

Review on green solvent supercritical carbon dioxide and its chemical reactions

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Abstract: This paper reviews on supercritical carbon dioxide SCCO_2 fluid which is the most extensively chosen solvent in green chemistry. SCCO_2 fluid has many intriguing characteristics like non-toxic, non-inflammable, non-polluting, inexpensive, readily available, chemically inert and having a capability of solubilizing lipophilic substances. Here, this review article provides an overview of SCCO_2 its properties and applications particularly in chemical reactions. This work focuses on novel advances in supercritical carbon dioxide chemical reactions. This review provides analysis in application of SCCO_2 as a green solvent and it has been recognized as one of the alternatives to water based conventional processes. We can conserve water by using SCCO_2 in dyeing method due to its remarkable low surface tension value compared to other liquids. This review includes chemical reactions using SCCO_2 , as a replacement to chemical solvents which cause harm to the atmosphere. Other advantages of carrying out reactions in supercritical fluids include regulating phase behavior and products, increase in reaction speed, and obtaining precise reaction channels. It is a simple and flexible solvent which provides favorable alternative to pernicious organic solvents. Thus, SCCO_2 has up and coming future prospects.

Index Terms: Green solvent, supercritical carbon dioxide, Non-toxic, Oxidation, metal extraction, Cage effect.

I. INTRODUCTION

In recent decades, Green Chemistry has become a field of significant concern in science for environment. Adopting green chemistry strategies have led to an appreciable minimization in waste. It is our main focus to consider those chemicals which are non-hazardous and gives greater efficiency. (Hobbs & Thomas, 2007) Unlike other volatile organic solvents SCCO_2 has many absorbing properties like inert, non-inflammable and nontoxic. Baron Charles Cagniard de la tour was the first scientist who described supercritical fluid (SCF) as a state of matter where liquid and vapor phase are indistinct. In this review paper our main focus is on the various types of chemical reactions which are reported utilizing SCCO_2 as a solvent. Currently, SCCO_2 has

been used in the following chemical reactions as a medium: enzyme-catalyzed reactions, polymerization, radical reactions, cycloaddition reactions, catalyzed metal transfer reactions. Heck and Stille reaction is carried out by Palladium-catalyzed reactions. (Gang et al., 2003) Oxidation, hydrogenation, hydroformylation, copolymerization, polymerization, metal extraction reaction is reviewed. This study aims at reviewing available knowledge of SCCO_2 to present worthwhile information.

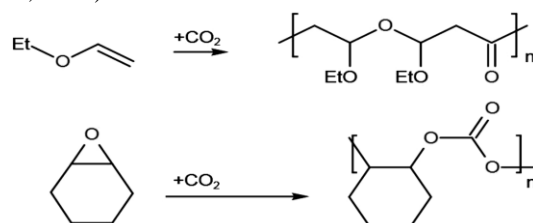
II. SUPERCRITICAL FLUIDS (SCFs) AND SUPERCRITICAL CARBON DIOXIDE (SCCO_2)

The term "supercritical fluid" refers to a substance in a non-condensing and single-phase fluid at an above its critical temperature (T_c) and critical pressure (P_c) (Burk, 1995). T_c and P_c are the highest temperature and pressure at which SCF can exist as vapor and liquid in equilibrium. SCF exhibits properties of gas and liquid both simultaneously. Moreover, we can modify SCFs transport properties by altering its temperature and pressure. SCF is used as an extracting agent as it possesses a good solvent power. (Topuz et al., 2020). Various gases that are commonly used as SCFs are CO_2 , C_2H_6 , NH_3 , H_2O etc. table 1 list some examples of substances used as supercritical solvents and their relative temperature and pressure (Lin et al., 2014; Akanda et al., 2012; Sunarso & Ismadji, 2009).

III. SUPERCRITICAL CARBON DIOXIDE AS A GREEN SOLVENT

For many non-polar low molecular weight compounds and a few polymers like amorphous fluoropolymers and silicones SCCO_2 is the best solvent. Much attention has been paid to situations where SCCO_2 is dissolved in polymers. The reviews by Cooper and Tomasko give substantial information on numerous applications of SCCO_2 to polymer synthesis and processing. The Lewis acidity of CO_2 is the foremost contributor to its solubility and many studies have been seen but there is no spectroscopic evidence shown of Lewis acid-base interaction between CO_2 and polymer.

