Reactions in supercritical carbon dioxide

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Use of conventional organic solvents often leads to the formation of hazardous waste, the disposal of which is a matter of environmental concern. Carbon dioxide is considered to be a green reaction medium and a good replacement for conventional organic solvents as it is benign and leads to elimination/reduction of hazardous wastes. Use of CO$_2$ at near/above critical conditions has several additional advantages as the reactions can be pressure-tuned to eliminate transport resistance, increase solvent power and heat capacity. Hence, there has been considerable interest in the use of supercritical carbon dioxide as either a replacement of conventional organic solvent or as a co-solvent in reactions. Herein, recent developments in this area during the last decade is reviewed, specifically in gas-liquid (organic hydrogenation, hydroformylation and oxidation) and liquid-liquid (carbon-carbon coupling, alkylation, acetylation, esterification) reactions.

Keywords: Hydrogenation, Hydroformylation, Oxidation, Alkylation, Supercritical carbon dioxide, Carbon dioxide

Supercritical carbon dioxide (ScCO$_2$) is considered to be a highly attractive modern solvent compared to traditional organic solvents. It is inexpensive, readily available, non-toxic and environmentally benign. The density, viscosity and diffusivity of ScCO$_2$ can be varied continuously between those of liquid and gaseous CO$_2$ by varying the temperature and/or pressure. The diffusivities of chemicals dissolved in ScCO$_2$ are higher and viscosities are lower than those of conventional organic solvents. The solubility of chemicals in ScCO$_2$ can be easily tuned by changing the temperature and/or pressure. The early applications of ScCO$_2$ were for extraction and separation. Decaffeination of roasted coffee beans using ScCO$_2$ pioneered by Kurt Zosel was the first major industrial application of ScCO$_2$. The focus eventually shifted to supercritical reactions and in 1999 a special issue of Chemical Reviews was dedicated to supercritical media. Properties of ScCO$_2$

Fluids near their critical point have dissolving power comparable to that of liquids, are much more compressible than dilute gases, and, have transport properties intermediate between gases and liquids. This unusual combination of physical properties has been exploited in reactions in supercritical media. Benefits of carrying out reactions in supercritical media are high rates, improved selectivity, and elimination of mass transfer problems. Increased reaction rates and selectivity result from the high solubility of reactant gases in supercritical fluids, rapid diffusion of solutes into, out of, and within the supercritical phase, weakening of the solvation around reacting species, local clustering of reactants or solvent and very large negative activation volumes near critical point, and, reduction of cage effect in radical reactions.

The use of supercritical fluid (SCF) as a medium for chemical reaction has an additional attraction in that its properties vary with density, which is highly sensitive to temperature and pressure in the critical region. Hence, SCFs provide an opportunity to engineer the reaction environment by manipulating temperature and pressure. ScCO$_2$ being non-inflammable, has significant safety advantage over organic solvents. The side reactions and byproduct formation in ScCO$_2$ mediated reactions are rare due to its inertness towards reactive compounds. Organic reactions in ScCO$_2$ are of two main
categories, viz., those in which \( \text{ScCO}_2 \) takes part in the reaction as a reactant, and, those in which \( \text{ScCO}_2 \) is used as a solvent or co-solvent.

There has been a surge in interest in reactions in \( \text{ScCO}_2 \) in recent times, primarily on hydrogenation reactions followed by hydroformylation and partial oxidation. Studies on liquid-liquid reactions (e.g. C-C coupling, alkylation, acylation, acetylation, esterification) are relatively less reported in literature. This review has considered the recent progress in the above types of reactions in \( \text{ScCO}_2 \). Although there is considerable interest in polymerization and photocatalytic reaction in \( \text{ScCO}_2 \), these are not covered here.

