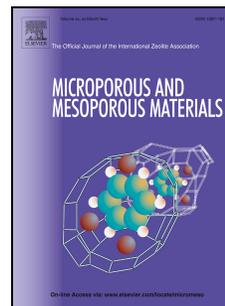


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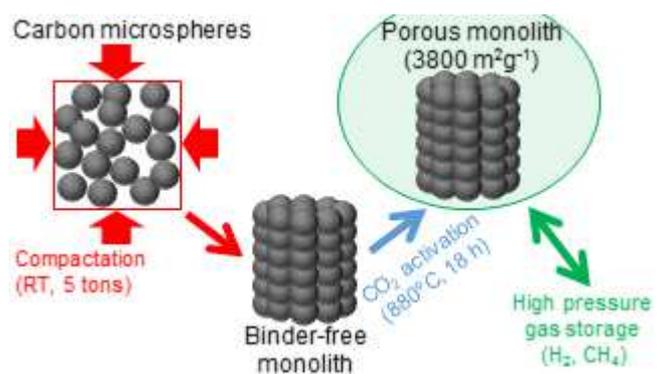
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Graphical abstract



Novel monoliths prepared from sucrose avoiding binder and thermal treatment.

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ABSTRACT

We present a process for the synthesis of binder-free carbon monoliths, which were prepared from carbon microspheres at room temperature. The microspheres were obtained through hydrothermal treatment of sucrose, and monoliths with a bulk density around 1 g cm^{-3} were prepared from them by a simple pressurization process. Subsequently, the monoliths were activated with CO_2 in order to increase their porosity. The activation preserved the monolithic shape and yielded maximum BET surface areas close to $4000 \text{ m}^2 \text{ g}^{-1}$. High pressure gas adsorption isotherms reveal that the activated carbon monoliths are interesting candidates for gas storage applications. High excess adsorption amounts are measured for hydrogen (1.2 wt. %) and methane (453 mg g^{-1}) at room temperature and for pressures up to 20 MPa. Taking into account the measured densities of the monoliths, a maximum volumetric excess adsorption amount of CH_4 of $230 \text{ cm}^3 \text{ cm}^{-3}$ is reached.

Keywords: spherical carbons, monoliths, gas storage.

1. Introduction

Carbon monoliths are key materials in a wide variety of applications, such as separation processes [1,2], electrodes of electrical energy storage devices [3,4], catalyst supports [5], gas storage materials [2,6], gas sensors [5], materials for purification of gas mixtures [7], dyes [8] and others.

For the preparation of carbon monoliths, different materials can be used as precursors, and usually three steps are involved: preparation of monolith, carbonization and activation. Literature has previously shown monoliths with different compositions and textural properties [1,2,8]. These properties have to be suitable for their use in each particular applications [1-8]. In these sense, to enhance their gases adsorption capacity, the bulk density of the monoliths is an important parameter, in addition to their textural properties. Therefore, the objective when preparing monolithic materials is usually to obtain high-density solid materials that can easily be handled. However, their synthesis is oftentimes laborious due to numerous preparation steps and, in the case of porous materials, the use of binders compromises the final porosity. Binder-free preparation of monoliths would preserve the initial porosity of the carbon material. Furthermore, it would be necessary to optimize the chemical and physical properties of carbon monoliths. Thus, inherent special properties, like porosity, surface chemistry and density, have to be optimized with respect to each potential application. For example, in the case of energy storage by high pressure adsorption of methane and/or hydrogen, monoliths with high contribution of micropores and high densities are required in order to improve their capacities [4].

Many investigations have focused on evaluating the density of the adsorbent and its important effect on the gases storage capacity [8]. The adsorbent has to be confined in a given volume, and the higher the adsorbent density, the higher the amount of material which can be confined in a tank and, hence, the higher the storage capacity [8]. Scarce some studies have highlighted the importance of the porosity and the density of the monolith on the gas storage capacity [8]. However, further research is required. Thus, for a given adsorbent, to get maximum gas storage capacities, both adsorption capacity and density have to be maximized. Regarding methane sorbents, targets are established by the DOE for optimizing, amongst others, the volumetric and gravimetric energy densities, and to find suitable strategies for sorbent packing, maximizing the system pressure and increasing the working capacity[8].

