38b Catalytic Hydroformylation of Higher Olefins in CO2-Expanded Media: Kinetic, Mechanistic and Economic Aspects

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Commercial processes for the hydroformylation of higher olefins are hampered by the syngas solubility limitqtions in the liquid phase reaction mixture and the tedious catalyst recovery steps that require the use of acid and alkali. We reported enhanced reaction rates during Rh catalyzed 1-octene hydroformylation in CO2-expanded acetone. At 30 and 60 oC, the turnover numbers (TONs) for aldehyde formation in CO2-expanded acetone were up to fourfold higher than those obtained in either neat acetone or dense CO2. The higher TONs in CXLs are attributed to enhanced syngas solubility (compared to neat solvent) and enhanced dielectric constant (compared to dense CO2). Other demonstrated advantages of using CXLs include significant replacement of conventional solvents (up to 80% by volume) by benign CO2 and process intensification at relatively mild pressures (compared to those required with scCO2). Recently, we demonstrated that the intrinsic solubilities of H2 and CO are higher in CXLs than those in neat organic solvents. A comprehensive study on catalytic hydroformylations in CXLs will be presented. Effects of several parameters including temperature, solvent media, concentrations of H2 and CO, and concentrations and types of various ligands will be investigated with in situ High Pressure ReactIR. An empirical correlation for the reaction kinetics will be developed and compared to those reported in literature. Economic and environmental impact analyses on the CXL-based hydroformylation processes will be discussed.