77b Investigations of Structure-Activity Relationships for Cobalt Oxygen Carriers as Radical Catalysts for Catalytic Oxidations in CO2-Expanded Liquids

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Selective catalytic oxidations play a significant role in the production of various intermediates for polymers, pharmaceuticals and consumer products of multi-billion dollar value. Most existing industrial oxidation processes present hazards and generate large amounts of waste. Recent studies in our laboratories have shown previously that CO2-expanded liquids (CXLs) as a reaction media allow for tunable solubilities, transport properties and enhanced oxygen solubilities compared to traditional organic solvents. CXLs are thus versatile reaction media for catalytic oxidations that may be exploited to provide optimal safety, environmental and reaction benefits. Specific cobalt complexes are known to act as efficient oxygen carriers by allowing reversible oxygen binding. These oxygen carriers significantly enhance oxidation reactions that use oxygen, as the terminal oxidant. The O2 solubility in organic solvents is often the rate limiting factor. Hence CXLs, in which the O2 solubility is significantly enhanced, are suitable media to study oxygen carrier catalysts. In this work, we relate structural variations of cobalt oxygen carriers to their catalytic activity in the oxidation of a substituted phenol to a quinone, using experimental methods guided by both mechanistic as well as computational inputs. In our preliminary investigations aimed at optimizing catalytic activity, we probe into the influence of various axial ligands on activity for a specific family of Schiff base cobalt carriers. The effects of various ligands on conversion, selectivity and TONs are investigated. Remarkable correlation is noted between the predicted O2 binding energies and catalytic activity. Experimental results will be presented along with relevant computational/mechanistic data.