CATALYTIC CYCLOCARBONYLATION IN COMPRESSED CARBON DIOXIDE: SOLUBILITY STUDIES

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Abstract

Among the current interests in organic synthesis are those reactions performing multiple C-C bond formation, in special when they undergo under catalytic conditions. As yet, its application has been limited to laboratory scale mainly due to: low yields in organic solvents and difficult product separation[1]. In this context, we have been working on the carbonylative cycloaddition of allyl halides and alkynes in acetone, mediated by nickel[2,3].

At present there is an increasing interest on the use of compressed fluids (CF), in particular, supercritical carbon dioxide ($scCO_2$) which is one of the most attractive fluids as an alternative reaction medium to environmentally unfriendly organic solvents[4]. Although metal-catalyzed homogeneous reactions in $scCO_2$ would be attractive, the low solubility of many catalysts is usually a barrier to their use in such processes[5]. Therefore, the solubility of metal complexes in $scCO_2$ is one of the key factors for determining the feasibility of homogeneous catalysis in supercritical fluid media. Unfortunately, only a small number of solubility measurements for metal complexes have been reported up to now.

We present herein a study that aims to a cleaner technology for the catalytic cyclocarbonylation reaction working with CF as the reaction medium, more specifically using mixtures of CO_2-expanded acetone. The conventional reaction is performed in acetone. For that reason, the solubility studies of the different components of the reaction have a great deal of interest in terms of phase behaviour predictions.

The purpose of the solubility experiments is to study the phase behaviour of different binary and ternary mixtures involved in the cyclocarbonylation reaction which will allow the prediction of the phase behaviour of a multicomponent mixture.

Preliminary solubility experiments were performed on the different components (catalyst + reactants) involved in the cyclocarbonylation reaction, both in pure CO_2 and CO_2-expanded acetone, at 298K and pressures between 6 and 10MPa. So far, the results confirm that both allyl halides and alkynes are highly soluble in CO_2-expanded acetone. The catalyst precursor solubility is currently under study. The analysis of phases at high-pressure has been carried out in a variable volume cell with sapphire windows, which allows visual inspection of the number of phases present.

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