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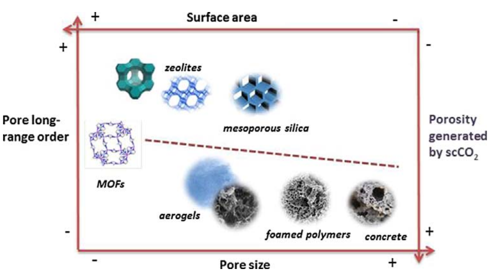
Features of supercritical CO_2 in the delicate world of the nanopores

Ana M. López-Periago, Concepción Domingo*

Instituto de Ciencia de Materiales de Barcelona (ICMAB-CSIC), Campus UAB s/n, Bellaterra 08193, Spain

GRAPHICAL ABSTRACT



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ABSTRACT

This contribution highlights the main characteristic that makes supercritical CO_2 ($scCO_2$) a highly interesting solvent to perform both physical processing and chemical reactions to build or modify delicate porous nanostructures. Historically, the most promising developments of the supercritical fluid technology in the field of porous materials have been foaming of polymers, processing and/or impregnation of aerogels, and surface modification of micro and mesoporous solids. More recently, the technology has evolved to the synthesis of porous materials by developing reactive processes in $scCO_2$. One example is the synthesis of empty-pore three-dimensional metal-organic frameworks (MOFs). This paper reviews process concepts of supercritical fluid methods applied to porous compounds, giving examples of materials produced in our own laboratory. The processing of disordered (polymers, aerogels, concrete) and ordered (zeolites, mesoporous silica's, MOFs) porous materials is addressed. Perspectives of future development of the technology in pharmaceutical formulations and CO_2 capture applications are given.

1. Introduction

The field of porous materials is, currently, at an exciting stage in its technological evolution. The research on ordered −including zeolites, zeotypes, metal-organic frameworks and mesoporous silica- and disordered −including ceramics, sintered metals and foamed polymers-porous solids [1] is among the most creative, fascinating and attractive fields of materials science. The supercritical fluid technology addressed the processing of porous matter from the beginning. Innovations in "porous materials and supercritical fluids" were compiled by A.I. Cooper in 2003 [2]. The basis of the developments of supercritical carbon dioxide ($scCO_2$) methodologies in porous materials is two-fold: first, the solubility of $scCO_2$ in polymers, with a pressure-dependent behavior, is substantial in comparison with conventional solvents; and second, the adsorptive behavior of $scCO_2$ in inorganic porous systems is insignificant when compared to liquid fluids, which allows the one-step design of surface grafting and impregnation processes.

$scCO_2$ technology applied to nanopores takes profit of the compressed CO_2 gas-like viscosity, high diffusivity and null surface tension, so capillary stresses are suppressed, converting this fluid in a non-damaging solvent for those structures, facilitating their synthesis and modification. The use of $scCO_2$ overcomes the limitations of diffusivity

* Corresponding author.
E-mail address: conchi@icmab.es (C. Domingo).

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and mass transfer of conventional solvents and can transfer an effective amount of materials into very small pores. Most importantly, pore collapse can be avoided because the expansion of $scCO_2$ directly as a gas does not give rise to a liquid-vapor interface. When the process is carried out from a liquid solution, the possibility of competition between solvent and solute molecules for the substrate adsorption sites often leads to the incorporation of both components into the internal surface of the porous system. Competition between the solvent and the solute for the substrate adsorption sites is reduced in $scCO_2$ with respect to liquid solvents, since supercritical fluids are essentially not absorbed. The adsorption by micropores, called micropore filling, is distinguished from capillary condensation that is molecular adsorption by mesopores, the later not possible in supercritical fluids. Only microporous materials are slightly effective at adsorbing $scCO_2$, as physical adsorption is enhanced by the overlapping of the molecule-surface interaction potentials from opposite pore walls. The null or little use of organic solvents, the straight preparation of dry products in confined autoclaves and the CO_2 intrinsic sterility are of particular interest to produce different nanoporous systems, their stabilization and formulation.

The production of bulk polymeric porous materials, which can be visualized as sponge-like substances with disordered pores, has been deeply studied using $scCO_2$ [3]. In these materials, the open porosity is not intrinsic; actually, it is generated during the supercritical treatment. An additional bulk key product developed using this technology is the aerogel, obtained from an organogel after a supercritical drying treatment, which ensures the characteristic properties of this mesoporous material [4]. Finally, pore densification by $scCO_2$ of structural concrete is a process that also deserves attention, due to the overwhelming success of the cement industry in our society since Roman times [5]. For ordered porous materials, $scCO_2$ has traditionally been used to modify the characteristics of their internal surface or empty volume. Microporous zeolites, with intrinsic uniform pores, are the most consumed substrates in industry [6]. However, certain limitations, such as zeolites small pore size and structural rigidity, have motivated the development of alternative ordered porous materials, such as mesoporous silica [7], flexible metal-organic frameworks (MOFs) [8] and hierarchical zeolites [9]. Those compounds can be modified using $scCO_2$ solvent; moreover, MOFs can be prepared in $scCO_2$ plus a cosolvent and/or in the presence of an ionic liquid [10]. Main applications of $scCO_2$ in the field of inorganic meso and microporous solid substrates are related to adsorption (e.g., high-value non-volatile organics separation, impregnation for drug delivery, protective coating and surface functionalization and CO_2 capture) and desorption (e.g., cleaning and drying, regeneration of sorbents and extraction) processes. Besides being used as a solvent, $scCO_2$ can also play other primary roles, such as antisolvent, solute or reaction medium, which offer a unique flexibility as a surface engineering technology [11].