Here, we present a simple and easy process for the preparation of carbon monoliths, which has several advantages, *e.g.*, it employs a natural precursor, it is binder-free, no heating is required, and the monoliths can be easily activated with CO₂. Furthermore, the application of the synthesized monoliths for energy storage to high pressure adsorption of hydrogen and methane is studied.

2. Materials and Methods

2.1 Materials

The precursor is a spherical carbon obtained from sucrose, which is an abundant, natural raw material.

2.2 Samples' preparation

The carbon microspheres were prepared by hydrothermal carbonization, following the procedure described in reference [11]: sucrose was mixed with 3.5 ml of distilled water to obtain a molar concentration of 1.6 M. Then, the mixture was placed in a 10 mL capacity Teflon-lined stainless steel autoclave in a programmable oven, which was heated at 473 K during 24 h. The solid product was recovered by filtration, washed with distilled water and dried in an oven at 383 K for 12 h. In this process, a powder mainly based on microspheres with diameters up to 12 μm was obtained. The preparation of the carbon monoliths were made by varying the procedure reported elsewhere [3,6]. 0.5 g of the powder were introduced into a stainless-steel mold with a diameter of 14 mm. Subsequently, the monoliths were assembled by submitting the mold to a pressure of 5 ton during 10 minutes at room temperature. In order to increase their porosity, the prepared monoliths were activated in a horizontal tube furnace under a CO₂ flow of 80 ml min⁻¹. The furnace was heated at 10 K min⁻¹ from room temperature to 1153 K, and different activation times of 10, 15 and 18 h were used.

2.3 Characterization

The morphologies of the materials were studied, using scanning electron microscopy (SEM) in two devices, JEOL JSM-840 and Zeiss Merlin VP Compact. The bulk densities of the monoliths were calculated from their degassed weights and geometries measured with a caliper gauge. The textural characterization was

performed after outgassing the samples at 523 K for 4 h, by N₂ adsorption-desorption at 77 K and by CO₂ adsorption at 273 K, in a volumetric Quantachrome Autosorb-6B apparatus. High pressure gas adsorption isotherms of hydrogen and methane were measured at 298 K and up to 20 MPa in a Sieverts-type equipment [12]. Previously, the samples were outgassed under vacuum at 523 K for 4 h.

3. Results and Discussion

In Table 1, the activation times, yields, textural properties and bulk densities of the synthesized monoliths are specified. The values of textural properties and mean micropore size have been obtained from N₂ adsorption-desorption isotherms at 77 K and the corresponding pore size distributions, which are included in the Supporting Information (Figure SI-2 and Figure SI-3). It can be observed that the non-activated monolith (sample MONO₀) has negligible BET surface area (S_{BET}) [13] and total micropore volume (V_{DRN_2}) [14]. However, it reveals an interestingly high density of 1.02 g cm⁻³, as well as a noticeable amount of narrow micropores (V_{DRCO_2}) [15]. This highly selective porosity, limited to the narrow micropore volume (pores with size smaller than 0.7 nm) could be very interesting for some applications, such as molecular sieves. In Figure 1, the change in the textural properties of the monoliths is plotted over the activation time. After CO₂-activation for 10 hours (sample MONO₁₀), all the porosity parameters increase significantly, and density decreases to less than 50 %. With increasing activation times, both BET surface area total micropore volume increase following a linear tendency up to the maximum activation time studied (18 h). Also, the mean micropore size increases when the activation time increases, in agreement with the pore size distributions reported in SI (see Figure SI-3). The narrow micropore volume remains almost constant for activation times longer than 10 h. The density notably declines up to 15 h, and then remains practically constant up to 18 h. The highest values of BET surface area of 3800 m²g⁻¹, (see SI for details on BET calculations), total micropore volume (V_{DRN_2}) of 1.38 cm³g⁻¹ and narrow micropore volume (V_{DRCO_2}) of 0.62 cm³g⁻¹ are achieved for MONO₁₈. For such highly microporous AC monolith, micropore volume is the most correct way to characterize its porosity. However, and taking into account that BET surface areas are usually included in this type of studies, to include this data is useful from a comparison point of view.

