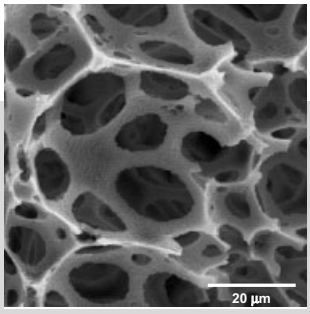
Porous Materials and Supercritical Fluids**

By *Andrew I. Cooper**



Porous materials are used in a wide variety of applications, including catalysis, chemical separation, and tissue engineering. The synthesis and processing of these materials is frequently solvent intensive. In addition to reducing organic solvent emissions, supercritical fluids offer a number of specific physical, chemical, and toxicological advantages as alternative solvents for the production of functional porous materials. The figure shows an electron image of a porous polyacrylate produced by the templating of a concentrated CO_2-in-water emulsion—a process that would otherwise be highly solvent intensive.

1. Introduction

1.1. Alternative Solvents

Almost 15 billion kilograms of organic and halogenated solvents are produced worldwide each year. The use of organic solvents in manufacturing and processing on this scale represents a major ecological problem. Similarly, both the generation of polluted aqueous waste streams and the energy used to remove water from products (i.e., drying steps) make significant contributions to global environmental pollution. As such, there is a real need to consider either solvent-free processes or alternative solvents.[1–3] In recent years, a number of research groups have proposed alternatives to conventional organic solvents or water. These include supercritical fluids (SCFs),[4,5] ionic liquids,[6] and fluorous solvents.[7,8]

This review focuses specifically on the use of SCFs for the synthesis and processing of porous materials. In particular, the aim is to highlight areas where the unique properties of SCF solvents can be exploited to generate materials that would be difficult or inconvenient to obtain by other routes. The general properties of SCFs in relation to chemical synthesis[4] and extraction[5] have been reviewed previously and will not be reiterated here. The specific benefits associated with SCFs in connection with porous materials will be discussed throughout.

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[**] The author thanks the Royal Society for provision of a Royal Society University Research Fellowship and acknowledges EPSRC for funding (GR/R15597, GR/N39999 and GR/23653). Mr. I. Hussain, Dr. K. Senoo, Dr. B. Tan, and Dr. H. Zhang are acknowledged for their help in preparing this review.

1.2. Supercritical Fluids in Materials Chemistry

SCF solvents are being evaluated in a diverse range of materials applications,[9,10] such as polymer synthesis,[11–13] particle formation,[14–16] coatings, lithography,[1,17] dyeing,[18] and waste management.[19,20] All of these applications exploit at least one of the unique properties associated with SCFs. There are several specific reasons to consider SCFs as alternative solvents for the synthesis and processing of porous materials:

i) The production of porous materials is often solvent intensive—more sustainable alternatives could offer significant environmental benefits.

ii) Drying steps can be energy intensive—with the exception of water, most of the SCF solvents studied so far are gases under ambient conditions.

iii) Pore collapse can occur in certain materials (e.g., aerogels) when removing conventional liquid solvents—this can be avoided by the use of SCF solvents, which do not give rise to a liquid–vapor interface.

iv) Porous structures are important in biomedical applications (e.g., tissue engineering) where there are strict limits on the amounts of residual organic solvent that may remain in the materials—this provides a strong driving force to seek non-toxic solvent alternatives.

v) Surface modification of porous materials frequently requires the use of solvents that will wet the pore structure efficiently—SCFs (and certain liquefied gases, such as CO_2) are extremely versatile wetting agents due to their low surface tensions (e.g., liquid CO_2 will wet Teflon).

vi) Surface modification or templating of nanoporous materials presents special problems because organic solvents are often too viscous to fill such small pores. Even gaseous species (when below the critical temperature) can condense within small pores, thus forming a relatively viscous liquid "plug" that blocks the pore to further penetration. SCF solvents have much lower viscosities than organic liquids and cannot condense into the liquid state. Moreover, mass-trans-

 DOI: 10.1002/adma.200300380

fer rates in SCF solvents tend to be high owing to low solvent viscosity.

vii) As a result of their compressed state, SCF solvents are highly suited to the generation of polymer foams. Moreover, polymer foaming requires that the material is either melted or highly plasticized—many SCF solvents are excellent plasticizing agents (while being non-solvents) for a wide range of polymers.

In many applications, more than one these considerations is important. As such, the synthesis and processing of porous materials is a particularly fertile area for SCF research. This review will summarize recent advances in the use of SCF solvents for the generation or modification of porous structures, with special attention to the points listed above.

To avoid confusion, we have restricted our use of the terms micropore, mesopore, and macropore to the definitions recommended by IUPAC,[21] i.e., micropores < 2 nm, mesopores 2–50 nm, and macropores > 50 nm.

2. Generation of Porous Materials by Supercritical Fluid Processing

2.1. Foaming

2.1.1. Microcellular Polymer Foams

SCFs are useful for the production of expanded microcellular polymer foams, as reviewed previously.[13] For example, "solvent-free"[22–29] approaches have been developed whereby a polymer is saturated with supercritical carbon dioxide ($scCO_2$) (usually at moderately elevated temperatures), followed by rapid depressurization at constant temperature (i.e., a pressure quench as opposed to a temperature quench). This method takes advantage of the large depression in the glass-transition temperature (T_g) found for many polymers in the presence of CO_2, which means that the polymer may be kept in the liquid state at relatively low temperatures. By lowering the pressure at a fixed temperature, the amount of diluent absorbed by the polymer is decreased. Thus, T_g begins to rise, eventually to the point where the T_g for the polymer is higher than the foaming temperature: at this point the cellular structure can grow no further and is locked in. The sudden reduction in pressure leads to the generation of nuclei due to supersaturation, and these nuclei grow to form the cellular structure until vitrification occurs.

