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Role of Supercritical Fluids in Chemical Reactions

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Abstract:

Recently, a great deal of attention has been directed towards finding alternatives to traditional solvents. An attempt has been made in this paper to focus on supercritical fluids (SCF's) as an alternative solvent system. The applications and advantages of these solvents are analyzed to determine whether or not SCF's are a viable replacement to the traditional solvents. SCF's are extremely versatile and have great environmental benefits relative to traditional organic solvents; however the use of these solvents is not widespread nor are they sufficiently developed to feasibly replace solvents used today. Regardless, SCF's present an area into which certain solvent uses can be diverted in order to mitigate the environmental effects of the current situation while searching for a more practical replacement.

Keywords

Supercritical Fluids, Traditional Solvents, Hydrogenation, Oxidation, Hydroformylation

1. Introduction

Presently, solvents occupy most of the focus in the realm of green chemistry, whether it is optimizing solid-state reactions, investigating ways to recycle solvent waste or conducting research on greener solvent systems. Motivating this work is the realization that while solvents play crucial roles in various chemical reactions they are not always necessary and in some cases may hinder optimal reaction conditions. Solvents are commonly employed for their benefits such as mass transfer, heat transfer, and dilution of reagents to ensure selectivity and potential stabilization of transition states.

Supercritical fluids (SCF's) are one of the green solvents which have received a fair amount of attention in the last two decades. Supercritical fluid is a term that refers to a substance exposed to temperatures and pressures above the corresponding critical point. Carbon dioxide ($ScCO_2$), water (ScH_2O), propane (ScC_3H_8), methanol ($ScCH_3OH$) and nitrous oxide (ScN_2O) are commonly studied SCF's. Among these, $ScCO_2$ is the usually used [1]. Most SCF's have very little environmental impact and is non-toxic, non-flammable and relatively cheap, making these solvents a great potential alternative to the systems already in place. This review seeks to present some of the applications of SCF's in some chemical reactions to assess their efficacy as replacements to traditional solvents.

2. Roles of SCF's in Chemical Reactions

SCF's, as a result of their versatile nature, have been examined in various reactions either as the solvent medium or as actively participating in the reaction. By adjusting certain properties, such as the density, pressure, dielectric constant and so forth it is possible to increase the reaction rate, yield and selectivity [2]. In fact, previous literature presents the study of SCF's in some outstanding chemical reactions [3]. Subsequently, the ability to tune the chemical properties of these solvents by changing the physical conditions exhibits certain experimental consideration that ought to be considered. Changes in the pressure under which the SCF is contained can affect the density of the fluid enormously and subsequently, the solvating ability of said fluid. Using SCF's it might be conceivable to complete customarily heterogeneous reactions in the homogeneous state. One illustration of this is reactions which involve polymeric substrates that experience rate restrictions when conducted heterogeneously. Likewise, it is important to consider the temperature under which the reaction will be carried out. For example, lower temperatures will cause the reaction rates to diminish while higher temperatures may cause catalytic decomposition [4].

On account of pyrolysis, it is spotted that conducting the reaction at lower temperatures can lessen undesirable by-products and has been shown to increase yield, selectivity and product separation [2]. Besides, it is important to consider the reactive nature of the SCF being utilized. One consequence of utilizing SCF's in chemical synthesis is that these solvents can play a part in the reaction under specific conditions. Be that as it may, this property is really used in specific reactions, for example, the hydrogenation of CO_2 to produce common organic molecules, such as formaldehyde. Of the many reactions that have been contemplated in SCF's, three of the most surely understood such as hydrogenation, hydroformylation and oxidation are presented here.