**Reactions Involving \( \text{CO}_2 \) as Reactant**

\( \text{CO}_2 \) is an inert molecule in most of the environments. However, it is a Lewis acid and reacts with strong bases (amines, phosphines, alkyl anions)\(^{25, 26} \). Pioneering studies on reactions in \( \text{ScCO}_2 \) involved the hydrogenation of \( \text{CO}_2 \) for formic acid and its esters\(^{2, 3, 27-28} \). \( \text{CO}_2 \) can be catalytically reduced to \( \text{CO} \) at temperatures greater than 343 K and with longer residence times\(^{3} \), which can poison the palladium catalyst used in hydrogenation reactions. High temperature catalytic hydrogenation of \( \text{CO}_2 \) produces \( \text{CO}, \text{CH}_4, \text{CH}_3\text{OH} \) and formic acid derivatives, depending on the reaction conditions and the catalyst\(^{29} \). Copolymerization of \( \text{CO}_2 \) with oxiranes to form poly(ether-carbonate) is considered to be a green alternative to the traditional phosgene route\(^{30, 31} \). Styrene carbonate has been synthesized (Scheme 1) with 100 % selectivity and 100 % yield from styrene oxide and \( \text{ScCO}_2 \) using \( \text{ZnBr}_2 \) and the quaternary salt, \( n-\text{Bu}_4\text{NI} \), as the catalyst\(^{32} \). \( \text{ScCO}_2 \) hydrogenation of methanol, ammonia and amines results in the formation of methyl formate and formamide derivatives respectively\(^{29, 33} \).

**Organic Reactions in \( \text{ScCO}_2 \) Medium**

Many conventional solvents used in organic reactions result in the formation of side products/hazardous wastes, leading to environmental concerns\(^{17} \). \( \text{ScCO}_2 \) is a benign solvent compared to conventional organic solvents. It enhances the miscibility of gaseous reactants, viz., \( \text{H}_2 \) and \( \text{O}_2 \) and eliminates inter-phase transport limitations, thereby enhancing catalyst activity and selectivity. Above all, the reaction can be pressure-tuned for optimizing catalyst activity, recovery, recycle and maximizing the product yield. This has been observed for both homogeneous and heterogeneous catalytic reactions\(^{25} \). These include hydrogenation, hydroformylation, oxidation, alkylation, disproportionation and esterification.

**Hydrogenation**

\( \text{ScCO}_2 \) is used as reaction medium for hydrogenation reactions in batch/continuous mode and homogeneous/heterogeneous phase. Improved reaction rates, higher catalyst efficiency, improved process safety, tunable selectivity are some of the advantages experienced on carrying out the reactions in \( \text{ScCO}_2 \). Large scale hydrogenation reactions are carried out both in fluid/gas and liquid phase. While fluid/gas phase reactions use solid catalyst in two-phase mode, liquid phase reactions are carried out in two or three phase modes. Liquid phase hydrogenations in two phase mode utilize a homogeneous catalyst and three phase mode has a heterogeneous catalyst in addition to the liquid reactant and gaseous hydrogen. Some of the hydrogenation reactions in \( \text{ScCO}_2 \) medium reported in literature are presented in Table 1. Representative hydrogenation reactions carried out in \( \text{ScCO}_2 \) medium are presented in Scheme 2.

Organic complexes of platinum, palladium, rhodium, ruthenium and iridium have been used as

![Scheme 1](image1)

Reaction of styrene oxide with \( \text{CO}_2 \) to styrene carbonate in presence of \( \text{ScCO}_2 \) [Based on Ref. 32]

![Scheme 2](image2)

(a) hydrogenation of nitrostyrene; (b) hydrogenation of \( \alpha \)-chlorobenzene