Ultralow-k dielectric materials have been produced by foaming polyimides (e.g., Matrimid) using $scCO_2$.[30] This approach allows the formation of both microcellular and bicontinuous, nanoporous structures, with dielectric constants as low as $k = 1.77$. A process was also developed for the production of porous polyetherimide monofilaments by semicontinuous solid-state foaming using a modified "pressure-cell" technique.[31] Dense, CO_2-saturated fibers were spun at rates up to 1 m s^{-1} with porosity being introduced at the spinning head (Fig. 1). The process was designed to allow the production of closed microcellular as well as open nanoporous filaments.

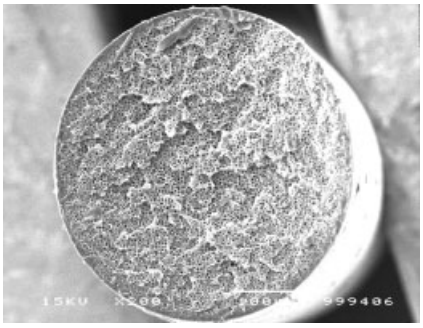

Fig. 1. Electron image of the cross-section of a foamed polyetherimide fiber, saturated for 8 h at 10 bar CO_2 saturation pressure and foamed at 180 °C for 30 s. Scale bar = 100 μm. Reproduced with permission; copyright 2002, American Chemical Society [31].

The generation of microcellular poly(vinylidene fluoride) (PVDF) foams using $scCO_2$ by continuous extrusion has also been described.[32] Both semicrystalline PVDF and blends of PVDF with polystyrene (PS) and poly(methyl methacrylate) (PMMA) were foamed using a single-screw extruder. For PVDF/PMMA blends, it was found that the cell density decreased (from 10^8 to 10^{10} cell cm^{-3}) and the bulk density increased (from 0.85 to 1.25 g cm^{-3}) as the foaming temperature was raised from 140 to 200 °C.[32]

Andrew Cooper obtained both B.Sc. (1991) and Ph.D. (1994) degrees in Chemistry at the University of Nottingham (UK). Upon completing his Ph.D., he was awarded an 1851 Research Fellowship which he held in the Chemistry Department at the University of North Carolina, Chapel Hill (USA) (1995–1996). He then held a Ramsay Memorial Research Fellowship in the Melville Laboratory for Polymer Synthesis, University of Cambridge (UK) (1997–1998). In 1999, he moved to the Chemistry Department at the University of Liverpool (UK) where he holds a Royal Society University Research Fellowship. He was recently awarded the Royal Society of Chemistry MacroGroup UK Young Researchers' Award (2002). His research interests include organometallic reaction mechanisms, dendrimers, supercritical fluids, polymer synthesis, porous polymers, emulsion-templated materials, and high-throughput approaches for accelerated materials discovery.

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2.1.2. Biocomposite Foams

It is clearly desirable to use non-toxic solvents for the synthesis or processing of biocomposite materials (e.g., for tissue engineering).[33,34] Carbon dioxide is an obvious choice for such applications, although SCF alkanes (e.g., ethane, propane) and certain hydrofluorocarbons (e.g., R134a)[35] could, in principle, fulfil similar requirements from a toxicological perspective. A major challenge in this area is to incorporate biologically active guest species into polymer hosts without loss of activity. For example, there are well-documented problems in maintaining protein activity under conventional processing methods due to either the presence of an organic–aqueous interface (e.g., double-emulsion techniques), elevated temperatures (e.g., polymer melt processing), or vigorous mechanical agitation. A further challenge is to control the morphology of the composites (e.g., to generate porosity that optimizes release characteristics or allows cell infiltration into a scaffold).

SCF mixing can be used to overcome many of these limitations in a single processing step. For example, CO_2-induced plasticization has been exploited to lower the viscosity of biodegradable polymers, such as poly(D,L-lactide) (PLA), polylactide-*co*-polyglycolide) (PLGA), and polycaprolactone, to such an extent that bioactive guests could be mixed into the polymer at temperatures close to ambient (e.g., 35 °C, 200 bar).[36] Foaming occurred upon venting the CO_2, which introduced a high degree of porosity into the composite materials. Biocomposites were formed encapsulating enzymes (e.g., ribonuclease A, catalase, β-D-galactosidase) and it was found that the enzyme activity was retained. Adenoviral osteoprogenitor constructs were also produced by $scCO_2$ foaming of PLA (Fig. 2).[37,38] The replacement of bone tissue is a major clinical and socioeconomic need, and again the avoidance of organic solvent residues is appealing.

Microporous PLGA foams containing encapsulated proteins (e.g., basic fibroblast growth factor) have also been prepared by SCF processing of water-in-oil (W/O) emulsions.[39]

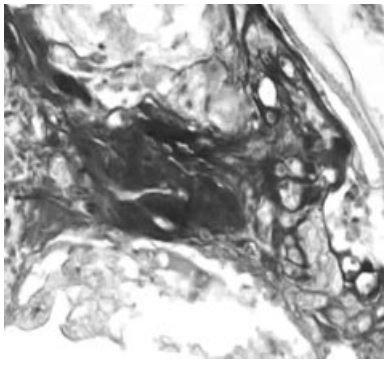

Fig. 2. Demonstration of sub-cutaneous new bone formation using human osteoprogenitor cells seeded onto a porous SCF-processed poly(lactic acid) scaffold, adsorbed with a bone growth factor (osteoblast stimulating factor-1) in MF1 nude mice. Note the extensive new woven bone formation (dark areas in image) as confirmed using birefringence microscopy demonstrating organized collagen and matrix formation. Scale bar = 1 μm. Reproduced with permission; copyright 2003; American Society for Bone and Mineral Research [38].