In polymerization, the reduction of the viscosity decreases the mass transfer resistance of the polymer. Reduction of viscosity depends upon the amount of CO_2 dissolved and the solubility of CO_2 in the synthesized polymer. Polymerization is given in Scheme 1 in which CO_2 act as monomer as well as solvent. The amount of copolymerization of ethyl vinyl ether increases because the carbocation gets extra stability due to SCCO_2 . (Nalawade, 2006)



Scheme 1: CO_2 Copolymerization reactions (Nalawade, 2006)

Numerous applications have been reported: polymer modification, polymer composites, polymer blending, microcellular foaming, particle production, and polymerization, where CO_2 plays the role of plasticizer or solvent or antisolvent. Additionally, fluorocarbon-based surfactant is most often used in the field due to high solubility of fluorocarbon chains in SCCO_2 solvents. Fluorocarbons are more CO_2 -philic than the hydrocarbons. The righteous properties of SCCO_2 as a solvent could be complemented further through the use of Ionic Liquids-in- CO_2 systems. (Peach & Eastoe, 2014)

IV. CHEMICAL REACTIONS INVOLVED IN SCCO_2

A. Hydrogenation reactions and hydroformylation reactions
By use of a SCCO_2 phase, in which a much higher concentration of hydrogen could be dissolved, contributes to a very high initial reaction rate, around 1,400 moles of formic acid per catalyst mole per hour. Leitner have documented efficient development of formic acid in a supercritical mixture of CO_2 and H_2 , containing the Ru (II) trimethyl-phosphine complex as a catalyst precursor. (Wai et al., 1998; Graf & Leitner, 1992) In liquid organic solvents, the rate of the same reaction under equal conditions is decreased by a considerable value. SCCO_2 liquid

Table 1: Critical points of some commonly used solvents

(Lin et al., 2014)

Gases	Critical temperature (K)	Critical pressure (MPa)	Critical density (g/mL)
Carbon Dioxide	304.17	7.38	0.448
Ethane	190.55	4.59	0.203
Methane	282.35	5.04	0.2
Ethylene	369.85	4.24	0.218
Propane	369.85	4.24	0.217
Nitrous oxide	309.15	7.28	0.45
Propylene	365	4.62	0.232
Xenon	289.7	5.87	0.118
Water	647.3	22.05	0.322
Ammonia	405.6	11.28	0.325
Benzene	562.1	4.89	0.302
Methanol	512.6	8.09	0.272
Ethanol	513.9	6.14	0.276
Acetone	508.1	4.70	0.278
Toluene	591.7	4.11	0.292

SCCO_2 is a single supercritical fluid phase in which the distinction between the liquid phase and gas phase disappears at and above the T_c (31.1°C) and P_c (72.8 atm) of carbon dioxide (Lin et al., 2014; Kohli, 2019). Figure 1 one shows the phase diagram. The triple point on this diagram is the point that represents all three phases of CO_2 together in equilibrium (Uwineza, 2020; Gopaliya, 2014). Above critical point with increase in pressure or temperature, the substance cannot be changed from liquid to gas or from gas to liquid (Uwineza, 2020; Gopaliya, 2014; Sapkale, 2010). SCCO_2 is one of the most broadly used supercritical fluids due to its striking properties such as being inert, non-inflammable, non-toxic, cost-efficient and readily available with high purity (Topuz, 2020).

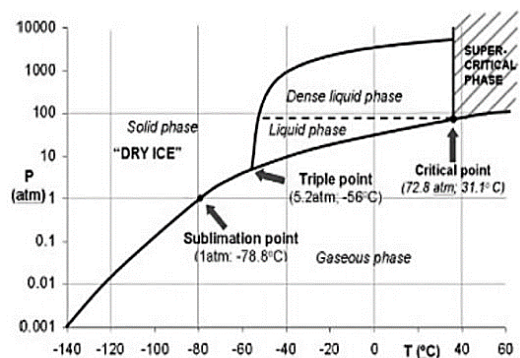
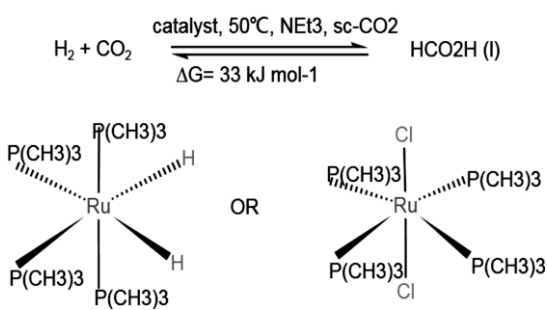