Hydrogenation reactions under \( \text{ScCO}_2 \) [Based on Refs 49 and 47]
homogeneous catalysts in hydrogenation reactions in liquid phase\textsuperscript{34, 35}. Neutral transition metal complexes and positively charged cationic complexes are usually used in homogeneous hydrogenation reactions\textsuperscript{3}. Neutral transition metal complexes dissolve readily in ScCO\textsubscript{2}. Cationic complexes, though more selective, do not easily dissolve in ScCO\textsubscript{2}. Perfluorination of these complexes with moieties such as C\textsubscript{6}F\textsubscript{13} have been successfully employed in substantially improving the solubility of cationic catalysts without disturbing the activity and selectivity\textsuperscript{34}. Often the substrate also acts as a co-solvent enhancing the solubility of the catalyst, increasing the reaction rates in ScCO\textsubscript{2}\textsuperscript{2}. Liquid phase hydrogenation in ScCO\textsubscript{2} eliminates H\textsubscript{2} diffusion resistance at the gas-liquid interface, increases solubility of H\textsubscript{2}, eliminates total transport resistance resulting in high reaction rates and improved yield. In hydrogenation reactions, it is possible to have kinetic control by controlling/varying the gas phase CO\textsubscript{2}/H\textsubscript{2} ratio. Improved selectivity is observed in asymmetric hydrogenations by replacing the organic solvent with ScCO\textsubscript{2}.

