

Recent developments in the use of supercritical CO₂ in synthetic organic chemistry

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- Résumé** **Avancées dans l'utilisation du CO₂ supercritique pour la chimie organique de synthèse**
 Les milieux supercritiques présentent l'avantage de permettre la découverte d'une large variété de phénomènes peu observés dans les milieux conventionnels. L'utilisation du CO₂ supercritique permet une séparation aisée des réactifs, des catalyseurs et des produits et peut constituer une alternative aux solvants traditionnels, plus acceptable car moins toxique pour l'environnement. Cependant, malgré des avantages certains, l'emploi du dioxyde de carbone pour la synthèse organique reste largement inexploité. Cet article présente les dernières avancées dans le domaine de la chimie organique en milieu CO₂ supercritique.
- Mots-clés** **CO₂ supercritique, chimie propre, catalyse en milieu homogène et hétérogène, réacteur en flux continu.**
- Key-words** **Supercritical CO₂, green technology, homogeneous and heterogeneous catalysis, continuous flow reactor.**

Because of a global increase in environmental awareness, the chemical industry is continually searching for new « cleaner » alternatives to its current processes [1-5]. Supercritical CO₂ (scCO₂) has considerable potential as a green solvent; it has several advantages over conventional hydrocarbon solvents, including low-toxicity, non-flammability, and low cost. As a result, supercritical fluids (SCFs) are playing an increasingly important role in many areas of chemistry, as illustrated by numerous recent reviews and books [6-12]. The book by McHugh and Krukonis [13] remains one of the best introductions to the field of SCFs. Here we describe some recent applications in organic synthesis.

Properties of supercritical fluids

SCFs are gases that are compressed until their densities are close to those of liquids. They are completely miscible with other permanent gases, such as hydrogen. SCFs only exist above the so-called critical temperature (T_c) and critical pressure (p_c), and with a density close to or higher than their critical density [9]. scCO₂ has relatively mild critical parameters (p_c of 73.8 bar and T_c of 31.1 °C). General properties and experimental considerations on the use of scCO₂ are well documented [7, 9, 13] and will not be discussed here. By varying the pressure and temperature, the density and solvation power of the SCFs become « tunable ». This key factor leads to an increased control over reactions rates and selectivity, with results often superior to those obtained using conventional solvents [6]. Carbon dioxide is chemically inert to most conditions, it is non-protic, not strongly Lewis acidic or basic, and is inert to radical and oxidising conditions. One major drawback to scCO₂ as a solvent for synthetic transformations is its incompatibility with primary or secondary amines, due to carbamate formation and precipitation of solid residues. However, scCO₂ is a non-polar molecule with poor

solubilising power (solvent power comparable to *n*-hexane), and this has considerably restricted the choice of catalysts, reagents, and substrates to a narrow range of nonpolar, nonionic, and low molecular weight compounds. Intensive research has been carried out over the last 5 years to overcome this problem. Research strategies employed to overcome this include: increasing the bulk density of the scCO₂ by increasing reaction pressure, the addition of co-solvents (modifiers such as MeOH or toluene undergo strong specific interaction such as hydrogen bonding with the solute), modification of the solute to make it more CO₂-philic (molecules with longer hydrocarbon, fluorocarbons or silicone chains) [14], careful choice of counterions ($[(3,5-(CF_3)_2C_6H_3)_4B]^-$, « BARF⁻ » [15-16] or CF₃SO₃⁻) for charged complexes. Recent reports of cheaper, more sustainable approaches to solubility enhancement are likely to have a significant impact in the future [17].

Hydrogenation reactions in scCO₂

Present studies on hydrogenation in supercritical media mainly capitalise on the enhanced mass transfer as a result of the increased solubility of hydrogen to SCFs. This often has a marked influence on the reaction rate and selectivity. Homogeneously catalysed reactions have been extensively reviewed [10, 18-19] and compared to analogous

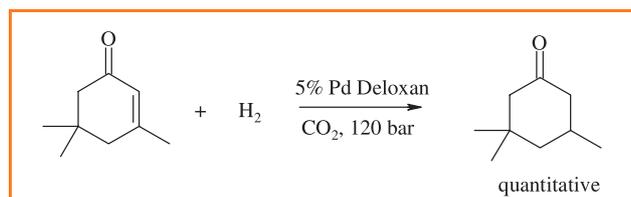


Figure 1.