In this process, an aqueous protein phase was emulsified in a concentrated solution of PLGA in methylene chloride followed by SCF extraction of the organic solvent and subsequent SCF foaming. Residual methylene chloride levels in the foams were found to be higher than the 600 $\mu g\,g^{-1}$ limit established by the US Pharmacopoeia, although it was suggested that these levels could be reduced by longer periods of SCF extraction,[39,40] or by prolonged vacuum drying.[39] The synthesis of PLGA by ring-opening precipitation copolymerization of lactide and glycolide monomers in $scCO_2$ using stannous octoate as the initiator was also reported.[41] Relatively low molecular weight PLGA (M_w ~3500 $g\,mol^{-1}$) was produced and the material could be recovered as an expanded porous foam after depressurization.

2.2. Crystallization of SCF-Swollen Crosslinked Polymers (CSX)

An alternative process for the generation of porous polymer structures is crystallization of swollen, crosslinked polymers, or "CSX".[42] Candidate materials for this process require i) a crystallizable block in the polymer; ii) chemical crosslinking between the polymer chains; and (iii) the possibility of swelling by an appropriate fluid. In the CSX process (Fig. 3), a preshaped, crosslinked polymer is heated above the crystal melting temperature (point 2) before a SCF solvent is added in order to transform the polymer into the swollen gel

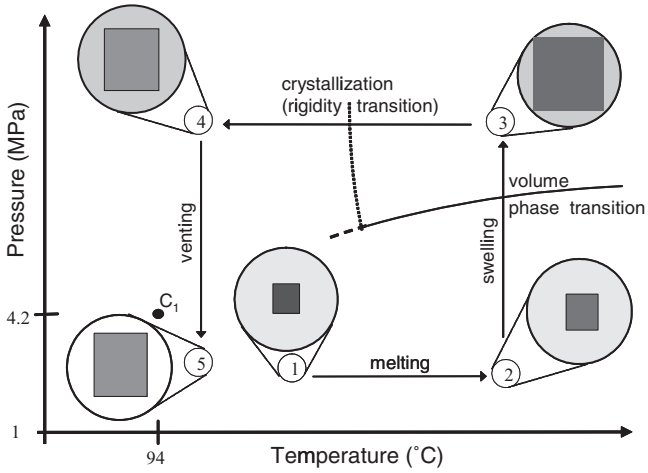

Fig. 3. Schematic pressure–temperature (P–T) diagram of the CSX process for generating porous structures through an intermediate gel state. The critical point (T_c, P_c) is denoted by "C_1". The various states are as follows: 1) initial polymer specimen; 2) amorphous network; 3) swollen gel; 4) bicontinuous structure of polymer and SCF; 5) porous polymer structure after venting of SCF. Reproduced with permission; copyright 2002, American Chemical Society [42].

state (point 3). Subsequent crystallization leads to the development of two continuous phases: a solid polymer-rich phase intertwined with a fluid phase (point 4). After removal of the fluid, a bicontinuous pore structure remains (point 5). It should be noted that this process is *not* a foaming process since the swollen CSX gel consists mostly of swelling fluid,

which does not expand or contract significantly during pore formation. This technique has been used to process linear low-density polyethylene (LLDPE) with a gel content of 15.9 % using supercritical propane to give materials with pore diameters in the range 10 nm–10 μm and void volumes of more than 80 % (Fig. 4).[42] The resulting pore structure was ultraclean, and preliminary results suggested that the materials were ready for biomedical applications (e.g., the culture of HEPG2 liver cells) without any further purification.

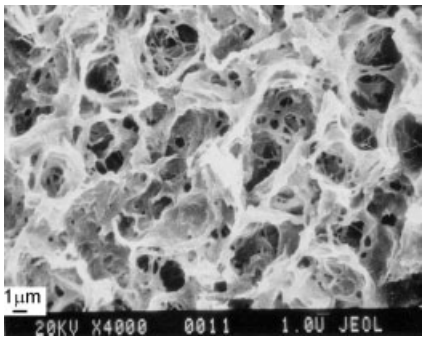

Fig. 4. Electron image of porous radiation crosslinked LLDPE (15.9 % gel content), produce by the CSX process outlined in Figure 3. Void volume = 83 %. Scale bar = 100 μm. Reproduced with permission; copyright 2002, American Chemical Society [42].

A different strategy is to crystallize polymer materials from *homogeneous* SCF solutions, although this may be somewhat limited in scope by solubility considerations.[43,44] An example of this approach is the production of mesoporous open-cell foams (surface area = 120–150 $m^2 g^{-1}$) by crystallization of isotactic polypropylene from homogeneous solution in supercritical propane.[45]

2.3. SCF Antisolvent-Induced Phase Separation

Since $scCO_2$ is such a poor solvent for common, organic hydrocarbon polymers,[44] it has broad potential as an antisolvent for the preparation of porous polymeric materials. Porous PS[46] (Fig. 5) and cellulose acetate[47] membranes were formed by precipitation from a suitable organic solvent. The membranes were prepared by a wet phase-inversion method, in which a homogeneous polymer solution is immersed in a non-solvent bath (in this case containing $scCO_2$). The approach is analogous to methods used to produce polymer particles (e.g., precipitation with a compressed fluid antisolvent or "PCA") except that the two solvents are mixed much more slowly. (In PCA, the organic polymer solution is typically sprayed rapidly into the antisolvent in order to produce particles, see Sec. 2.5 below.) As in the case of the CSX process,[42] the porosity in the membranes was not generated by foaming: turbidity was observed in the solutions after addition the $scCO_2$ and little change was observed during depressurization, suggesting that the porous structures were formed by antisolvent-induced phase separation rather than by physical expansion.[46]

2.4. Non-Reactive Gelation of SCF Solutions Using Organogelators

The formation of low-density porous materials with nanoscopic features by using low molecular mass organic gelators (LMOGs) is currently a subject of considerable interest.[48] Materials produced by this route are often highly fragile and subject to structural collapse during drying because of capillary forces. As such, SCF solvents offer a distinct advantage for the synthesis and processing of these materials, for the same reasons that SCFs are used to dry silica aerogels.[49,50] Low-density microcellular fluorinated materials were generated by a one-step process which uses $scCO_2$ and requires no organic solvents.[9,51,52] Highly fluorinated, low molar mass compounds[51,52] and polymers[52] were synthesized which dissolve in $scCO_2$ and then associate to form gels. Upon removal of the CO_2 phase, the gels produced free-standing foams with average cell diameters smaller than 1 μm and density reductions of 97 % relative to the parent compound (Fig. 6). This technique combines gelation and foaming in one process. It is likely that less expensive, non-fluorinated gelators (e.g., based on peracetylated sugar derivatives[53]) could be developed in the future for similar applications.