Table 1—Hydrogenation reactions in ScCO\textsubscript{2}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Benefit of ScCO\textsubscript{2}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereoselective hydrogenation of itaconic esters</td>
<td>Rhodium-organic catalyst</td>
<td>Improved selectivity, high rate</td>
<td>34</td>
</tr>
<tr>
<td>Enantioselective hydrogenation of (N)-(1-phenylethylidene) aniline</td>
<td>Chiral iridium</td>
<td>High rate (20 times faster than in organic solvent)</td>
<td>35</td>
</tr>
<tr>
<td>Hydrogenation of tetralin</td>
<td>Rh\textsuperscript{7}-Al\textsubscript{2}O\textsubscript{3}, Rh/C</td>
<td>High rate and high cis-decalin yield with Rh/C catalyst</td>
<td>36</td>
</tr>
<tr>
<td>Hydrogenation of sertraline</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>High selectivity towards cis products</td>
<td>37</td>
</tr>
<tr>
<td>Hydrogenation of tert-butylphenols</td>
<td>Rh/C</td>
<td>Higher cis ratio (0.95)</td>
<td>38</td>
</tr>
<tr>
<td>Hydrogenation of 4-alkylphenols</td>
<td>HCl-Rh/C and (H_3PO_4)-Rh/C</td>
<td>cis-4-isopropylocyclohexanols</td>
<td>39</td>
</tr>
<tr>
<td>Hydrogenation of 4-isopropylphenol</td>
<td>Pd/alumina</td>
<td>Efficient reaction, high rate</td>
<td>41</td>
</tr>
<tr>
<td>Isophorone to trimethylcyclohexanone</td>
<td>Pt/Al\textsubscript{2}O\textsubscript{3}</td>
<td>High selectivity for unsaturated alcohol</td>
<td>42</td>
</tr>
<tr>
<td>Hydrogenation of unsaturated aldehydes</td>
<td>Pd/C</td>
<td>Switchable selectivity to 5 different products by varying the reaction conditions</td>
<td>43</td>
</tr>
<tr>
<td>Hydrogenation of vegetable oil and fatty acid</td>
<td>Nickel based catalyst</td>
<td>High yield</td>
<td>44, 45</td>
</tr>
<tr>
<td>Hydrogenation of pinene</td>
<td>Pd/C</td>
<td>Significantly faster reaction rates, safer operation</td>
<td>46</td>
</tr>
<tr>
<td>Cyclohexene to cyclohexane</td>
<td>Pd/C</td>
<td>High catalyst activity and catalyst life</td>
<td>16</td>
</tr>
<tr>
<td>\textit{o}-Chloronitrobenzene to \textit{o}-chloroaniline</td>
<td>Pd/C</td>
<td>High reaction rate and product selectivity</td>
<td>47</td>
</tr>
<tr>
<td>Tetrahydrofurfural alcohol to 1,5-pentanediol</td>
<td>Rh/MCM-41</td>
<td>High conversion, selectivity under mild conditions</td>
<td>48</td>
</tr>
<tr>
<td>Nitrostyrene to aminostyrene</td>
<td>Pt/TiO\textsubscript{2}</td>
<td>Increase in reaction rate, selectivity</td>
<td>49</td>
</tr>
<tr>
<td>Styrene oxide to 2-phenyl ethanol</td>
<td>Pd-Cu catalyst encapsulated with polyurea</td>
<td>100 % conversion, 100 % selectivity</td>
<td>50</td>
</tr>
<tr>
<td>Aldol condensation followed by hydrogenation in a single reactor</td>
<td>Bifunctional Pd-acid catalyst</td>
<td>High activity, selectivity, long catalyst life</td>
<td>51 – 54</td>
</tr>
<tr>
<td>\textit{In situ} generation of ScCO\textsubscript{2} by decomposition of HCO\textsubscript{2}H and hydrogenation (alkenes, ketones, aldehydes)</td>
<td>Platinum</td>
<td>Yields similar to those obtained from conventional ScCO\textsubscript{2} reaction</td>
<td>55</td>
</tr>
<tr>
<td>Hydrogenation of 2-butyne-1,4-diol</td>
<td>5 wt% Pd/C</td>
<td>High rate, 100 % selectivity to butane-1,4-diol</td>
<td>56</td>
</tr>
<tr>
<td>Hydrogenation of isoisororone</td>
<td>Rh, Pt, Pd on charcoal</td>
<td>High activity for Rh/charcoal, Pt/charcoal catalysts</td>
<td>57</td>
</tr>
<tr>
<td>Hydrogenation of diphenyl</td>
<td>Rh/C, Ru/C</td>
<td>&gt; 99 % yield, TON = 1490 for Rh/C</td>
<td>58</td>
</tr>
<tr>
<td>Ring Hydrogenation of Phenol and cresol</td>
<td>Rh/charcoal</td>
<td>Increase in catalyst activity, enhanced mass transfer</td>
<td>59</td>
</tr>
<tr>
<td>Ring hydrogenation of naphthalene and \textit{1}-napthol</td>
<td>Rh, Pd, Pt, Ru supported on C or Al\textsubscript{2}O\textsubscript{3}</td>
<td>High selectivity to decalin over Rh/C</td>
<td>60</td>
</tr>
<tr>
<td>Ring hydrogenation of phenyl ethanols</td>
<td>Rh, Pd, Pt, Ru supported on C or Al\textsubscript{2}O\textsubscript{3}</td>
<td>High selectivity (&gt;80%) to cyclohexyl ethers over supported Ru catalysts</td>
<td>61</td>
</tr>
<tr>
<td>Hydrogenation of naphthalene</td>
<td>Rh, Pd, Pt, Ru supported on C or Al\textsubscript{2}O\textsubscript{3}</td>
<td>High activity for Rh/C catalyst, high TOF</td>
<td>62, 63</td>
</tr>
<tr>
<td>Hydrogenation of 1,2-epoxyethylbenzene</td>
<td>Pd/C, Pt/C</td>
<td>Suppression of dehydroxylated product</td>
<td>64</td>
</tr>
</tbody>
</table>
Due to ease of catalyst separation, regeneration and recycle, the trend has been changing to the use of heterogeneous catalysts instead of soluble metal complex as catalysts. The catalysts, Pt, Pd, Rh, Ru and Ni, supported on different inorganic materials have been used for the hydrogenation reactions in ScCO₂. Carbon in various forms (charcoal, active carbon, graphite) has been the most popular material for supporting the catalyst\textsuperscript{16,36,38,40,43,46,47,56-64}. The other supports reported in literature include alumina\textsuperscript{36,41,42,60-62}, calcium carbonate\textsuperscript{37}, TiO\textsubscript{2}\textsuperscript{49}, MCM-41\textsuperscript{48} and polyurea\textsuperscript{50}.