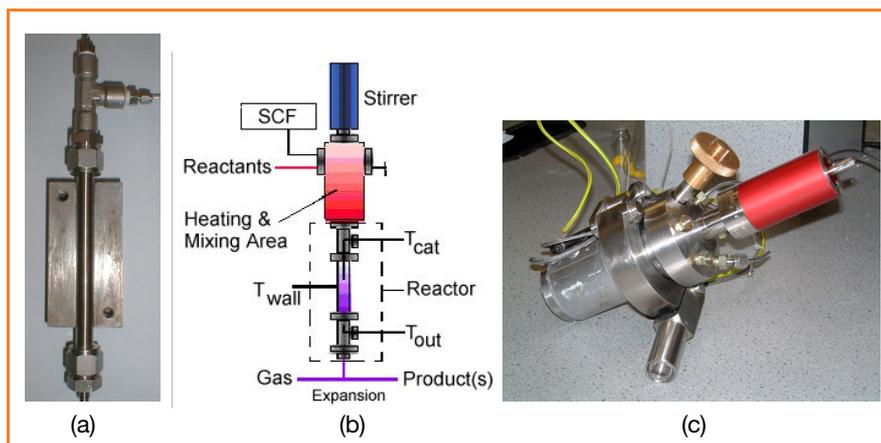


Figure 2 - (a) and (b): illustration of the typical layout of a continuous flow supercritical reactor. The close-up photograph of the actual reactor (a) represents the area within the dotted box in (b). The actual reactor is 10 cm in length. Picture (c) represents a batch reactor, equipped with a quick release clamp system and a safety valve.

heterogeneously catalysed reactions [8, 20]. scCO_2 has already been successfully employed as both the reaction medium and reactant in the synthesis of formic acid and its derivatives [21-23] with reaction rates comparing favourably with those achieved in conventional solvents. The homogeneous catalytic synthesis of *N,N*-dimethylformamide (DMF) and methyl formate (MF) from carbon dioxide are also reported [8, 23-26]. Heterogeneous variants of the above solvent-free homogeneous processes have also been designed [21, 27]. Indeed, the hydrogenation of cyclopropene by $\text{MnH}(\text{CO})_5$ via a radical mechanism was the first example of scCO_2 being employed as a solvent in such reaction systems [28]. Custom designed Rh complexes have been described as active catalysts for hydrogenation reactions [29-30]. Homogeneous enantioselective asymmetric hydrogenation of prochiral α -enamides [15], and hydrogenation of α,β -unsaturated carboxylic acids such as tiglic acid have been reported [31]. Leitner also reported the use of scCO_2 as a reaction medium for the homogeneous iridium catalysed enantioselective hydrogenation of prochiral imines [32]. Poliakoff and co-workers have developed a system for the continuous hydrogenation in SCFs, over a range of supported noble metal catalysts [25]. The selective catalytic hydrogenation of a number of organic functionalities including aromatic and aliphatic alcohols, aldehydes, ketones, nitro-compounds, imines, oximes, olefins and acetylenes have successfully been carried out in this continuous system (figure 1) [33-34]. Continuous reactors for SCFs have the advantage over batch reactors that they do not require depressurisation to feed in the reactants or to recover the products. The design of one type of fixed bed continuous reactor and one batch reactor are shown in figure 2. The hydrogenation of oleochemicals [35-36], and mechanistic aspects of dihydrogen activation and transfer during asymmetric hydrogenation in scCO_2 have been reported [37]. Selective hydrogenation of maleic

anhydride to either γ -butyrolactone or succinic anhydride over simple Pd/ Al_2O_3 catalyst in scCO_2 has been described for the first time [38]. Water-soluble trialkylphosphine-ruthenium(II) complexes have also been reported as efficient catalysts for hydrogenation in scCO_2 [39].

Hydroformylation reactions in scCO_2

Hydroformylation is the catalytic addition of CO and H_2 (« syn-gas ») to olefinic precursors. In 1991, Rathke described the first example of the homogeneous hydroformylation in scCO_2 [40]. Subsequently, Leitner reported that a CO_2 -soluble Rh complex with a polyfluoroalkyl-substituted triarylphosphine ligand facilitated the hydroformylation of 1-octene to linear

aldehyde in a good yield with 82% selectivity [41], with very little evidence of side reactions such as hydrogenation or isomerisation of the olefin. In 1998, the same group reported the asymmetric hydroformylation of styrene [42]. A continuous process for the selective hydroformylation of higher olefins in scCO_2 can also be found [43]. Recently, Xiao and co-workers synthesised a fluorinated polymeric phosphine which when combined with scCO_2 and rhodium, effects unprecedented, fast and highly chemoselective hydroformylation of acrylates, one of the least reactive olefins in hydroformylation reactions (figure 3) [44-45].