Also, the increase in the activation time is accompanied by a decrease in the bulk density of the monoliths, 0.45 g cm^{-3} for MONO₁₀ and 0.34 g cm^{-3} for MONO₁₅, being the lowest bulk density the one for MONO₁₈, 0.33 g cm^{-3} , reached for the longest activation time, 18 hours.

The obtained porosities are interestingly high and the pore size distributions indicate that these materials, especially MONO₁₈, could be employed in several applications, *e.g.*, for energy storage, where such properties play a key role [16,17].

Table 1. Textural properties and densities of the monoliths

Sample	$t_{\text{Act.}}$ (h)	Yield %	$S_{\text{BET}}^{\text{a}}$ (m^2g^{-1})	$V_{\text{DRN}_2}^{\text{b}}$ (cm^3g^{-1})	$V_{\text{DRCO}_2}^{\text{c}}$ (cm^3g^{-1})	Mean micropore size ^d (nm)	Density (g cm^{-3})
MONO0	-		9	0.00	0.14	--	1.02
MONO10	10	36.0%	1535	0.74	0.59	1.1	0.45
MONO15	15	16.6%	2886	1.21	0.59	1.4	0.34
MONO18	18	10.2%	3800	1.38	0.62	2.6	0.33

a) S_{BET} : Apparent (BET) surface area.

b) V_{DRN_2} : Total pore volume (Dubinin-Radushkevich).

c) V_{DRCO_2} : narrow ($< 0.7 \text{ nm}$) micropore volume (Dubinin-Radushkevich).

d) Mean micropore size obtained applying the non-local density functional theory (NLDFT) to the N_2 adsorption isotherms at 77 K for the three activated monolith samples.

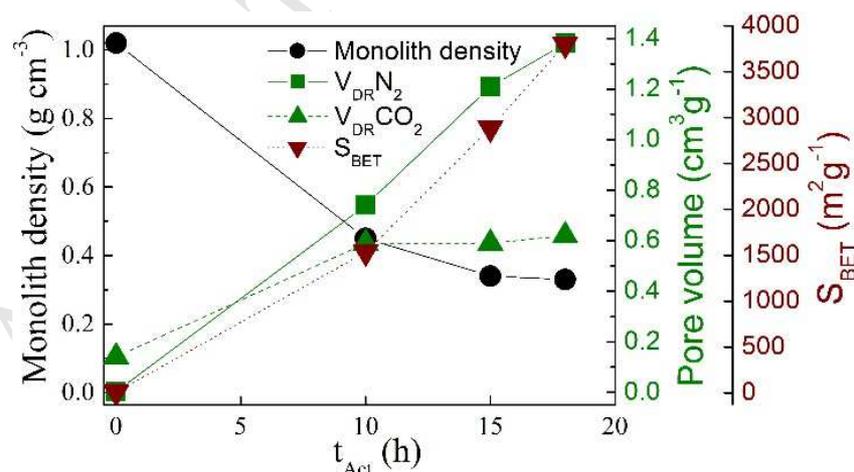


Figure 1. Textural properties (S_{BET} , V_{DRN_2} , and V_{DRCO_2} micropore volumes) and densities of the monoliths plotted over the activation time (t_{Act}).

In Figure 2, the SEM images of the samples are shown. Figure 2a confirms that the initial powder sample consists of interconnected microspheres with diameters up to 12 μm . For MONO18, which was activated during 18 h, Figure 2b reveals the defined shape of the monolith despite no binder was used for its synthesis. Optical images to see the complete monolith, before and after the activation process, have been included in the supporting information (see Figure SI-1). Interestingly, the enlarged picture of sample MONO18 in Figure 2c shows that the spherical morphology of the precursor was not modified neither by the high mechanical pressure nor by the activation process. Therefore, MONO10 and MONO15 samples are expected to have structures similar to that for MONO10. The structure of interconnected spheres and hierarchical channels in-between them could improve the access of gas molecules to the porous texture.