Stereo-selective hydrogenation in ScCO₂ favors the cis-product with high selectivity and yield\textsuperscript{25-40}. Switchable selectivity to five different products has been reported in the hydrogenation of furfural, just by varying the reaction conditions\textsuperscript{43}. Hydrogenation of alkenes and alkyne are highly exothermic and control of hydrogen concentration by CO\textsubscript{2} is the key to hydrogenation reactions in ScCO\textsubscript{2}\textsuperscript{3,46}. \textit{In situ} generation of CO\textsubscript{2} can reduce the inventory and compression cost. This has been tried successfully for the hydrogenation of alkenes, aldehydes and ketones by generating CO\textsubscript{2} through decomposition of formic acid\textsuperscript{55}. Yields similar to those obtained for reactions in ScCO\textsubscript{2} have been reported. Another development in hydrogenation reaction is to carry out two reactions in sequence in the same reactor under ScCO\textsubscript{2}. Aldol condensation followed by hydrogenation in the same reactor using a bi-functional palladium catalyst led to high activity, selectivity and long life of the catalyst\textsuperscript{51-54}.

CO poisoning of noble metal catalyst at temperatures greater than 343 K and prolonged residence time is one of the problems associated with hydrogenation reactions in ScCO\textsubscript{2}\textsuperscript{16}.

\section*{Hydroformylation}

Addition of equivalent amounts of CO and H\textsubscript{2} to an alkene to produce oxygenated organic compounds, mainly aldehydes, is known as hydroformylation. It is also known as oxosynthesis. A brief history of hydroformylation and the on-going research has been presented by Bektesevic and co-workers\textsuperscript{65}. Rhodium and cobalt complexes are the most employed catalysts in hydroformylation reactions. In addition, metal complexes with manganese and ruthenium are also being considered for hydroformylation reactions in ScCO\textsubscript{2}\textsuperscript{65}. Although earlier studies were focused on homogeneous phase reactions, the problems in the recovery of the expensive metal complex catalysts directed research on heterogenization of the complex soluble catalysts. The active catalysts were chemically bonded to inorganic and polymer supports. Heterogeneous catalysts are expensive and are used in reactions where selectivity is of prime importance, e.g. pharmaceutical products\textsuperscript{65}. Silica, MCM-41, carbon, etc., have been studied as supports for hydroformylation catalysts. Leaching of the active metal complex from the supported catalyst is a major problem faced by many of these catalysts.

Niesse and Woelk\textsuperscript{66} have reviewed the developments in hydroformylation reactions in supercritical fluids and the application of NMR spectroscopy in understanding the reaction. Recently, ScCO\textsubscript{2} hydroformylation reactions were also carried out in combination with ionic liquids (IL)\textsuperscript{67,68}. A review of hydroformylation in room temperature ionic liquids (RTIL) has been presented by Haumann and Riisagar\textsuperscript{69}. These systems are reported to work well for gas-phase reactions and reactions where CO is produced \textit{in situ} from CO\textsubscript{2}. Increase in reaction rate is reported for rhodium complexes catalysed hydroformylation of olefins\textsuperscript{70}. Rh/(R,S)-3-H\textsubscript{2}\textsuperscript{16}. BINAPHOS as catalyst in the hydroformylation of styrene gives high conversion and selectivity and has a long catalyst life\textsuperscript{71}. Increased catalyst stability is reported in the conversion of 1-hexene to heptanal with rhodium complex\textsuperscript{72}. High activity is observed in the hydroformylation of long chain alkenes with homogeneous and immobilized rhodium complex and of 1-octene with tris-(3,5-bis[trifluoromethyl]phenyl) phosphine-modified rhodium\textsuperscript{73,74}. Increase in reaction rate and regioselectivity with increase in ligand concentration and high TOF, similar to that in organic solvents on use of ScCO\textsubscript{2}, are observed in the hydroformylation of 1-octene with rhodium complex\textsuperscript{75,76}. General reaction for the hydroformylation of alkene to aldehyde is presented in Scheme 3a and the hydroformylation of 1-hexene to heptanal is presented as Scheme 3b.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme3.png}
\caption{Scheme 3}
\end{figure}
Oxidation