Diels-Alder cycloaddition reactions in scCO_2

Using a series of alternative dienes and dienophiles, with differing steric and electronic properties, the Diels-Alder reaction was investigated in scCO_2 . In 1987, Paulaitis and Alexander reported the Diels-Alder reaction of maleic anhydride with isoprene; it was one of the earliest reported synthetic reactions in a SCF media [46]. In all of the investigated cases, regioselectivities similar to those observed in conventional solvents were achieved. In 1998, Chapuis *et al.* reported the first SCF Diels-Alder reaction controlled by a chiral auxiliary [47]. Danheiser reported a silica catalysed

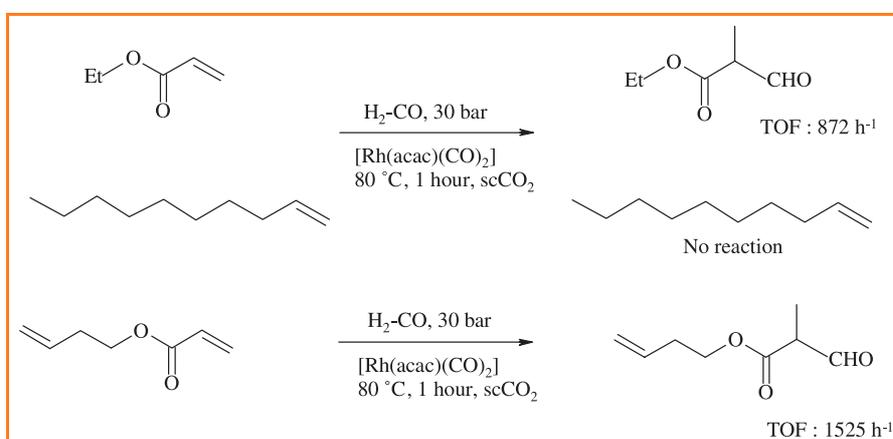


Figure 3 - Chemoselective hydroformylation of C=C bonds in scCO_2 .

Diels-Alder reaction in scCO_2 [48]. Kobayashi reported the application of scandium perfluoroalkanesulfonates as Lewis acid catalysts in Diels-Alder reactions [49]. Roberts investigated the effect of pressure on the bimolecular rate constant of the Diels-Alder reaction between maleic anhydride and isoprene [50], a further discussion of the kinetics of this reaction has been described [51].

Oxidation reactions in scCO_2

A wide range of studies of heterogeneously catalysed oxidations in SCFs can be found, in contrast to homogeneously catalysed oxidations. Recent papers have reviewed catalytic oxidations in dense CO_2 [8, 52]. Functionalisation of alkanes by oxidation has been of interest both in liquid solvents and in SCFs. The aerobic oxidation of cyclohexane in the presence of an iron-porphyrin catalyst $\text{FeCl}(\text{tpfpp})$ ($\text{tpfpp} = 5,10,15,20\text{-tetrakis(pentafluorophenyl)porphyrin}$) and acetaldehyde in scCO_2 was reported by Koda [53]. Jiang reported a palladium(II) catalysed oxidation of acrylic esters to acetals [54]. Recently, Wei and co-workers have shown that CO_2 -expanded solvents provide optimal properties for maximising oxidation rates [55]. Epoxidation of alkenes by hydroperoxides in scCO_2 in the presence of $\text{Mo}(\text{CO})_6$ [7, 56-57], or other transition metal catalysts have also been examined [57-59]. A continuous epoxidation of propylene with oxygen and hydrogen over a Pd-Pt/Ts-1 catalyst has been developed [60]. Recently, Leitner reported the steel-promoted oxidation of olefins using oxygen in the presence of aldehydes [61]. The diastereoselective epoxidation of olefins has also been reported [62].

Palladium-mediated coupling reactions in scCO_2

Palladium-catalysed coupling reactions in scCO_2 have received much recent attention. Tumas reported work on the development of the Heck and Stille coupling reactions in scCO_2 [63]. Stille cross-coupling reactions catalysed by perfluoro-tagged and un-tagged Pd complexes have been developed [64]. Recently, intramolecular Heck cyclisation reactions in scCO_2 were reported, suppressing the double bond isomerisation reaction often present in conventional solvents [65]. Arai detailed a Heck reaction employing water-soluble catalysts in a scCO_2 -water biphasic system [66]. The reaction of aryl iodides with a variety of olefins in scCO_2 in the presence of triethylamine and an immobilised palladium catalyst has been reported [67-68]. Carroll and Holmes [69] prepared unusual polyfluoroalkylphosphine ligands to enhance the solubility of Pd(II) catalysts for coupling reactions of phenyl iodide. Dendrimer-encapsulated nanoparticles have also been shown to be versatile catalysts for both the hydrogenation of styrene and Heck heterocoupling of iodobenzene and methacrylate [70]. However, the few studies done so far suggest that most cyclisation and coupling reactions (Suzuki and Sonogashira couplings) are neither faster nor offer greater yields in scCO_2 than in liquid solvents, Heck reactions being the possible exception. Jessop suggested that the potential advantage to using SCFs for these reactions might lie in the tunable dielectric constant [71] or local solute/solute clustering effects that have been beneficial in non-catalysed reactions [72].