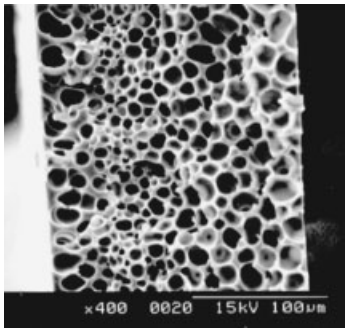

Fig. 5. Porous PS membrane produced by wet phase inversion from toluene using $scCO_2$ as the antisolvent (25 °C, 20 wt.-% polymer solution in toluene, $M_w = 280\,000$ g mol^{-1}). Reproduced with permission; copyright 2001, Elsevier Science [46].

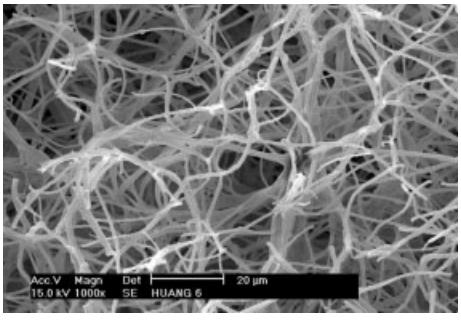

Fig. 6. SEM image of a free-standing foam produced from a CO_2-soluble trifunctional urea by gelation of a 5 wt.-% solution in $scCO_2$ (scale bar = 20 μm). Bulk density of the foam is approximately 0.09 g cm^{-3}. Reproduced with permission; copyright 1999, the American Association for the Advancement of Science [51].

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Similarly, LMOG aerogels have been produced from 2,3-didecyloxyanthracene, both by SCF drying of gels formed in ethanol, and by direct gelation of $scCO_2$ without the use of any organic solvents.[54]

2.5. Porous Particle Formation

The preparation of micrometer-sized particles using SCFs is particularly useful for the processing of pharmaceutical formulations.[55] Broadly speaking, there are two main strategies to achieve this; rapid expansion of supercritical solutions[14,56,57] (where the material must be soluble in the fluid) and antisolvent precipitation[15,58,59] (where the material should be insoluble). Antisolvent precipitation has potential for generating porous microparticles from a wide variety of substrates, particularly since it does not require that the starting material is soluble in the SCF solvent (see also discussion on membranes,[46,47] Sec. 2.3).

Porous PS microspheres and microballoons (hollow microspheres) were produced by spraying a toluene solution of PS through a capillary into CO_2 vapor to form droplets, which then fell into liquid CO_2 where they were rapidly dried and vitrified.[60] Both the thickness and porosity of the microcellular shells could be controlled by changing the initial solution composition. The cell sizes and surface areas of the microspheres were approximately 1–20 μm and 3–40 $m^2 g^{-1}$, respectively.

A non-steroidal drug, $Cu_2(indomethacin)_4L_2$ [L = dimethylformamide (DMF)] was formulated into micrometer-sized particles using both gas antisolvent (GAS) techniques and aerosol extraction systems (ASES).[61] In both cases, DMF was used as the solvent and CO_2 as the antisolvent. Under certain conditions, the material processed by ASES could be isolated as large (> 50 μm), porous spheres.

The main requirement for these processes is that the solvent and the SCF antisolvent are miscible. While the approach is therefore quite general, a disadvantage is that the use of organic solvents is not avoided.

3. Chemical Synthesis of Porous Materials Using Supercritical Fluids

3.1. Chemical Gelation of SCF Solutions

The use of SCF solvents to avoid pore collapse during drying of inorganic, organic, and organic–inorganic hybrid aerogels,[51] and other nanoscale porous materials such as semiconductors,[62] has been reviewed by others and will not be discussed in detail here. In the supercritical state there is no liquid–vapor interface so capillary stresses are suppressed, although other stresses can occur because of differential strain between the SCF in the pores and the porous matrix.[62] More recently, the same advantages have been exploited to allow the preservation of high-aspect-ratio, nanometer-sized features in microlithography using $scCO_2$ as the developing solvent (Fig. 7).[1]

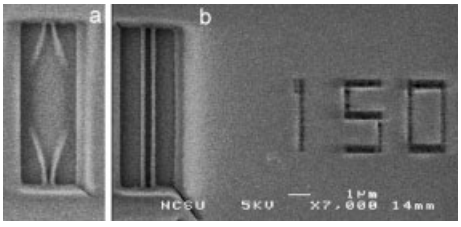

Fig. 7. Electron images of 150 nm microlithographic features (6:1 aspect ratio) developed by a) aqueous-based development and b) $scCO_2$-based development using appropriate adjuncts. The use of a SCF solvent for pattern development avoids feature collapse, in a similar way that pore collapse is avoided in the SCF drying of aerogels. Scale bar = 1 μm. Provided by Micell Technologies and reproduced with permission [1].

In addition to the use of SCF solvents for the controlled drying of preformed porous materials, researchers have exploited SCF solvents as media for the in-situ preparation of porous materials by chemical *reaction* (i.e., direct chemical gelation of SCF solutions). The primary advantages of this approach are that separation is simple and that it is possible to avoid the use of large volumes of organic solvents, both in the synthesis step itself and by eliminating further solvent usage during sample purification.