Oxygen and CO$_2$ are completely miscible under supercritical conditions at all concentrations. Also, CO$_2$ cannot be oxidized further during catalytic oxidation. Hence, oxidation reactions in ScCO$_2$ eliminate side product formation due to oxidation of organic solvents. CO$_2$ also acts as a diluent when molecular oxygen is used as the oxidant, providing safer operating conditions for the reaction. Transition metal catalyzed homogeneous phase oxidations have a minimum of four critical components, viz., catalyst, substrate, terminal oxidant and the medium. Molecular oxygen from air, H$_2$O$_2$ and hypochlorite salts are cheap and benign oxidants, extensively used as terminal oxidant in the oxidation reactions. However, relatively expensive oxidants, viz., iodosobenzene and its variants, peroxy acids (e.g. chloroperoxybenzoic acid, monoperoxyfuranic acid), alkyl peroxides (e.g. $t$-BuOOH) and amine oxides have also been successfully used in oxidation reactions. Manganese based catalysts are used with H$_2$O$_2$, O$_2$ and NaOCl as a terminal oxidants. Rhenium, titanium, vanadium and molybdenum complexes use H$_2$O$_2$ and its derivatives as terminal oxidant. Cobalt, ruthenium, iron, chromium use oxygen and iron, chromium complexes use aqueous NaOCl as terminal oxidant along with suitable co-solvents. The advantages of each system have been reviewed by Musie et al. It has been found that a judicious mixture of solvent and CO$_2$ can optimize the reaction performance as compared to the solvent or ScCO$_2$ used in isolation. Use of ScCO$_2$-expanded solvent media offers enhanced oxidant solubility without altering the catalyst solubility.

Continuous/semi-continuous oxidation reactions in heterogeneous phase in ScCO$_2$ use a range of oxide and mixed metal oxide catalysts. These are carried out at higher temperature (typically at or above 473 K) and use oxides of Co, Mo, W, Ni, Si, Cu, Mn etc., in different combinations supported on Al$_2$O$_3$ or carbon, Pt/TiO$_2$. Typical reactions involve partial oxidation of aliphatic and aromatic hydrocarbons to respective alcohols and aldehydes, olefin epoxidation, olefin to alcohol and alcohol to ether. Problems associated with continuous mode of operation and some solutions have been discussed in the tutorial review by Han and Poliakoff.

A pressure dependent increase in reaction rate, linked to the phase behavior of the reaction mixture, has been observed when CO$_2$ is used as solvent. Catalytic oxidation of several organic substrates in ScCO$_2$, both in homogeneous and heterogeneous phases, has been extensively studied. Photocatalytic oxidation in ScCO$_2$ is another area of increasing interest. Beneficial effects of oxidation reactions in ScCO$_2$ have been reported in several studies, e.g., production of H$_2$O from H$_2$ and O$_2$, oxidation of benzyl alcohol, and oxidation of alcohols. Representative reaction schemes for the conversion alcohol to aldehyde in ScCO$_2$ are presented in Scheme 4 (a & b).

C-C bond formation, alkylation, acetylation and esterification

The mechanism of C-C bond formation in ScCO$_2$ is similar to that in organic solvents. Earlier work on metal-catalyzed C-C formation in ScCO$_2$ has been reviewed by Ikariya and Kayaki. These include cyclotrimerization of alkynes, Heck-Mizoroki olefination of aryl halides, Suzuki-, Sonogashira- and Stille-coupling reactions using Co or Pd complexes. Conversion and selectivity comparable to or better than the reactions in organic solvent have been observed in presence of ScCO$_2$, which is a green reaction medium. Reaction scheme for $t$-butylation of naphthalene is presented as Scheme 5.
Biodiesel production by esterification/transesterification of fatty acids/triglycerides in ScCO₂ has been gaining increasing research interest. Esterification of oleic acid with methanol in ScCO₂ over different catalysts has been compared by Michael Jackson & co-workers ¹⁰⁰. They reported that immobilized lipase (Novozym 435) gave very high activity under ScCO₂, compared to sulfonic acid functionalized silica, standard acidic resin and Amberlist 15.

