

BOOSTING CO₂ AS A RENEWABLE CARBON SOURCE: NEW OPPORTUNITIES PROVIDED BY HIGH PRESSURE CONDITIONS

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ABSTRACT

One of the most promising CO₂ applications as a renewable carbon source is in the production of carbonates through epoxides carboxylation. This reaction is efficiently catalysed by ionic liquids, namely tetrabutylammonium bromide (TBABr). In this work, the ability of supercritical CO₂ to decrease TBABr melting point temperature was explored with the purpose of using it, as a liquid heterogeneous catalyst phase. Two different biphasic systems (a CO₂-rich and an epoxide-rich) were investigated and a direct comparison between homogeneous and heterogeneous catalysis was performed. Styrene oxide was selected as a model substrate. Reactions were performed at 353.2 K and at 15 and 18 MPa. Conversion of epoxy groups to carbonates, was monitored quantitatively by using ¹H-NMR spectroscopy.

INTRODUCTION

CO₂ capture and storage, although surrounded by controversy, will mostly likely become a practical reality in the near future. It will generate very large amounts of compressed pure CO₂, which must then be stored, unless alternative uses of high-pressure CO₂ as a raw-material are found [1-3]. The possibility of producing valuable organic compounds through CO₂ chemical fixation, is therefore, an increasingly “up-to-date” goal.

Indeed, the incorporation of CO₂ as an available, cheap, non toxic and renewable carbon resource into an organic substrate is a good example of a “sustainable process” and can contribute to a “sustainable growth” by providing more environmental benign routes to produce chemicals. In this respect, epoxides carboxylation with CO₂, to produce carbonates is one promising application [4-6]. Nevertheless, most published works focuses exclusively on reactions at low-pressures, disregarding advantages of high-pressure CO₂ properties.

Unique properties of high-pressure CO₂ have been extensively used in chemical catalysis, namely to control equilibrium and kinetics of reactions [7]. Successful examples in literature highlight characteristics that make high-pressure CO₂ and its mixtures, attractive [7]. However, because these are non-conventional characteristics, their role is not clarified for many cases and particularly not for the case of epoxides carboxylation with CO₂.

Especially interesting is the combination of ionic liquids with CO₂, because ionic liquids are practically not soluble in CO₂, while CO₂ presents a high affinity and consequent solubility in various types of ionic liquids. They are both more environmentally acceptable than volatile organic solvents, and they are both tunable solvents, which means that physico-chemical properties can be adjusted to specific needs, either by varying the cation/anion combination (for ionic liquids) or by varying pressure and temperature conditions (for CO₂). [8]

Furthermore, because supercritical CO₂ is able to decrease ionic liquids melting point, some organic salts can become liquid at much lower temperature (some melting point depressions exceed 100 K), and in this case, some salts can also be used as ionic liquids under a supercritical CO₂ atmosphere. [9,10] Several authors have been investigating this phenomenon, namely the influence of the structure of cation/anion on the melting behavior. [8-10]

In this context, Scurto et al. [10] measured the melting point depression effect caused by high pressure CO₂ in numerous ammonium salts. For the case of tetrabutylammonium bromide (TBABr) a melting point depression from around 373K to 353K at 15MPa was found out. In this work, the ability of supercritical CO₂ to decrease TBABr melting point temperature was explored with the purpose of using it, as a liquid heterogeneous catalyst phase. Two different biphasic systems (a CO₂-rich and an epoxide-rich) were investigated at constant temperature: i) For the CO₂-rich biphasic system, the addition of CO₂ solubilizes the epoxide in the vapour phase and melts the catalyst (heterogeneous catalysis); ii) On the other hand, for the epoxide-rich biphasic system, as CO₂ is added, it incorporates into the liquid phase originating a CO₂-expanded liquid, in which the catalyst is dissolved (homogeneous catalysis).

Reactions were performed at 353.2 K and at pressures of 15 and 18 MPa. Conversion of epoxy groups to carbonates, was monitored qualitatively and quantitatively by using ¹H-NMR spectroscopy.

MATERIALS AND METHODS

High purity carbon dioxide 99.998 mol% was supplied by Air Liquide. Styrene oxide 97% and tetrabutylammonium bromide ≥98% were purchased from Sigma-Aldrich.

Experiments on the CO₂ carboxylation of styrene oxide were performed in a high-pressure apparatus [11]. The apparatus is composed by a stainless steel cylindrical cell with an internal volume of approximately 5 cm³ and two sapphire windows at the tops allowing a direct visual observation of the number of phases of the reaction mixture. Temperature control is achieved by immersing the cell inside a thermostated water-bath, heated by means of a controller that maintained temperature within ± 0.1°C. Temperature is measured with a mercury thermometer with a precision of ±0.1 °C. The pressure inside the cell is measured with a pressure transducer 204 Setra calibrated between 0 and 34.3 MPa and with a precision of ±0.1%. The cell has an internal magnetic stirrer for efficient mixing of the components.