3.1.1. Sol–Gel Polymerization of Alkoxysilanes in SCFs

Aerogels have been synthesized by sol–gel polymerization of alkoxysilanes in $scCO_2$.[50] Instead of forming gels in alcohol solvents before exchanging the alcohol for CO_2, $scCO_2$ was used directly as the sol–gel polymerization solvent. Standard sol–gel formulations require large quantities of water (typically 2–3 equivalents) for the hydrolysis and condensation of the alkoxysilane monomers.[51] Alcohols are good solvents for these processes because they are capable of dissolving both water and non-polar alkoxysilane monomers. Since the solubility of water in CO_2 is very low, an alternative water-free method was used.[50] Alkoxysilanes such as tetramethoxysilane or 1,4-bis(triethoxysilyl) benzene were polymerized at 35–45 °C in $scCO_2$ (410 bar) in the presence of 13–36 wt.-% formic acid. Gelation occurred within 12 h and the gel was aged for a further 12–18 h. At the end of the reaction, the CO_2 pressure was released to yield silica aerogels in almost 100 % yield to give materials with surface areas in the range 250–600 $m^2 g^{-1}$.

3.1.2. Free-Radical Polymerization using $scCO_2$ as a "Pressure-Adjustable" Porogen

We have investigated the formation of permanently porous crosslinked poly(acrylate) and poly(methacrylate) monoliths using $scCO_2$ as the porogenic solvent.[63,64] Materials of this type[65,66] are useful in applications such as high-performance liquid chromatography, high-performance membrane chroma-

tography, capillary electrochromatography, microfluidics,[67] molecular imprinting,[68] and high-throughput bioreactors.[69] In our process, no organic solvents are used, either in synthesis or in purification. It is possible to synthesize the monoliths in a variety of containment vessels, including chromatography columns and narrow-bore capillary tubing. Moreover, we have exploited the variable density associated with SCF solvents in order to "fine-tune" the polymer morphology. Figure 8 shows the variation in the Brunnauer–Emmet–Teller (BET) surface area for a series of crosslinked poly(trimethylolpropane trimethacrylate) monoliths synthesized using $scCO_2$ as the porogen over a range of reaction pressures.[70] The average pore size and surface area in these materials could be tuned continuously over a considerable range (BET surface area = 90–320 $m^2 g^{-1}$) just by varying the SCF solvent density. It is interesting to note that a minimum in surface area (and a maximum in the average pore diameter, not shown) was observed at a reaction pressure of around 2600 psi (~18 MPa). This can be rationalized by considering the variation in solvent quality as a function of CO_2 density and the resulting influence on the mechanism of nucleation, phase separation, aggregation, monomer partitioning, and pore formation.[71] We have also applied the same concept to the synthesis of well-defined porous, crosslinked poly(methacrylate) beads (diameters = 100–200 μm) by suspension polymerization, again without the use of any organic solvents (Fig. 9).[72] The surface area of the beads could be tuned over a wide range (5–500 $m^2 g^{-1}$) by varying the CO_2 density. Both of these techniques demonstrate how the variable density associate with SCF solvents can be exploited to precisely control the structure of porous materials produced by reaction-induced phase separation.

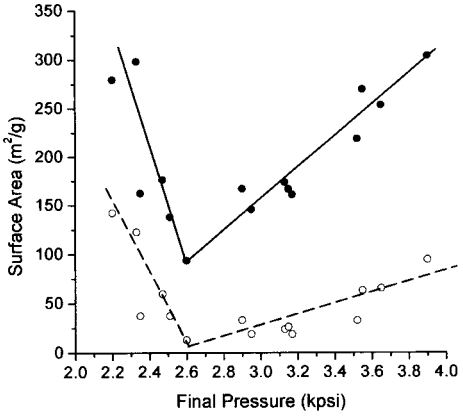

Fig. 8. Variation in BET surface area (●) and micropore surface area (○) as a function of reaction pressure for a series of porous poly(trimethylolpropane trimethacrylate) monoliths synthesized using $scCO_2$ as the porogen. The variable density associated with SCF solvents can be used to "fine-tune" porous structures. Reproduced with permission; copyright 2002, American Chemical Society [70a].

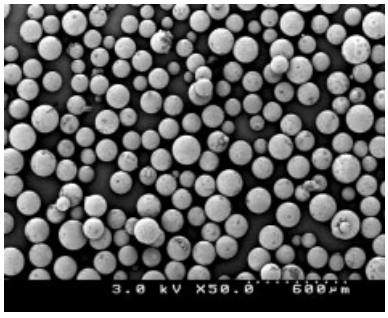

Fig. 9. Macroporous polymer beads synthesized by suspension polymerization using $scCO_2$ as the porogen (scale bar = 600 μm). Reaction pressure = 300 bar. Average pore size = 100 nm. BET surface area = 253 $m^2 g^{-1}$. Average bead diameter = 130 μm. Reproduced with permission; copyright 2001, American Chemical Society [72].