3. Hydrogenation

The rate of numerous hydrogenation reactions is reliant on the concentration of hydrogen in solution and also the diffusion of H_2 once dissolved. However, this is constrained by the immiscibility of H_2 in many organic solvents [5]. On account of the miscible nature of SCF's with some gases, it is conceivable to significantly increase the concentration of hydrogen in solution. Besides, the expanded diffusivity exhibit in most SCF's enables the reaction to proceed at significantly increased rates [4- 6]. Previous studies have demonstrated that this increase in rate lies solely with the increase in hydrogen concentration as catalytic activity is not shown to increase when the reaction is carried out in SCF's [6]. Besides, SCF's have been beneficial in the production of many hydrogenation products including, fats and oils, small organic compounds and enantio selective products. Considering that the transformation of vegetable oils into saturated fats is an immense industry, using SCF's would be extraordinarily advantageous. The across the board utilization of SCF's would at first outcome in the substitution of customary solvents and ultimately an extensive reduction in the environmental impact caused by such solvents. Hence, the ability to supplant the present solvents with ScCO2, which is non- combustible, non-toxic and environment friendly would present many *green* advantages [5, 7].

4. Hydroformylation

This process is fundamentally the same as hydrogenation in that it conventionally uses liquid solvents, gaseous reagents and a solid catalyst and presents incredible modern significance as the products of this reaction go onto many secondary applications [4, 7]. Unlike the hydrogenation reaction, the reaction rate for hydroformylation is not extraordinarily altered when done in SCF's since the reaction is homogeneous when carried out in organic solvents. However, there have been observed increases in catalytic selectivity when performing the reaction in SCF's with the end goal that the desired product is obtained in higher yields [3, 4, 6].

5. Oxidation

There have also been numerous studies where SCF's are utilized as a part of oxidation reactions, some of which have yielded certain heterogeneous catalyzed reactions, for example, the steel catalyzed oxidation of cumene, the CoO catalyzed oxidation of toluene or supercritical water oxidation as already talked about [4]. The advantage here, like the previous examples, is the miscibility of O_2 with most SCF's allowing for more prominent mass transfer [3, 7]. A few studies have been performed on homogeneous oxidation reactions with SCF's, for example, epoxidation reactions that can allow enantio selective products within the presence of specific catalysts, sulfoxidation reactions where the application of an SCF propels diastereoselectivity and even oxidation of alkanes to produce functionalized molecules, for example, the transformation of cyclohexane to cyclohexanone yet in cut down yields [3, 4]. Another fascinating use of SCF's, as for oxidation, is the use of partial oxidation. Methane has been studied as a potential fuel source, anyway there are challenges related with the storage and transport of this material. Partial oxidation of methane yields methanol and other higher order hydrocarbons, which are easier to transport and store. Regrettably, this reaction is yet to be improved and shows exceptionally poor yields [5]. In addition to the synthetic pathways described above, there has also been research put into the use of SCF's to increase total aerobic oxidation of organics [3].

In spite of the fact that not explicitly discussed herein, there are a countless number of reactions in which SCF's have been substituted in order to observe the effect on reaction rates, selectivity, yield and so on. As presented, it is clear that in some cases it is beneficial to a great extent to employ SCF's in place of the conventional solvents not only for their ecological advantages, as well as for their capability to enhance the metrics related with the reaction of interest.

6. Conclusion

Solvent use contributes enormously to the ecological effect of most chemical industries. Solvents are utilized as a part in the pharmaceutical industry, automotive industry, textiles, dry cleaning, paints, plastics, rubbers and so on. However, it is clear that simply halting the production of solvents would accomplish harm than good. Therefore, it is important to discover a few other options to the conventional methods used; whether greener solvents are introduced, solvents are expelled from the procedure by and large or alternative solvent systems are adopted. The numerous applications previously introduced demonstrate that there is a possibility for SCF's to supplant customary solvents in some features. All the more particularly, the utilization of SCF's as the mobile phase in some usual analytic procedures, the potential use of SCF's in the pharmaceutical industry, the capacity to treat waste using SCF's or substituting SCF's in well-known reactions all in an attempt to supplant the solvents conventionally used. Regrettably, there are some applications where it is not feasible to simply replace the solvent with a SCF. Therefore, SCF's can clearly offer a replacement to conventional solvents in numerous aspects and in these cases it would be significantly valuable to supplant the solvents. However, SCF's cannot entirely substitute the solvents used today and solve the existing crises.

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