All prepared and analyzed samples have shown good properties to be applied in gas storage. However, MONO18 has been selected for gases adsorption tests since, based on its characterization, it is the most adequate sample for a potential energy storage application. Thus, this sample has the highest value of BET surface area, total micropore volume and narrow micropore volume, a moderate bulk density and a micropore size distribution showing a large proportion of pores with the optimum size for gases storage (see Table 1 and Figure SI-3). Figure 3a shows the H_2 adsorption isotherm of sample MONO18 (please refer to the SI regarding details on the calculation of high pressure excess adsorption amounts and storage capacities). At room temperature (298 K) and 20 MPa, gravimetric excess adsorption reaches a maximum of around 1.2 wt. %. This value is interestingly high, especially taking into account that the volume of narrow micropores in the sample, a parameter which has proved to mainly control H_2 adsorption under these conditions[12], is not very high in comparison with other samples from literature [6,12,16]. The total volumetric storage capacity, that is the total amount of H_2 which can be stored in a given storage volume [18], reaches a maximum value of 16.4 g l^{-1} at room temperature and 20 MPa. This is a high value in comparison with other carbon monoliths recently prepared [20], even more considering the reduced density of sample MONO18. Due to its elevated total porosity, at cryogenic temperatures very high adsorption values would be expected.

The methane excess adsorption isotherm at room temperature (298 K) of sample MONO18 is plotted in Figure 3b. At a pressure of around 18.8 MPa the isotherm goes through a maximum of 31.2 wt. % (453 mg g^{-1})

'). Both values, the excess adsorption amount, as well as the pressure at which it is reached, are interestingly high when compared with other materials [17–19] and with the DOE targets (500 mg g^{-1} , and $p_{\text{max}} = 25 \text{ MPa}$) [8]. Considering the monolith density, the volumetric excess adsorption amount at 18.8 MPa reaches $230 \text{ cm}^3 \text{ cm}^{-3}$, a value that is comparable [19,20,23], or even higher [24,25] than those obtained with a large number of MOFs. Taking into account a residual pressure of 0.48 MPa in a methane tank filled with sorbent [8], the maximum deliverable capacity can be estimated from the adsorption data, being around $200 \text{ cm}^3 \text{ cm}^{-3}$ (see SI for further details). The volumetric total storage capacity of CH_4 has been calculated using the last CH_4 adsorption point from the isotherm, the monolith (bulk) density, 2.22 g cm^{-3} as the real density, and the formulas given in reference [18]. This volumetric total storage capacity of CH_4 , 278 g l^{-1} , is higher than those for other materials, such as other carbon monoliths prepared with binders [26,27] or MOF [28], and corresponds to 13.9 MJ l^{-1} , which clearly exceeds the DOE target of 12.5 MJ l^{-1} for sorbent materials[8].

It should be mentioned that total storage capacities on a gravimetric basis, as they are often reported (*e.g.*, in reference [28]), are not useful values due to the fact that they increase with decreasing bulk densities [18]. Thus, an assumption of too low bulk density values leads to an overestimation of the void volumes, and to the over assessment of the contribution of non-adsorbed molecules present in them, leading to erroneously overestimated and unrealistic gravimetric storage capacities [18].