3.2. Templating of Supercritical Fluid Emulsions

Emulsion templating is useful for the synthesis of highly porous inorganic[73–76] and organic materials.[77–79] In principle, it is possible to access a wide range of porous hydrophilic materials by reaction-induced phase separation (i.e., chemical "locking") of concentrated oil-in-water (O/W) emulsions. In practice, a significant drawback to this approach is that large quantities of a water-immiscible oil or organic solvent are required as the internal phase (typically > 80 vol.-%). Moreover, it may be difficult to remove this oil phase from the templated material after the reaction. Inspired by studies on SCF emulsion formation and stability,[80] we have developed methods for templating high internal phase CO_2-in-water (C/W) emulsions to generate highly porous materials in the absence of any organic solvents—only water and CO_2 are used.[81] Providing that the emulsions are sufficiently stable (which depends strongly on the surfactant system), it is possible to generate low-density materials (~0.1 $g\,cm^{-3}$) with relatively large pore volumes (up to 6 $cm^3 g^{-1}$) from water-soluble vinyl monomers such as acrylamide and hydroxyethyl acrylate. Figure 10 shows a crosslinked polyacrylamide material synthesized from a high internal phase C/W emulsion, as characterized by scanning electron microscopy (SEM) and confocal microscopy (scale = 230 × 230 μm). Comparison of the two images illustrates quite clearly how the porous structure shown in the SEM image is templated from the C/W emulsion (as represented by the confocal microscopy image of the pores). In general, the confocal image gives a better measure of the CO_2 emulsion droplet size and size distribution immediately before gelation of the aqueous phase. From analysis of the confocal images, cell densities in the materials were found to be in the range 0.5×10^8–5×10^8 cells cm^{-3}. Initially, we used low molecular weight (M_w ~ 550 $g\,mol^{-1}$) perfluoropolyether ammonium carboxylate surfactants to stabilize the C/W emulsions,[81] but a significant practical disadvantage is that this surfactant is expensive and non-degradable. We have subsequently shown that it is possible to use inexpensive hydrocarbon surfactants to stabilize the C/W emulsions and that these emulsions can also be templated to yield low-density porous materials.

3.3. Nanoscale Casting

A wide variety of nanoporous structures can be formed by templating both natural and synthetic materials.[82–86] The

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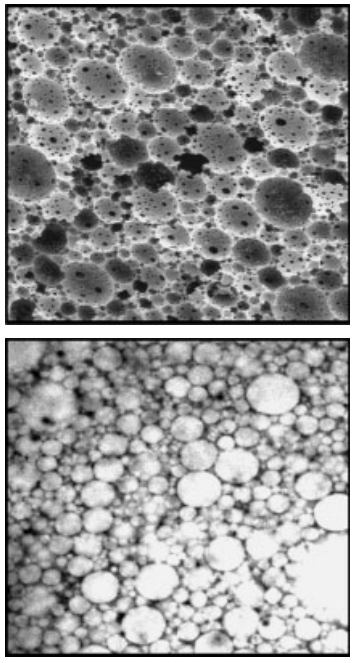

Fig. 10. Emulsion-templated crosslinked polyacrylamide materials synthesized by polymerization of a high internal phase CO_2-in-water emulsion (C/W HIPE). a) SEM image of sectioned material. b) Confocal image of same material, obtained by filling the pore structure with a solution of a fluorescent dye. As such, (a) shows the "walls" of the material while (b) shows the "holes" formed by templating the $scCO_2$ emulsion droplets. Both images = 230 × 230 μm. Ratio of CO_2/aqueous phase = 80:20 v/v. Pore volume = 3.9 $cm^3 g^{-1}$. Average pore diameter = 3.9 μm. Adapted from Butler et al. [81].

viscosities and surface tensions associated with conventional liquid solvents and reagents may prohibit the replication of very small features. Even gaseous reagents, when used below the critical temperature, may capillary condense into the liquid phase within nanometer and sub-nanometer-sized pores. As such, SCF solvents possess specific advantages for templating structures on the nanometer scale since they have low viscosity, high diffusivities, and never condense into the liquid phase. A number of porous inorganic materials have been prepared by the process of "nanoscale casting using SCFs" (Fig. 11).[87–92] In this technique, low molecular weight precursors such as tetraethyl orthosilicate (TEOS),[87,90] platinum acetylacetonate $[Pt(acac)_2]$,[88] titanium isopropoxide $[Ti(O-iPr)_4]$,[91,92] and aluminium acetylacetonate $[Al(acac)_3]$[91] were dissolved in $scCO_2$ and contacted with porous template materials such as activated carbon[87–92] and palm nutshell.[89] After treatment in the SCF, the samples were recovered and the template material was removed by calcination or oxygen plasma treatment. Using this method, it was possible to produce templated nanoporous platinum,[88,89] silica,[87,89,90] titania,[89,91,92] and alumina materials.[91] In the case of silica, it was shown that the samples prepared using solutions of TEOS in $scCO_2$ had much higher surface areas (900–1400 $m^2 g^{-1}$) than samples which were produced by immersion in neat liquid TEOS (440–540 $m^2 g^{-1}$).[87,89,90] Nitrogen adsorption–desorption isotherms for the materials formed by immersion in neat TEOS did not exhibit a manifested step corresponding to the existence of micropores or mesopores.[89] It was assumed that silica only covered the entrances of the mesopores and micropores in the activated carbon template because of the high viscosity of the neat precursor medium. By contrast, the SCF-assisted approach led to silica penetration of the smallest pores in the activated carbon template.

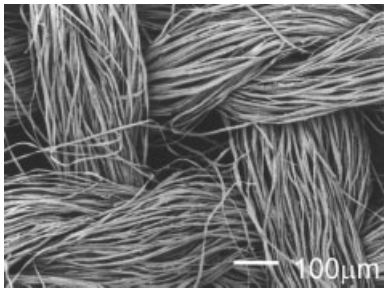

Fig. 11. Electron image of porous titania sample produced by nanoscale casting using supercritical fluids. An activated carbon cloth was treated with a solution of titanium isopropoxide in CO_2 and the carbon template was then removed by calcining in air at 873 K (scale bar = 100 μm). This method can be used to replicate features on the macro-, meso-, and microscopic length scales. Reproduced with permission; copyright 2001, Elsevier Science [91].

4. Modification of Porous Materials Using Supercritical Fluids

In addition to generating porous structures by processing and chemical synthesis (Sects. 2,3), it is also possible to modify preformed porous materials using SCFs.

4.1. Chemical Deposition within Porous Substrates

Several groups have investigated the reactive deposition of metals, polymers, and other materials in order to modify the properties of porous substrates by using SCFs. Potential advantages include rapid mass transfer, easy separations, and the ability to fill even small mesopores and micropores.