Vegetable oils are rich sources of fatty acids. Enzyme catalyzed/non-catalytic transesterification of several vegetable oils (castor oil ¹⁰¹, linseed oil ¹⁰¹, sesame oil ¹⁰², mustard oil ¹⁰², corn oil ¹⁰³, sunflower oil ¹⁰⁴, menhaden oil ¹⁰⁵, rapeseed oil ¹⁰⁶, etc.) with methanol/ethanol are reported to result in an enhancement in catalyst activity and rate of reaction when carried out in ScCO₂. Low conversion (< 7 %) was observed in the non-catalytic transesterification of linseed oil in ScCO₂ ¹⁰⁷. Conversion increased to 50 %, when the same reaction was carried out in supercritical methanol and to 37 %, when the reaction was conducted in supercritical ethanol ¹⁰¹. Higher conversions (100 %) are also reported in the enzyme catalyzed transesterification of sesame and mustard oil in supercritical alcohols (methanol and ethanol) as compared to the same reactions in ScCO₂ (conversion: 70 %) ¹⁰². Continuous synthesis of fatty acid methyl esters (FAME) using immobilized Novozym 435 catalyst in ScCO₂ is a potential process for biodiesel production due to high yields and faster kinetics ¹⁰⁰, ¹⁰⁴.

Acetylation of starch with acetic anhydride and sodium acetate is reported to have an enhancement in the degree of substitution (DS) when carried out in ScCO₂ ⁹⁹. The increase in DS was also related to the size of starch particles.

Catalytic functionalization of methanol in ScCO₂ at 313 K has been reported recently ¹⁰⁰. Silver catalyst bearing perfluorinated ligands has been used for activation of methane and C-C bond formation between methane and ethyl diazoacetate producing ethyl propionate. The authors have attributed the success of methanol activation and C-C bond formation to the use of ScCO₂ as solvent.

**ScCO₂ in Material Synthesis**

Supercritical carbon dioxide has been successfully employed as a ‘green solvent’ in material synthesis for the synthesis of metal nanoparticles, high performance polymers, porous organic materials, etc. The developments in the synthesis of porous organic materials have been reviewed by Cooper ¹⁰⁸. This review covered the use of ScCO₂ as a solvent or foaming agent for porous organic materials, use of ScCO₂ as a developing solvent for lithography, ScCO₂ in the synthesis of metal nanoparticles, and, materials for controlled drug delivery. Synthesis of metal nanoparticles and thin films in ScCO₂ and use of ScCO₂ in polymer material synthesis was later reviewed by Beckman ¹⁰⁶. Developments in environmentally friendly synthesis of high-performance fluorinated polymer materials in ScCO₂ for different applications were discussed by Du et al. in a recent review ¹⁰⁹. The materials synthesized in ScCO₂ were reported to have properties superior or comparable to those prepared in conventional organic solvents or water.

**Concluding Remarks**

Supercritical CO₂ is an environment friendly, benign solvent that is increasingly used as a replacement of conventional organic solvents. It has an added advantage that near critical conditions, its properties (e.g. solvent power, diffusion resistance) can be altered significantly by small changes in pressure. Initial research in this area was on gas-liquid hydrogenation/hydroformylation and oxidation reactions where ScCO₂ led to the formation of homogeneous dense phase, eliminating mass transport resistance at the interface. The focus has been on the development of soluble complex catalysts and its modifications for enhancing the solubility. This shifted to heterogenization of homogeneous catalysts, use of metal oxide catalysts in heterogeneous phase and continuous mode of operation. Technology development and commercialization has not kept pace with the accumulation of new research findings in this field. This has been attributed to the huge energy costs for compressing CO₂, in case a side stream of the required pressure does not already exist in the plant. Innovative ways of overcoming this include sequencing of multiple reactions in the same reactor and in situ generation of CO₂ by appropriate decomposition reaction (e.g. decomposition of formic acid). ScCO₂ mediated hydrogenations in ILs and ScCO₂ expanded solvent media for oxidation reactions are also reported to have synergetic effects on reactions as compared to either ScCO₂ or IL/solvent used in isolation.

**References**

MAYADEVI: REACTIONS IN SUPERCritical CARBON DIOXIDE