Experimental procedures were replicated for all experiments, as follows. Briefly, the water bath was first brought to the desired temperature of 353.2 K. The cell was then loaded with styrene oxide (0,2 or 2 ml) and TBABr (0,1% mol in relation to the epoxide). The cell was connected to the apparatus and immersed in the water bath. CO₂ was liquefied and pumped into the cell up to the desired pressure, under stirring. After six hours of reaction, the reactor was gradually cooled to room temperature and depressurized to atmospheric pressure. The cell was opened, and the contents analyzed by ¹H NMR spectroscopy.

RESULTS

Two different biphasic systems (a CO₂-rich and an epoxide-rich) were investigated and a direct comparison between homogeneous and heterogeneous catalysis was performed at the exactly same conditions of temperature and pressure. Figure 1 illustrates what happens to both systems as CO₂ is introduced into the cell and pressure increases.

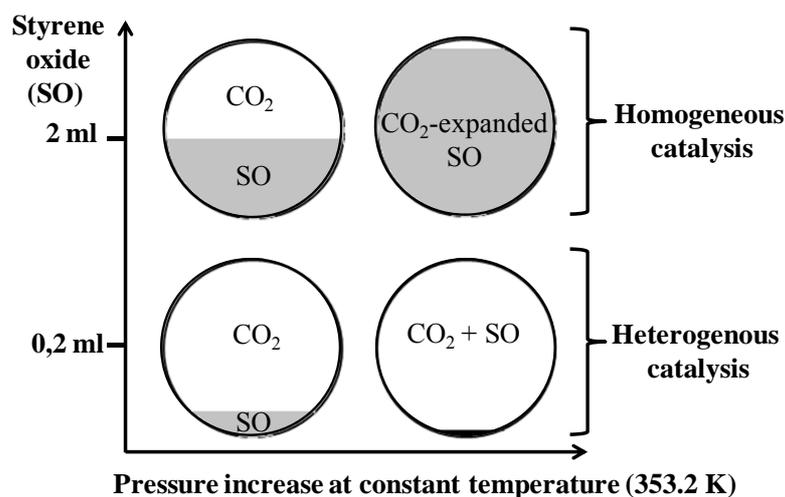


Figure 1: The effect of pressure addition to a CO₂-rich and an epoxide-rich system

At 353.2 K, for the CO₂-rich system, as pressure increases, the epoxide is solubilized in the CO₂-rich phase and at 15MPa the catalyst melts into a liquid phase (heterogeneous catalysis). On the other hand, for the epoxide-rich system, the pressure increase will have a completely different effect on the system, causing the appearance of an expanded liquid phase, where the catalyst is dissolved (homogeneous catalysis). As described at the materials and methods section, the high-pressure cell is cylindrical and has two sapphire windows at the tops that allowed a direct visual observation of the number of phases of the reaction mixture.

High-pressure reactions were performed at 353.2 K for six hours using TBABr as catalyst (1% mol in relation to the epoxide). The formation of the cyclic carbonate groups was monitored by ¹H-NMR spectroscopy.

Figure 2 illustrates an example of the conversion of styrene oxide to styrene carbonate. New signals between 4.25 and 6.00 ppm correspond to the cyclic carbonate groups. Due to the decreased signal intensity of the epoxy groups between 3.25 and 4.00 ppm, the conversion of styrene oxide could be monitored.

