Designing Safer, Sustainable Fully Recyclable Homogeneous Catalysts Systems

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Homogeneous catalysis is a powerful tool in developing greener more sustainable synthetic chemistry. However, both catalyst recycling and the use of solvents because solvents are issues of concern. Solvents, for example, are an integral and major component of any homogeneous catalysis system. While we have a history of developing catalyst recycling with conventional solvents and polymeric catalysts, our more recent work has focused on exploring how we can recycle catalysts while at the same time using inexpensive safer, separable, and recyclable solvents. In this talk, I will focus on our work where we use polyolefin oligomers both as catalyst (or reagent) supports and as solvents. We believe we have shown in this work that low viscosity, commercially available poly(α-olefin)s (PAOs) - fractionated hydrocarbon mixtures with 20-48 carbons - have considerable potential as solvents in catalysis and in separation chemistry. These PAOs fulfill several criteria for green and sustainable chemistry. They are readily separable from polar solvent phases by a gravity separation. They are safer solvents. While they are presently petroleum derived, they could conceivably be derived from biosourced fatty acids. PAOs also serve as separation media, extracting trace pollutants from polar phases in systems where the PAO itself or PAO with additives serves as a recyclable, regenerable sequestering phase. Most importantly, PAO phases with PAO-soluble catalysts, reagents, and sequestrants can be quantitatively recycled multiple times in catalysis, synthesis, and separation chemistry without significant contamination of the isolated organic products or of a separable polar solvent phase. While PAOs have advantages, they of course have disadvantages too. First, they are more viscous than a low molecular weight solvent. Second, they are simply alkanes with the polarity and solubility properties of hexane or heptane. In some reactions, that is problematic. Fortunately, PAOs with as little as 1 M of a low molecular weight cosolvent or a PAO-anchored cosolvents exhibit microheterogeneity and such solvent mixtures have properties much like the pure cosolvent. This leads to cosolvent systems that are in effect polarized alkanes. This can facilitate catalysis and has the potential to lead to recyclable tunable organic solvent systems that employ ‘designed’ solvents.