Features of supercritical CO_2 in the delicate world of the nanopores

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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.

INTRODUCTION

The supercritical fluid technology addressed the processing of porous matter from the beginning. 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 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 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 [1]. Herein, some of the most prominent classes of disordered and ordered inorganic 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.

RESULTS AND DISCUSSION

1. Aerogels

Aerogel is a general terminology referring to any material derived from organic, inorganic and hybrid molecular precursors that prepared by a supercritical drying technology results in a highly porous solid 3D network. Common types of aerogels are constituted by silica, metal oxides, carbon and synthetic polymers and polysaccharides. In our laboratories, we have focus the research in aerogels of graphene oxide (GO). GO combines the textural advantages of graphene with convenient hydrophilicity and fascinating surface chemistry. The presence of functional groups enables the exfoliation of GO sheets in polar liquids, including ethanol, leading to stable colloidal dispersions. Although several techniques have been proved to successfully produce high surface area GO aerogels, a method integrating the advantages of efficiency, environmental friendly, safety and low-cost together is still being pursued. For GO aerogels, supercritical fluid technology has mainly been applied at the critical point of ethanol. The method developed in our laboratory is devoted to the formulation of GO aerogels directly from GO dispersions using exclusively low temperature $scCO_2$ technology (333 K at 20 MPa), avoiding the use of any cross-linking agent. The aerogel monoliths obtained by simultaneous $scCO_2$ gelation and drying have a very low density and high specific surface area, which rivals with that of most light-weight graphene aerogels reported in the literature. These aerogels are formed under mild conditions which fosters the stability of the functional groups during the procedure.

2. Zeolites

Zeolites are crystalline aluminosilicates with a structure based on an open 3D network formed by interconnected micropores and channels, giving an enormous degree of structural and compositional diversity. In various domestic and industrial fields, like catalysis, petrochemical industry, detergents, filtration or separation, molecular sieving and adsorption, a matured technology is settled around zeolites with pore sizes lower than 1 nm. Zeolites are also used to perform reactions in restricted space, where the dimensions of the reaction vessel are comparable to those of the reactants. For instance, target molecules that are too large to diffuse through the zeolite pore opening, but are of the correct size to be housed into the intrazeolite large cavities, can be incorporated by ship-in-a-bottle reactive post-synthesis methods. In this particular case, suitable precursors penetrate by diffusion from a solvent thought the zeolite channels and are further transformed into the final compound by reaction in the large cavities. The replacement of liquid solvents by $scCO_2$ in this novel synthetic method was a successful process developed in our laboratory with the aim of reducing diffusion times. In contrast to the conventional long and multiple-step procedure, the developed supercritical ship-in-a-bottle methodology is a one-pot reaction with a duration of only few hours.

3. Mesoporous ordered silica

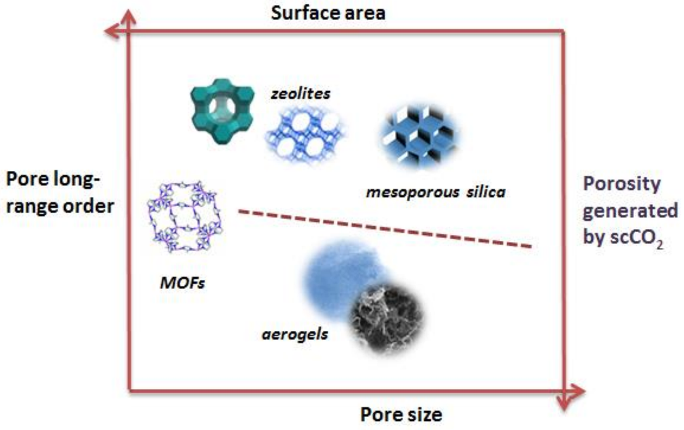
Since their description in the late 1990s by Mobil Company, amorphous mesoporous silicas have attracted much attention due to their unique properties, such as ordered pore structures, reactive pore walls with a hydroxyl surface density of 4-6 $OHnm^{-2}$, and very high specific surface areas, up to 1000 m^2g^{-1} and higher. They find applications in waste water remediation, indoor air cleaning, catalysis, drug delivery, CO_2 capture, etc. In our research group, we have studied the grafting of different organic molecules in the internal surface of MCM-41 with pores of 4 nm diameter. We have performed a detailed study the silanization of the mesoporous substrate MCM-41 with aminosilanes for the particular application of CO_2 capture. The essence of the supercritical silanization method with aminosilanes consists of performing a preliminary study to determine the best operating conditions that avoid the formation of insoluble carbamate species by reaction between the amine (primary or secondary) and CO_2. For a monoamine, those conditions were found to be conformed by low pressures (7.5-9.0 MPa) and relatively high temperatures (373-408 K), using pure CO_2 or CO_2 plus a cosolvent. Aminosilane grafted densities as high as 3-4 molecules per nm^2 were reached.