Miscellaneous catalytic synthetic reactions in supercritical fluids

scCO_2 has been shown to be a unique solvent in which to perform polymer synthesis, reflected in the commercialisation of a number of supercritical polymerisation processes. DeSimone and co-workers are responsible for a large proportion of the research in this area [18, 73-74]. Recently, the ionic ring-opening polymerisation of several heterocycles in scCO_2 has been described for the first time [75]. Hydrosilylation of poly(methylhydrosiloxane) with a fluorinated olefin in scCO_2 using a Pt catalyst has been successfully demonstrated [76]. Catalytic intermolecular Pauson-Khand reactions in scCO_2 have been described [77]. Transition metal-catalysed olefin metathesis, and ring-opening metathesis polymerisation (ROMP) of a number of cyclic olefins in both liquid CO_2 and scCO_2 are reported [78-79]. The chemical yield and molecular weight of the polymers are comparable to those in conventional solvents. Leitner found that some carbene complexes effected ring-closing metathesis (RCM) of even functionalised dienes to cyclic olefins [29, 78]. Yoshida reported the use of scCO_2 both as the reaction media and carbonyl source for the production of urethanes from amines [80]. This is an attractive catalytic one-pot alternative to the use of phosgene in urethane synthesis. Poliakoff, Ross and co-workers used a fixed bed heterogeneous supported acid catalyst to perform continuous Friedel-Crafts alkylation of aromatics in SCF media [81]. Using the same continuous flow reactor apparatus, the acid catalysed dehydration of alcohols in scCO_2 was also investigated [82]. SCFs can also greatly reduce the coking contamination of catalysts in reactions such as alkylation and Fischer-Tropsch synthesis [83]. Tumas reported a Rh catalysed alkene hydroboration reaction in scCO_2 [84]. Li Fan investigated the effect of SCFs on alkylation reactions on Y-type zeolites [85]. Finally, the prospect of using enzymes as heterogeneous catalysts in SCF media has created a significant interest since the mid 1980s. A large amount of literature exists, reporting enzymatic catalysis in scCO_2 , performing hydrolyses, oxidations, esterifications and transesterification reactions [86]. The application of synthetic organic building blocks in SCFs is the subject of an excellent recent review by Oakes [12].

Conclusion

SCFs, and scCO_2 in particular, are rapidly emerging as versatile media for carrying out a diverse range of synthetic organic reactions, and we are only just beginning to see the real potential and benefits they offer in addition to environmental aspects. Used either as solvents or reactants, SCFs provide several opportunities to enhance and control homogeneous and heterogeneous catalytic reactions. Johnston [87-88] showed that specific aqueous micro-emulsions may extend the use of dense carbon dioxide as a solvent for hydrophilic substances and ions. Despite the high costs of supercritical process technology, the reactivity of SCFs will continue to be explored in the fixation of gases, the recovery of catalysts and many other aspects. Furthermore, several classical spectroscopic techniques are becoming amenable to high-pressure investigations. SCFs have already established themselves as useful solvents in materials applications [89], in pharmacy [90], and in industry, in several classical industrial processes (ethylene polymerisation [91], ammonia synthesis [92], and methanol



Figure 4 - View of the reactors in the Thomas Swan and Co. Ltd. scCO₂ plant in Consett, Co. Durham (UK).

Photograph, courtesy of Thomas Swan and Co. Ltd.

synthesis [93]) and for the extraction of hops, spices, flavours, perfumes and for the decaffeination of coffee [94-96]. Dupont have build a \$40M development plant for producing fluoropolymers in scCO₂ [97]. Hydrogenation in the fine chemicals industry is carried out on a relatively modest scale, and it is here that the prospects look best for the most immediate commercialisation of SCF catalysis. This year, a « world first » 1000 t per annum multi-purpose plant using SCF for a new generation of faster, cleaner and more selective synthesis has been commissioned in the UK by Thomas Swan & Co. Ltd. in conjunction with the University of Nottingham (figure 4). The key chemical technologies include hydrogenation, Friedel-Crafts alkylations and acylations, hydroformylations and etherification [98].

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