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Facile synthesis of soft-templated carbon monoliths with hierarchical porosity for fast adsorption from liquid media

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ABSTRACT

An easy synthesis of carbon monoliths with hierarchical porosities is presented here combining phenolic sol-gel and soft-templating methods (use of amphiphilic surfactant Pluronic F127 as mesopores template). By varying the synthesis conditions, purely microporous or micro-mesoporous or micro-meso-macroporous carbon materials were obtained. While micropores and mesopores arise during the carbonisation, macropores formation occurs during the gelling step through a controlled macroscopic phase separation process. The same pyrolytic temperature was used to ensure comparable surface chemistry (proved by FTIR and TGA-MS measurements for the templated samples), textural properties were investigated by a group of techniques: TEM, CO_2 and N_2 sorption, Hg porosimetry and SAXS. The benefit of the different porosities was evidenced on blocs of 1–2.5 mm diameter by studying adsorption kinetic of phenol and methylene blue aqueous solutions. Due to comparable surface chemistry of the templated samples, only their difference of porosity was considered as a decisive factor for the kinetics of adsorption. The relative role of each porosity was evidenced and quantified. It was found that mesopores are crucial for a fast transport of adsorptive into the adsorption sites (micropores/smaller mesopores) while the additional presence of macropores further accelerates the rate of sorption for both adsorptives.

1. Introduction

Porous carbonaceous materials are nowadays extensively used in several different areas such as depollution of water [1–5], electrochemical energy storage (supercapacitors) [6,7], or in catalysis as support of catalysts [8]. Their great success is related to their usually low price, nontoxicity and possibility of tuning their properties (porosity, surface chemistry, graphitization level) according to the targeted applications. These properties, based mainly on their high surface area, are largely determined by their preparation process and therefore also by the choice of carbon precursors. The latter can be biosourced [2,9–11], synthetic [1,12] or derived from various coals [13]. Shape of the carbon materials is also of great importance for the applications, carbon materials can be processed in the form of powder, films, fibres and large pieces (monoliths or membranes) [7,14,15]. Monoliths possess some advantages over fine powders such as an easy handling, limited attrition and powder toxicity. Moreover, they can be shaped directly during the synthesis if appropriate synthesis like the sol-gel process is used [16].

Nevertheless, these materials can face drastic problems related to the diffusiveness of fluids through them (e.g. slow diffusion, pressure drop, limited access to their whole porous structure). These drawbacks can be partly circumvented by the appropriate design of a porous network associating different pore sizes (hierarchical porosity) with the appropriate architecture. Each pore size contributes to a specific manner: micropores yield mainly to the high surface area where adsorption can take place whereas larger pores (meso- and macropores) promote fast diffusion throughout the whole porous network. Moreover, it has been shown that presence of both interconnected macropores and mesopores plays a key role on the transportation of species to the active sites in micropores either in liquid or gaseous media for applications in catalysis, adsorbent and supercapacitor electrode materials [1,17]. This is particularly true in liquid phase for mesopores as exemplified with adsorbate species, having a size larger than phenol or iodine (e.g. tannin acid), which are adsorbed in micropores [18]. In this case, a clear improvement of the adsorption capacities correlated with the mesopore volume was observed by Hsieh et al. [18]. It is proposed that mesopores enable a more efficient access to the inner and narrow micropores with therefore adsorption on site of higher energy. Macropores are also particularly useful when aqueous

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solution/electrolyte are used since poor liquid penetration could be encountered due to the possible hydrophobic nature of the surface [7]. If impact of the different porosities on the adsorption properties (capacity, kinetics) is well documented for zeolite-based materials [19], there are not so many studies probing the specific influence of mesopores and/or macropores in hierarchical monolithic carbon materials on kinetics of diffusion in adsorption-related process (depollution, supercapacitor). This is mainly related to the difficulty to synthesize model porous carbon materials with tailored porosities at different scales. Indeed, most of the study dealing with carbon are adapted to produce monoliths with two pore scales (meso-macropores [20], micro-macropores [21]) and more rarely with three type of pores (micro-meso-macropores) [22]. Another reason is based on the fact that most kinetic of diffusion studies rely on activated carbons (powder or granule forms), either in gas [23,24] or liquid state (electrolyte [7] or aqueous media [25–30]), where the individual role of mesopores or macropores could not easily be investigated due to difficulty to modulate each porosity.

The sol-gel process is a well-known route to prepare carbon monoliths *via* carbon aero/cryo/xerogels. These materials, developed approximately 30 years ago by Pekala and Kong [31], are synthesized classically by polycondensation of aromatic compound such as resorcinol, phenol or phloroglucinol and aldehyde (formaldehyde, furfural) [14,15,32]. Biosourced precursors such as cellulose and its derivatives, glucose, starch etc. [9,33] or tannin [10,34] can also be used. The resulting gel contains nanometric or micrometric voids filled by the solvent and delimited by the 3D polymeric structure. During drying, the different voids need to be preserved to yield to meso- and macroporosity. Among others, supercritical drying is the gentlest way of drying which avoids pore shrinkage or closure [35,36] but this process is time consuming and expensive. By using faster and cheaper kind of drying (freeze drying, normal pressure drying), preservation of the porous structure is difficultly ensured [35,36] and shrinkage of the materials associated with cracks may occur. Generally, if porous dried gels often contains both meso- and macropores [36], the pores are rather broadly distributed in size and the difficulties to precisely control the distribution width arise. During pyrolysis, meso- and macropores are not strongly modified regarding their size while micropores are created due to evolution of enormous amounts of pyrolytic gasses. Template-based processes offer an alternative for introducing control of the pore size [25].