4.1.1. Deposition of Metal Nanoparticles in Porous Materials

There are a number of reports of the synthesis[93–95] or purification[96,97] of metal nanoparticles using SCF solvents. Recent results suggest that this is an area where fine control over solvent properties (e.g., by varying solvent density) may offer distinct advantages. For example, silver and gold nanocrystals, sterically stabilized with dodecanethiol ligands, were dispersed in supercritical ethane.[96] Since the van der Waals attraction between the nanocrystal cores increases significantly with size, an increase in ethane density and thus solvent strength was found to disperse larger nanocrystals with size selectivity. A reduction in ethane density precipitated the nanocrystals, again with size selectivity. This suggests that SCF solvents may be useful for size separation of metal nanoparticles, which is important in a number of emerging technologies.[96,97]

Metal nanoparticles have been synthesized in situ within non-porous, SCF-swollen polymer substrates (e.g., poly(4-methyl-1-pentene), polytetrafluoroethylene, polyethylene).[98,99] This approach takes advantage of plasticization and swelling effects associated with SCF solvents. It is also possible to synthesize metal nanoparticles within permanently porous structures,[100,101] thereby exploiting wetting behavior, pore filling, and low viscosity. For example, silver nanoparticles have been introduced into the pore structure of porous crosslinked PS beads and silica aerogels by $scCO_2$-assisted impregnation of silver coordination complexes followed by depressurization and subsequent addition of H_2 (1000 psi (~6.9 MPa), 60 °C, 24 h) in order to reduce the complexes to metallic silver.[100] Mass increases of 2–10 % were observed, and mean particle diameters were found to be in the range 20–40 nm.

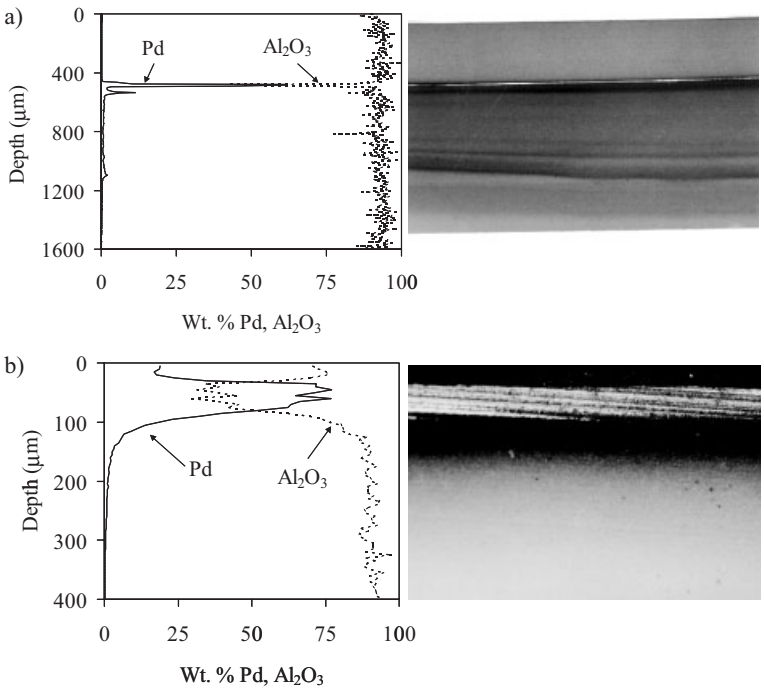

Fig. 12. Electron probe microanalysis (EPMA, left) and optical microscopy cross-section analysis (right) of palladium films deposited within porous α-alumina disks by reduction of a CO_2-soluble precursors in $scCO_2$ solution. a) Precursor= $CpPd(\pi\text{-}C_4H_7)$, 0.53 wt.-% in CO_2, 0.47 wt.-% H_2 in CO_2. b) Precursor= CpPd(hfac) (hfac= hexafluoro acetylacetonate), 0.76 wt.-% in CO_2, 0.61 wt.-% H_2 in CO_2. Note that the more concentrated precursor solution gives rise to a thicker Pd film. The position of the film can be controlled by varying the relative concentrations of precursor and H_2. Reproduced with permission; copyright 2001, American Chemical Society [105].

4.1.2. Chemical Fluid Deposition of Thin Metal Films in Porous Supports

Thin metal films are important for a wide variety of applications involving optics, microelectronics, sensors, membranes, and catalysis. Micrometer-thick metal films do not have the mechanical integrity to be freestanding and must be supported in some manner. In an extension of studies involving the chemical fluid deposition (CFD) of thin metal films on surfaces,[102–104] thin palladium films have been formed within porous alumina disks by in-situ H_2 reduction of CO_2-soluble organopalladium compounds.[105] The film position in the disks was controlled by adjusting the relative concentrations of H_2 and the palladium precursor (π-2-methylallyl(cylopentadienyl)palladium or palladium hexafluoroacetylacetonate) on opposite sides of the alumina substrate (see Fig. 12). Palladium films between 2 and 80 μm thick were deposited at prescribed depths between 80 and 600 μm, as measured from the metal precursor side. The deposition of supported thin metal films *within* the bulk of a porous substrate (rather than on the surface) has certain advantages (e.g., the film is protected from abrasion and is less likely to suffer from adhesion problems). Hydrogen has low solubility in most organic solvents but is highly soluble in $scCO_2$,[106,107] thus facilitating the reduction step. This process genuinely exploits the gas–liquid "hybrid" properties of $scCO_2$: it is solution-based (therefore, eliminating precursor volatility constraints) while retaining most of the rapid transport properties and conformal coverages associated with chemical vapour deposition. A potential restriction for CFD is that the reduction chemistry must proceed readily at low temperatures.[102–104]