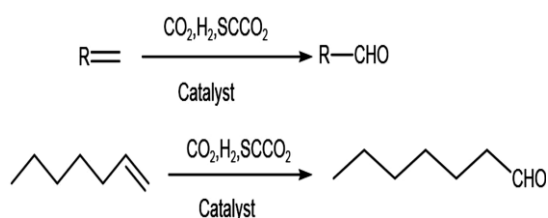
Fig 1. The phase diagram of CO_2 (Lin et al., 2014; Sunarso & Ismadji, 2009)

phase hydrogenation removes H₂ diffusion resistance at the gas-liquid interface, improves H₂ solubility, eliminates total transport resistance, leading to high reaction rates and increased yield. (Mayadevi, 2012) An even more development in the hydrogenation reaction is that, under SCCO₂, two reactions are performed in sequence in the same reactor. Aldol condensation followed by hydrogenation in the same reactor using a bifunctional palladium catalyst led to high activity, selectivity and long life of the catalyst.



Scheme 2. Ruthenium (II)-catalyzed hydrogenation of CO₂ in the supercritical fluid phase (Wai et al., 1998).

Hydroformylation is the addition of equivalent amounts of CO and H₂ to an alkene to create oxygenated organic compounds, mostly aldehydes. Niese and Woelk (2007) examined the advancements in supercritical fluid hydroformylation reactions and its application. For rhodium complexes catalyzed Olefins Hydroformylation an increase in reaction rate was observed. (Koch & Leitner, 1998; Mayadevi, 2012)



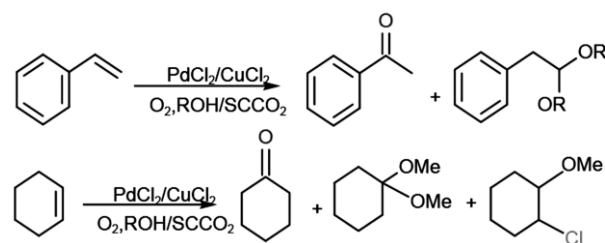
Scheme 3: a) Hydroformylation reaction b) Hydroformylation of 1-Hexene in SCCO₂ (Tadd et al., 2003; Mayadevi, 2012)

Scheme 3a represents the general reaction for Alkene to Aldehyde Hydroformylation and 1-Hexene to Heptanal hydroformylation is given in Scheme 3b.

B. Oxidation reactions

In oxidation we have observed the Wacker reaction in which the alkene is oxidized to aldehyde or ketone. Lloyd and Luberoff (1969) stated that in n-propanol, the oxidation reaction of 1-octene gave 2-octanone, 3-octanone and 4-octanone a yield of 68%, 9%, & 3%, respectively. 1-Octene oxidation in SCCO₂ has greater selectivity to give methyl ketone as the major product. The study of the Wacker process in Styrene and Cyclohexene gives Acetophenone and Cyclohexanone but with SCCO₂ the

small amount of acetal has also obtained. So, it can be concluded that use of SCCO₂ as a reaction media could give regioselective reaction and the effect of electronegativity or substituting group on oxidation regioselectivity could also be revealed. When CO₂ is used as solvent a pressure-dependent increase in reaction rate, correlated with the phase activity of the reaction mixture has been observed. (Han & Poliakov, 2012; Caravati et al., 2006) Usage of solvent SCCO₂-expanded media provides improved oxidant solubility without altering the catalyst solubility. Pd²⁺/ (Cu⁺ or Cu²⁺)-catalyzed Methyl acrylate oxidation process can also be productively carried out to provide high conversion (99.4%) with a 96.6% yield of Dimethyl acetal as the main product. (Zou Gang et al, 2003; Jia et al., 1999; Li et al., 1999) Several studies have documented beneficial effects of oxidation reactions in SCCO₂, such as development of H₂O₂ from H₂ and O₂ (Munshi & Bhaduri, 2009), Benzyl alcohol oxidation, and alcohol oxidation. The reactions gave promising performance when CO₂ in supercritical or in liquid condition is used in oxidation reactions using Alkyl ethers as the substrates.



Scheme 4: Oxidation of Styrene and Cyclohexene (Mayadevi, 2012).