Hard-template process, also called nanocasting, is using a porous template as a mould. Its filling by a carbonaceous precursor, further conversion to carbon and etching of the mould leads to the negative porous structure of the template with pores size determined by the wall thickness of the mould. This process enables to produce micropores, mesopores and also macropores by using zeolites [37–40], mesoporous silica (e.g. MCM-48 or SBA-15 matrices) [12,26,41–43] and silica opal [44,45], respectively. However, hard-templating is a time-consuming process which requires harmful chemicals during the hard-template removal (e.g. hydrofluoric acid). Soft-templating process for porous carbon material is rather dedicated to mesopores formation. It is mainly based on the use of organic templates which are pyrolysable species and yield gasses by thermal decomposition with formation of mesopores. One of the most commonly used soft-template is the amphiphilic triblock copolymer of the commercial Pluronic type (e.g. F127 or P123). This type of substance has two hydrophilic polyethylene oxide (PEO) blocks at the ends of the chain and one hydrophobic polypropylene (PPO) block in-between [14]. Pluronic polymers tend to form micelles and mesophases which ensure the creation of the future mesopores. Unlike sol-gel process, the future mesopores are still filled with the soft-template during drying. The template is easily thermally removed during pyrolysis at temperatures below 400 °C without need of special chemicals [15]. Thus, soft-templating seems to be easier and more environmentally friendly than hard-templating. The greatest advantage of both hard- and soft-templating processes is the possibility to precisely control porosity in the narrow range, e.g. 2–5 nm [2], 1–10 nm [22], 200 nm [44].

Both hard- and soft-template processes allow, in well-defined conditions, to prepare monolithic porous carbon materials with mesopores and macropores control. Processes are either based on a mesoporous silica monolith used as a hard-template [46,47], a mixture of a polymeric foam (hard-template) coated with a layer of soft-templated carbon [48] or based solely on soft-template (use of amphiphilic surfactant). In the latter case, hydrothermal [22] or "dual phase separation" approaches [7,49] were required to produce both meso- and macropores. The dual phase separation process relies on the use of a glycolic solution to control the spinodal phase separation. Glycol is here the predominant solvent (with minor amount of water) but also the macropore template by forming a continuous liquid network. Moreover, when glycol is added to mixture of Pluronic and polyphenolic-based resin in water media, it is compatible with the soft-template for possible mesophases formation and it avoids uncontrolled macroscopic phase separation (with decantation of an organic-rich phase) [11,49] that leads to absence of macropores. Soft-template process taking advantage of this macroscopic phase separation to produce macropores, without the use of any additives like glycol, could be interesting to develop.

Our main aim was to develop quick and facile synthetic route to produce carbon monoliths with hierarchical porosity by combination of sol-gel and soft-templating method but with omission of using excessive additives (glycolic solutions) or hydrothermal process [22]. The second objective was to prove and quantify how mesopores or macropores are responsible for faster diffusion of adsorbed species (phenol, methylene blue) to the active sites during adsorption because this phenomenon is generally not documented in the literature for carbon materials.

2. Experimental

2.1. Synthesis of carbon monoliths

Carbon monoliths were prepared by sol-gel process from resorcinol (R) and formaldehyde (F) as starting compounds. To introduce mesoporosity in a controlled manner, an amphiphilic surfactant (called soft-template (ST) here, a triblock poloxamer Pluronic F127, $(PEO)_{106}(PPO)_{70}(PEO)_{106}$) was introduced in the sol-gel process to behave as a porogen agent. This soft-template process, when associated with basic sol-gel process developed for the preparation of carbon gels, led to rapid macroscopic phase separation with an aqueous rich supernatant and polymer-rich decanted phase. In order to take advantage of the solvent as a macropore porogen agent and to avoid using any additives (e.g. ethylene glycols – TEG, PEG etc.) which allow controlling spinodal phase decomposition for macropore formation [7,49,50], a simple addition of ethanol was performed in order to slow down macroscopic phase separation during the gelling step. It is worth to note that macroscopic phase separation occurs only in the presence of surfactant and water (W). With the appropriated amount of ethanol (E), this phenomenon can be strongly limited and only liquid/liquid phase separation at the micrometric scale occurs with formation of a cloudy solution. We tested three different E/W ratios 2:1, 1:1, 1:2.

To evaluate the influence of the soft-template, four carbon monoliths were prepared with different amounts of Pluronic and one without any template as a reference (denoted NT as non-templated). The soft-templated samples were denoted as ST/R X/Y where X/Y represent the weight ratio between surfactant F127 (ST) as soft-template and resorcinol (R) used (ST/R 2/1, ST/R 1.5/1, ST/R 1/1 and ST/R 1/1.5). After preliminary investigations, the samples ST/R 2/1 and ST/R 1/1 where selected for further in-depth analysis and comparisons. The samples were generally synthetized as follows. Firstly, the mixture of E (96%, p.a., Mach chemikálie), W and copolymer Pluronic F127 (bio reagent, Sigma-Aldrich) or the mixture of E and W only (in the case of the non-templated sample) was stirred for 1 h. Secondly, R (98%, Mach

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