4.1.3. Supercritical Fluid-Mediated Metallization of Mesoporous Silica

Mesoporous aluminosilicates are important as solid acids and ion exchangers.[108] A key requirement in these applications is hydrothermal stability. Postsynthesis aluminization offers potential advantages over directly synthesized materials with respect to accessibility of active Al sites and structural ordering, but there are difficulties to be overcome in obtaining a uniform distribution of Al throughout the host silica. This arises from the fact that the Al is first contacted with the outer surface of the host silica during grafting before being transported into the internal pore structure, or bulk. The low viscosity and high diffusivity inherent to SCFs are ideally suited to rapid transport of reagent species into mesoporous substrates. For example, MCM-41 silica materials have been aluminized by reaction with aluminium isopropoxide using either $scCO_2$ or supercritical propane as the solvent (reaction temperature = 40 °C for CO_2, 110 °C for propane).[109] The samples were then calcined at 600 °C for 4 h to obtain the Al-grafted materials.[27] Al magic-angle spinning (MAS) NMR spectroscopy indicated that ca. 40 % of the Al in the dry samples was tetrahedrally coordinated, increasing to at least 60 %

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after calcination. The samples showed very high stability after steaming at 900 °C for 4 h, with both samples retaining 80–85 % of their surface area and pore volume, and 80 % of their acid content. To investigate whether or not there was any specific advantage of using the solvents in the supercritical state, an Al-grafted material was synthesized under the equivalent conditions but using liquefied propane instead of SCF propane.[109] This material was found to have lower hydrothermal stability, suggesting that the SCF route led to better dispersion of the Al, a change in the way that the Al interacts with the host silica surface, or a combination of both.

4.1.4. Growth of Dimensionally Ordered Nanowires within Mesoporous Silica

Nanoscale structures of semiconductor wires are expected to play a role as materials in emerging technologies because of their unique optical, electrical, and mechanical properties.[110,111] Akanethiol-coated gold nanocrystals (2.5 nm diameter) have been used as uniform seeds for the growth of defect-free silicon nanowires from SCF solution.[112] It was found that the orientation of the nanowires could be controlled by varying the reaction pressure, once again taking advantage of the variable density associated with SCFs. More recently, semiconductor silicon nanowires have been synthesized within the pores of surfactant-templated mesoporous silica using $scCO_2$ as the solvent.[113,114] Diphenyl silane was degraded within the pore structure at 500 °C to create silicon nanowires. The low viscosity of the SCF phase enabled rapid diffusion of the reactant precursor into the mesoporous structure. Discrete transitions in the UV-vis absorption spectrum suggested quantum confinement effects.[114]

4.1.5. Synthesis of Conducting Polymer Foams

The polymerization of monomers within non-porous SCF-swollen polymer hosts to form polymer blends has been described for a number of monomer–polymer combinations.[115–119] Related techniques have been applied to the formation of porous composite materials such as foams. For example, conducting polypyrrole–polyurethane composite foams have been formed by SCF impregnation of polyurethane substrates with an oxidant, $Fe(CF_3SO_3)_3$, followed by exposure to pyrrole vapor.[120–122] The in-situ precipitation polymerization of pyrrole in $scCO_2$ and in supercritical fluoroform has also been reported.[123]

4.1.6. Porous Coordination-Polymer Crystals

Very recently, Kitaura et al. reported the synthesis of copper-based coordination polymers that show fascinating adsorption behavior for "supercritical gases" such as CO_2, CH_4, O_2, and N_2.[124] In particular, these materials exhibit "gate-opening" and "gate-closing" pressures (i.e., the microporous structure is pressure-responsive). Because of the relatively flexible nature of these materials, the channels can open and close reversibly with pressure. Hysteretic adsorption is observed because the gas molecules stabilize the porous phase. In principle, SCF solvents such as $scCO_2$ could be versatile media for the structural modification of microporous coordination polymers, although solubility considerations (e.g., the relative insolubility of most metal salts and complexes) may restrict the types of reactions that are readily achieved.

4.2. Surface Treatment Porous Materials with Low Surface Energy Coatings

The protection of historical buildings and other structures made of stone can be achieved by coating with perfluoropolyethers. These polymers are water repellent and stable to corrosive acids, high temperatures, UV radiation, and oxidizing agents. The materials are also transparent and colorless, thus maintaining the appearance of natural stone. A practical drawback is that these materials are not soluble in common organic solvents. By contrast, perfluoropolyethers are readily soluble in chlorinated fluorocarbons (CFCs) and in CO_2.[125] Perfluorinated polyether coatings have been applied onto surfaces of marble, sandstone, and limestone by spraying from solutions in $scCO_2$.[126] The penetration depth of the fluorinated coating was found to strongly depend on the mean size and porosity of the stones. These results suggest that CO_2 could be used for the application of weather-proof fluorinated coatings for which there are no other viable, environmentally acceptable alternatives.

5. Conclusions

This review has shown that there are a number of specific benefits that can be derived from the use of SCFs for the synthesis and modification of porous materials. SCFs are useful for the production of microcellular foams, both by expansion and by using crystallization or antisolvent phase-separation routes. In the case of biocomposite foams, the introduction of toxic solvent residues into the final product can be avoided. For materials that possess nanoscale pores or features (e.g., aerogels, LMOG foams, nanolithographic images), supercritical drying can avoid feature collapse due to the lack of capillary forces. Likewise, templating of nanoscale features and surface modification of nanoscale porous structures using SCFs holds promise because these solvents penetrate small pores more effectively than liquid solvents. Direct gelation of SCFs and templating of SCF emulsions are two new routes to produce low density porous materials. In the case of chemical gelation of SCF solutions, the variable density associated with SCFs can be used to fine-tune the resultant pore structure. Lastly, all of these processes offer the potential of reducing organic solvent usage in the production of porous materials and

composites. This is particularly important for processes that currently use large volumes of organic solvents (e.g., O/W emulsions, organic sol–gel routes, suspension polymerization, etc.). SCF routes to porous materials that exploit more than one of these specific advantages are likely to be profitable subjects for future research.

Received: January 8, 2003
Final version: April 16, 2003

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