38e Heterogeneous Catalysis of Methyl Acetate Formation in Compressed Carbon Dioxide

Stephan Schwinghammer, Matthäus Siebenhofer, and Rolf Marr

The use of supercritical fluids in chemical synthesis has gained increasing interest among the chemical and materials research community during the past two decades. High-pressure gases and supercritical fluids are attractive substitutes for organic solvents in a wide range of industrial application in the food industry. High-pressure carbon dioxide is particularly attractive as a substitute for organic solvents due to its characteristic of being an environmentally benign solvent. The solvent supercritical/compressed carbon dioxide is not classified as hazardeous. It is potentially useful in industry for environmental protection and for economic reasons due to energy savings in the evaporation of bulk solvents. Carbon dioxide is also non-flammable, non-toxic and relatively inexpensive. Compared with liquids mass-transfer in compressed CO_2 is better. Supercritical carbon dioxide can either act as active component of a chemical reaction or act as solvent for reactants, catalysts and products. It can dissolve reactants and catalysts of different physical state to provide homogenous operating conditions during chemical reaction, while separation of products from reactants, catalysts and unwanted by-products may evolve from changing the pressure and/or temperature of operation. Several reactions have been performed successfully in liquid and supercritical CO_2 with rates and selectivities comparable or better than in conventional solvents [1]. The solvent properties of CO_2 can be altered by selecting appropriate operating conditions. In addition, this specification of compressed CO_2 enables fine-tuning of the reaction environment and as a result optimization of the rate and selectivity of reaction. By adjusting temperature and pressure and as a consequence the solvation power of CO_2 many applications in separation and purification processes can be solved. Because the solubility of many substances is rather low in carbon dioxide, high pressure may be needed to achieve reasonable concentrations. As CO_2 may not equally dissolve products and reactants, high pressure is needed routinely to guarantee homogeneous single-phase reaction processes. In the present project we focused on the properties of compressed carbon dioxide as reaction carrier for esterification reactions. Reversible chemical reactions, such as esterification reactions, are a preferred field of application for the solvent compressed CO_2 because solubility of the participating reaction components can be altered by pressure tuning. As a consequence the product yield of equilibrium reactions can be improved. The use of the alternative solvent carbon dioxide results in shifting the reaction equilibrium composition to the desired product side of the reaction. In the present project esterification of methanol with acetic acid in compressed carbon dioxide has been investigated because esterification of carboxylic acids with alcohols is representative for reversible reactions. While esterification in conventional reaction media is well reported [2] few studies have been done on specific chemical equilibrium reactions in compressed carbon dioxide such as esterification reactions [3]. The positive effect of the solvent CO_2 itself on the yield of methyl acetate formation has been investigated in a previous work [4]. The current project focuses on investigation of heterogeneous catalysts on esterification in compressed carbon dioxide. The effect of silica gel on esterification of acetic acid with methanol in compressed carbon dioxide has been investigated. It is a useful desiccant because of the porosity and chemical nature. Elimination of the reaction product water from the reaction system shifts equilibrium composition to the product side of the esterification reaction and therefore enhances the formation of methyl acetate. The experiments have been carried out in a high-pressure reaction cell with two inspection glasses at front and back side of the cell over the whole height enabling permanent visual control of experiments. As mentioned control of the water balance of the esterification reaction was expected from adding silica gel while actually experimental results showed no positive effect on the yield of esterification due to blocking of silica gel with acetic acid. In a next step the silica gel was modified with ferric ions. The influence of ferric endowed silica gel on the formation of methyl acetate was investigated for system pressures up to 9.1 MPa and system temperatures up to 328 K. Comparison with silica gel showed a significant increase of the yield.

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