C. Co-polymerization

Fluoropolymers are highly soluble in SCCO₂, which provides an appealing alternative to chlorofluorocarbons (CFCs) for the synthesis of these fluoropolymers and telomers in a homogeneous solution. In 1992, DeSimone's group reported the first successful synthesis of fluoropolymers in SCCO₂ using homogeneous free-radical polymerization of extremely fluorinated acrylic monomer 1,1-dihydroperfluorooctyl acrylate (FOA) with AIBN [2,2-azobis (iso butyronitrile)] as an initiator. (Wai et al., 1998; Burk, et al., 1995) The decomposition rate of the initiator AIBN estimated in SCCO₂ was approximately 2.5 times lower than that observed at atmospheric pressure in benzene. The reason for this can be attributed to low viscosity of SCCO₂, that does not generate the essential "cage effect" which otherwise encourages the formation of a new primary radical pairs. Copolymerization of water-soluble polymer, monomers and hydrophobes normally creates hydrophobically modified water-soluble polymers. These polymers have broad use in the treatment of water, food, cosmetics, personal care products, etc. The copolymerization of FOA, (figure 2) with acrylic acid in SCCO₂ gives a polymer in the form of a dry white powder with diameter of about 0.2 μm. The copolymer solutions exhibit high thixotropy, i.e. its viscosity decreases sharply under constant

shear rates; the viscosity improves again when the shear is stopped. Instead of fluorine-containing monomer we can use siloxane-containing monomer which is TMSPMA (3-(Trimethoxy silyl) propyl methacrylate (figure 3) because it is less expensive. Copolymerization of TMSPMA with acrylic acid was also successfully carried out.

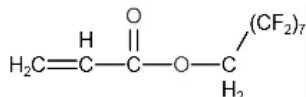


Fig. 2: FOA

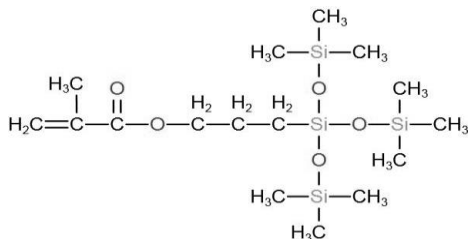
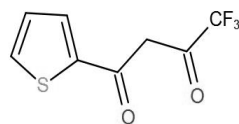


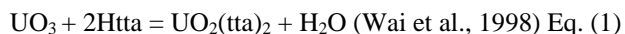
Fig. 3. TMSPMA (Zou Gang et al., 2003)

V. METAL EXTRACTION IN SCCO₂

Owing to the charge neutralization requirement and the weak solute-solvent interactions, metal ions are insoluble in SCCO₂ but metal ions can be made soluble by forming neutral metal chelates with the organic solvents. The potential of SCCO₂ to remove uranium ions from nitric acid solutions in the presence of tributyl phosphate (TBP) is of major relevance. (Wai et al., 1998; Burk et al., 1995) The uranyl ions isolated from SCCO₂ are likely to be formed as UO₂(NO₃)₂.2TBP, which is identical to kerosene. In reprocessing, the acid and the organic waste is produced containing fission products and transuranic elements which is harmful for the environment. SCCO₂ can be used to substitute kerosene for uranium and plutonium extraction, thereby decreasing the formation of organic solvent waste. Existing research has also shown that dissolving of UO₃ crystals in SCCO₂ containing fluorinated β-diketone, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta) is possible without using any acid. So, using SCCO₂ technology would result in the minimizing nuclear waste materials. The following reaction is



Htta



Other chemical reactions involving SCCO₂ as a solvent are synthesis of organometallic compounds, preparation of nanoparticles (Tadros et al., 1998), Chemical reaction with transition metals using SCCO₂ (Skouta, 2009), synthesis of silver and copper nanoparticles in water-in-SCCO₂

microemulsion (Ohde et al, 2001), free-radical reactions etc. (Suppes et al., 1989)

CONCLUSION

Supercritical fluid carbon dioxide has many outstanding properties, which makes it a very strong solvent as we have observed in the hydrogenation and hydroformylation. The findings showed greater conversion and selectivity with SCCO₂ in traditional organic solution conditions as observed in the oxidation reaction. SCCO₂ decreases the decomposition rate of AIBN initiator in the polymerization reaction by eliminating the cage effect due to its low viscosity property. The viscosity of copolymer gets improved after the shear is stopped when we used FOA with acrylic acid in SCCO₂. The reduction in acid waste and nuclear organic waste is observed as the neutral chelate complex gets solubilized in SCCO₂, which indicates no need of acid solutions for the extraction of metals. As a conclusion from this review, the use of a harmful material can be minimized by using SCCO₂ fluid. SCCO₂ as an alternative solvent for green chemistry is convincingly substantiated by its use in many chemical processes and hence for the future. Chemical reactions in supercritical fluids might continue to become an emerging area of research and technology and could, over the next decade, result in more effective, economical and environmentally sound processes for chemical production.

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