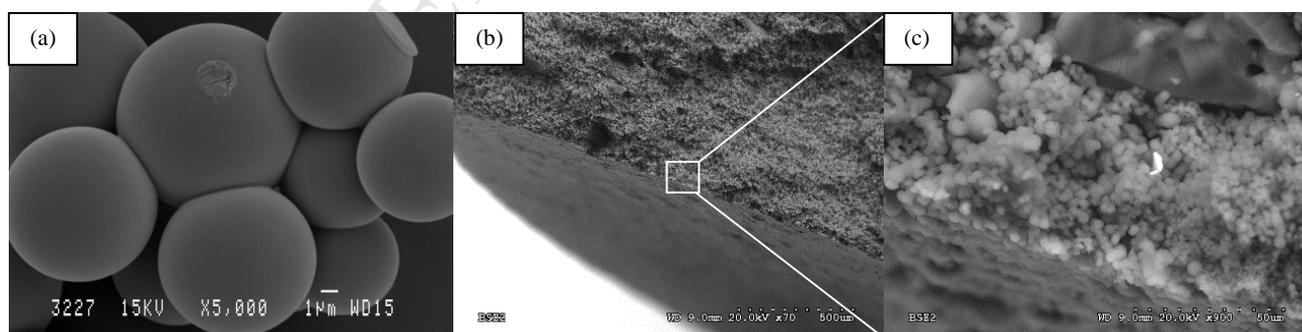


Figure 2. SEM images of spherical carbon (a) and activated carbon monolith MONO18 (b and c).

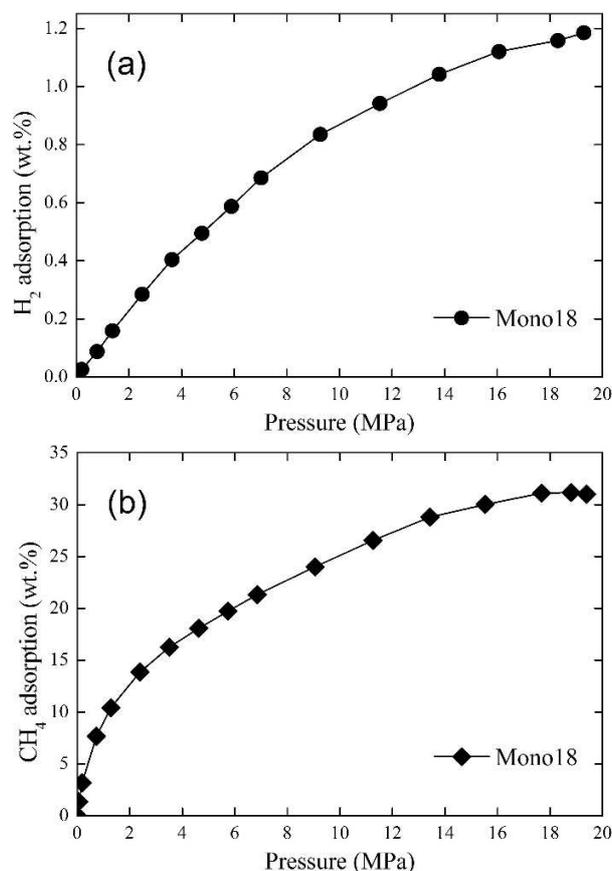


Figure 3. High pressure excess adsorption isotherms for sample MONO18 at room temperature (298 K) with hydrogen (a) and methane (b).

4. Conclusions

In summary, a simple procedure for the synthesis of monoliths from carbon microspheres is presented. Upon activation with CO₂, the monolithic geometry and the microspherical structure were preserved and very high porosities, with BET surface areas up to 3800 m²g⁻¹, were generated. It has been proved that the activated monoliths are interesting candidates for the storage of gases, such as H₂ or CH₄. In the future, other applications for the synthesized monoliths should also be taken into account, for example as electrodes in electrochemical energy storage devices. For such applications, not only the high porosity, but also the presence of interconnected microspheres in the structure of the materials could be advantageous because of their electrical conductivity and their interaction with the electrolytes.

ASSOCIATED CONTENT

Supporting Information

Supplementary data associated with this article can be found, in the online version: optical images, nitrogen adsorption isotherms, calculation of BET surface areas, properties of initial microspheres, calculation of gas excess adsorption amount and storage capacities.

Notes

The authors declare no competing financial interests.

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Highlights.

- Binder-free carbon monoliths prepared from carbon microspheres at room temperature.
- Easy activation procedure produces monoliths with interesting properties and high bulk density.
- High excess adsorption amounts are measured for hydrogen and methane at room temperature and pressures up to 20 MPa
- High hydrogen (1.2 wt.%) and methane (453 mg g⁻¹) adsorption capacities are achieved
- A volumetric excess adsorption amount of CH₄ of 230 cm³cm⁻³ is reached