4. Crystallization of MOFs in $scCO_2$

Recently, several new microporous solids have entered the scientific scene, highlighting the metal-organic frameworks (MOFs), covalent organic frameworks, and porous organic polymers. From them, MOFs are the most studied compounds also in regard of $scCO_2$ use. MOFs are a class of crystalline materials produced by the coordination of transition-metal cations with multidentate organic linkers, forming extended frameworks that often are highly porous. These are materials primarily proposed for adsorption applications in H_2 and CO_2 storage and gas purification and separation, but also for catalysis, sensing, and biomedical uses. The solvothermal technique is the most commonly employed method for their synthesis. However, this is an energetic and time-consuming approach performed in polluting organic solvents, which needs extensive cleaning, drying, and activation periods after product crystallization. One important drawback for the use of these materials is channel collapse upon solvent removal or channel blockage due to solvent retention. It has been shown that $scCO_2$ drying leads to substantial, or in some cases spectacular (up to 1200 %), increase in N_2-accessible surface area, avoiding pore collapse. The use of compressed CO_2 in the field of MOFs has been mainly limited to post-synthesis activation by cleansing entrapped undesired byproducts or solvents, performed either by batch solvent exchange/$scCO_2$ treatment or directly from the solvated crystals by flowing $scCO_2$. On the basis of the analysis of the state of the art in $scCO_2$ crystallization and conventional MOFs synthesis, we thought that the successful preparation of open-pore MOFs is a real possibility through the right choice of building blocks. $ScCO_2$ appears as an attractive medium to synthesize these materials due to the potential solubility of numerous MOF precursors in this fluid, including organometallic compounds and some typical organic bridging molecules such as pyridine-based linkers, thus allowing their formation by reactive crystallization. This open new avenues in the use of $scCO_2$ for the synthesis of complex nanostructured products. Preliminary studies have shown that the straight precipitation of 3D porous MOFs in $scCO_2$ is a feasible chemical process. Moreover, amazing crystal shapes are obtained, which can be analyzed from a crystal growth mechanistic point of view by taking into account nonclassical routes of crystallization. Some representative results for 3D porous MOFs already obtained by us in $scCO_2$, correspond to a known phase (ZIF-8) and a new curcumin-MOF. It is worth mentioned that the synthesis of 3D MOFs often involves high molecular weight or polar molecules with low solubility in $scCO_2$ which, in principle, would discard many synthetic possibilities. However, our work has demonstrated that the synthesis protocols in $scCO_2$ could be extended to 3D structures, in some cases, requiring the addition of a cosolvent.

CONCLUSIONS

The following scheme shows graphically some important porous products studied in our research group during the last years. They are classified as a function of pore size, pore order and interaction with $scCO_2$.



In addition to the use of $scCO_2$ solvent for foaming and the controlled drying of preformed porous materials, like aerogels, we thought that the unique properties of this solvent can be easily exploited for the *in situ* preparation of porous materials by chemical interaction and/or reaction. Examples are the non-reactive gelation of dispersions (1D MOFs, graphene) and the reactive crystallization of MOFs. These approaches reduce significantly solvent usage, simplify phase separation and avoid the need of purification.

REFERENCES

[1] LOPEZ-PERIAGO, A.M., DOMINGO, C., Features of supercritical CO2 in the delicate world of the nanopores, 30th year Special Issue of J. Supercrit. Fluids 2018; https://doi.org/10.1016/j.supflu.2017.11.011

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