The aim of this article is to cover areas where the unique properties of $scCO_2$ are exploited to generate porous materials with characteristics difficult to obtain by other routes, highlighting the specific benefits associated with the use of this fluid in relation to composition, purity, physiochemical properties, porosity and effectiveness in chosen applications. Herein, some of the most prominent classes of disordered and ordered porous materials are analyzed in detail, from both a synthetic and applied point of views, by focusing in examples of supercritically produced porous materials in our laboratory during the last two decades.

2. Current state

2.1. Polymers

From the beginning, polymers precipitation, modification and synthesis had constituted some of the most active areas of research in supercritical fluid technology [12–14], which soon led to its utilization in the production of polymeric foams [15]. First studies were focused on the foaming of high-viscosity amorphous polymers, such as polystyrene (PS) or polyethylene (PE) and their blends [16,17], which are some of the most widely used commodity polymers for insulation and packaging applications. Nowadays, because of environmental concerns, the industry is favoring the use of biopolymers derived from renewable resources. These materials are frequently used in applications related to health care, specifically in tissue engineering and drug delivery. For instance, biodegradable poly(D,L-lactide) (PLA) and polylactide-co-polyglycolide (PLGA) have been deeply evaluated to prepare 3D scaffolds, together with some relevant biocompatible stiff polymers, such as polycaprolactone (PCL) and polymethylmethacrylate (PMMA) [18].

In conventional technology, the high viscosity of polymers is overcome by foaming them at high temperatures, and the process is aided by the addition of organic solvents and/or physical blowing agents, such as chlorofluorocarbons and hydrocarbons with a high ozone depletion effect. In handling polymers, $scCO_2$ has been found to be an excellent replacement for organic solvents and blowing agents, simultaneously. $ScCO_2$ can reversibly swell glassy and rubbery polymers, reducing the viscosity of the polymer melts up to an order of magnitude. The Lewis acid-base interactions formed between CO_2 and polymers were evidenced by Raman analysis [19]. After polymer saturation with compressed CO_2, a pressure reduction step is used to generate supersaturation, nucleation of CO_2 bubbles and pore growth until vitrification of the network. The inner morphology is determined by the thermophysical and rheological properties of the polymer, the level of saturation with CO_2 at the chosen pressure and temperature, the rate and profile of pressure reduction and the depressurization temperature that fix the polymer vitrification conditions [20,21]. Extrusion assisted by $scCO_2$ is a continuous method designed for the microcellular foaming of polymers, which provides rapid mixing and dissolution of CO_2 in the polymer melt. $ScCO_2$ is injected in the extruder barrel to melt the polymer at reduced temperature, also acting as the blowing agent at the exit of the spinneret [22].

The foaming of polymeric microspheres has been studied simultaneously with the impregnation process to achieve systems adequate for controlled drug delivery [23–26]. For tissue engineering applications, the architecture of the scaffold would play an important role in modulating tissue growth. A correct architecture of a scaffold would be the one that mimics the natural extracellular matrix, i.e., with high nanoporosity and an interconnected 3D macroporous network necessary for cell proliferation. Scaffolds can be produced using conventional techniques, such as solvent casting, foaming, physical separation and freeze drying, or advanced processing methods, such as rapid prototyping technologies, in which the scaffolds are built layer by layer from a computer-aided design model [27]. The main drawbacks of conventional scaffolds production methods involve a reduced capability to control pore size and the presence of residual toxic organic molecules. Although the use of $scCO_2$ has been found to be very convenient to prepare porous polymers for this application, the pressure quenching foaming procedure, previously optimized for PS, generates closed microcellular core structures (interconnectivity $< 30\%$) encased by a nonporous skin, characteristics not adequate for scaffolds used in tissue engineering [28–31] (Fig. 1a). Scaffold textural properties can be improved by blending the polymer with a particulate porogen, e.g., NaCl or gelatin which are leached out with water, or by adding appropriate plasticizers to $scCO_2$, e.g. biocompatible ethyl lactate or ethyl acetate, as investigated in our laboratories [32] (Fig. 1b). These polymers can also be foamed *via* high-pressure extrusion [33]. Moreover, foams with multiscale pore structures can be manufactured by the optimization of the depressurization rate and mode. In general, the two-step depressurization mode is suitable for the fabrication of porous polymeric materials with bimodal pore size distribution, involving pores in the macro and nanometer scales [34] (Fig. 1b). The melting of the polymer during the $scCO_2$ treatment allows the dispersion of biocompatible nanofillers, such as hydroxyapatite, which enhances tissue growth bioactivity [35].