CO_2-Responsive polymers and their use in catalysts

This seminar covers two unique applications of CO_2-responsive polymers covering both heterogeneous and homogeneous catalysis. CO_2-responsive materials have found use across a wide range of different applications including switchable solvents, polymers, and surfaces. These materials have tunable properties allowing for control over changes to charge, morphology, assembly, and hydrophilicity based on the addition of CO_2 into the system. Switching of these materials is typically achieved through the reversable acid-base reaction of a substituted organic tertiary amine and aqueous CO_2 (as carbonic acid) forming a bicarbonate salt. This reaction creates a transition from an uncharged and typically hydrophobic amine to a charged, hydrophilic ionic salt group. Using this switchability, CO_2-responsive polymers were applied in two ways: controlling the activity of heterogeneous catalysts and facilitating the recovery of homogeneous catalysts.

CO_2-responsive polymers were used in heterogeneous catalysis as the insoluble support for metal nanoparticles (NPs). It was demonstrated that the activity and selectivity of supported NPs used in hydrogenation reactions can selectively controlled by the addition of CO_2 into the system. Using CO_2-responsive polymer-grafted silica as the support for ruthenium NPs selective hydrogenation of carbonyl groups and bicyclic heterocycles was achieved. Rhodium and palladium NPs supported on CO_2-responsive gels showed similar but unique selective activity with the addition of CO_2 into the hydrogenation reaction.

In homogeneous catalysis, CO_2-responsive polymers were used to facilitate the recovery of a tethered catalytic ruthenium-phosphine complex post-reaction. To couple responsive polymers to an active catalytic center, a novel all-in-one ATRP radical initiator and ligand: “InnitPhos” was developed. This ligand when coordinated to a ruthenium metal center can catalyze its own functionalization through an ATRP reaction. This new polymer-tethered catalyst can then be taken and used in further hydrogenation reactions. Upon completion of the reaction the polymer catalyst can be recovered using CO_2-responsive selective solubility from aqueous solutions.