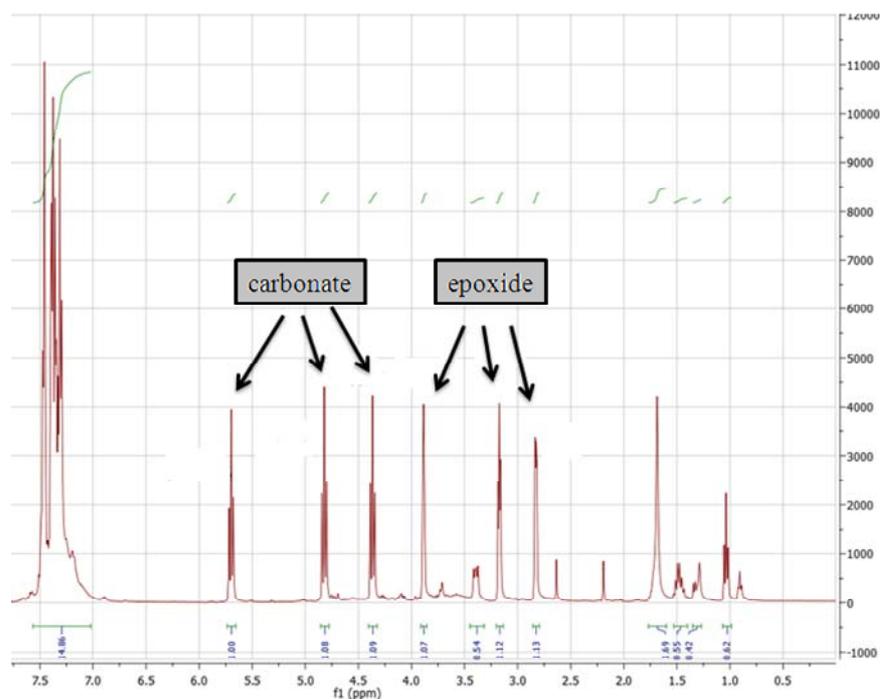


Figure 2: ¹H-NMR spectroscopic monitoring of styrene oxide carboxylation at 353.2 K, for 6 hours, using TBABr as catalyst (1 mol %).

Results obtained are presented in Figure 3. Percentages of carbonate formation for heterogeneous catalysis were always higher than those obtained for homogeneous catalysis. Furthermore, the addition of CO₂ and consequently pressure increase, had a positive effect for both systems under study.

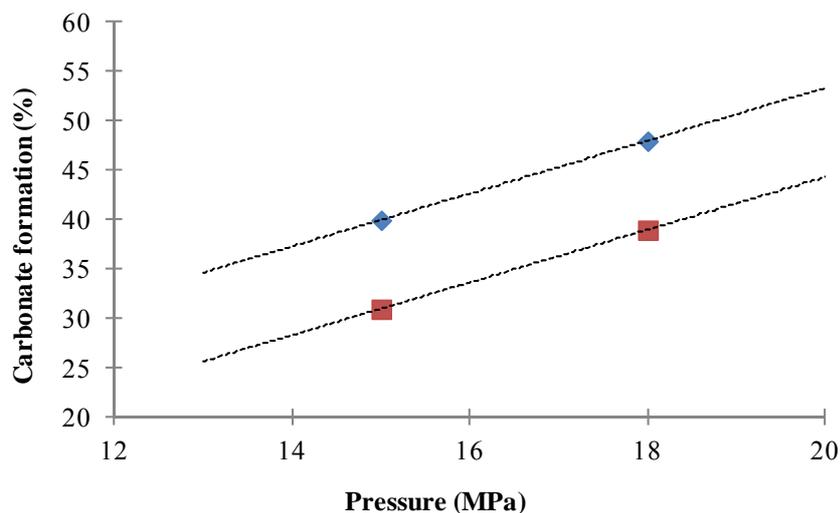


Figure 3: Comparison of styrene carbonate formation for different volumes of substrate. ♦ 0,2 cm³ (heterogeneous catalysis), ■ 2 cm³ (homogeneous catalysis). All reactions were carried out at 353.2 K, over 6h, using TBABr as catalyst (1 mol %). Dashed lines are just a guide to the eye.

Although at the exactly same conditions of temperature and pressure, reactions under study occurred at different biphasic systems depending on the quantity of substrate used (CO₂-rich or epoxide-rich). For the CO₂-rich system, the reaction occurred at the interface between liquid catalyst and the vapour phase where both reactants are solubilized. Due to reported high affinity of CO₂ for ionic liquids, mass transfer does occur and it seems to be favoured by pressure increase.

On the other hand, for the epoxide-rich system, the reaction occurred at the expanded liquid phase. It is well described in literature, that for these cases, pressure increase, has complex effects on the reaction kinetics, considerably altering reactant ratios in contact with catalysts as well as diluting the reaction mixtures. Results obtained in this work showed a beneficial effect on carbonate formation by increasing CO₂ pressure. Nevertheless, vapour-liquid equilibrium experiments are needed to a better understanding of these effects.

CONCLUSION

In this work, the unique properties of high pressure CO₂ and its mixtures, allowed a direct comparison of homogeneous versus heterogeneous catalysis at the exactly same conditions of pressure and temperature. Styrene oxide carboxylation with CO₂ to produce styrene carbonate, was catalysed by i) CO₂-induced liquid TBABr (heterogeneous catalysis) or by ii) TBABr dissolved in a CO₂-expanded styrene oxide phase (homogeneous catalysis). Results were always slightly better for heterogeneous catalysis, allowing to conclude that, due to high affinity of CO₂ for ionic liquids, an efficient mass transfer occurred between the liquid catalyst and the vapour phase where the reactants are solubilized. This result allows to explore the possibility of using TBABr as catalyst for CO₂ carboxylations of substrates in which TBABr is not soluble, without the need of increasing temperature above 373K or using an organic solvent.

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