25 °C and a quasi-backscattering configuration