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## Polymer-Supported Rhodium Catalysts Soluble in sc-CO<sub>2</sub>

In organic syntheses utilising homogeneous catalysts, the catalysts are dissolved in a suitable solvent which also acts as the reaction medium. These solvents are often toxic organic liquids, so there is a growing need to replace them with environmentally benign solvents, such as water or supercritical carbon dioxide (sc-CO<sub>2</sub>). At present, the majority of organic syntheses are solvent-sensitive and most homogeneous catalysts are not soluble in either water or sc-CO<sub>2</sub>.

Separating and recovering the homogeneous catalysts at the end of the reaction is also a major problem. To overcome this, increasing attention is being directed at developing polymer-supported ligands for complexing with homogeneous metal catalysts for straightforward membrane separation.

Researchers at Texas A & M University, U.S.A., have now succeeded in developing a homogeneous catalyst that is soluble in sc-CO<sub>2</sub> solvent (Z. K. Lopez-Castillo, R. Flores, I. Kani, J. P. Fackler and A. Akgerman, *Ind. Eng. Chem. Res.*, 2002, 41, (13), 3075–3080). They did this by attaching a homogeneous rhodium (Rh) catalyst to the backbone of a fluoroacrylate copolymer.

The polymer was prepared by polymerisation of the monomer 1H,1H,2H,2H-heptadecafluorodecyl acrylate (zonyl TAN) and *N*-acrylosuccinimide (NASI); zonyl TAN increases the solubility in sc-CO<sub>2</sub> while NASI provides attachment sites for the catalyst. NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (DPPA) was then used to exchange the NASI groups in the polymer. Finally, this was reacted with [RhCl(COD)]<sub>2</sub> to obtain the sc-CO<sub>2</sub> soluble, polymer-supported Rh catalyst. As the polymer is a very large molecule it was easily separated by a membrane.

Catalyst hydrogenation activity was evaluated using 1-octene and cyclohexene at different molar ratios of substrate:Rh and different temperatures. Most reactions were performed at 173.4 bar pressure for 12 hours. Conversion of 1-octene to *n*-octane was nearly 100%. Conversion of cyclohexene increased with temperature: at 368 and 393 K, the maximum conversions were 39 and 51%, respectively. For this hydrogenation, the catalyst was Rh(TAN)<sub>15</sub>(DPPA)Cl with a Rh dimer:polymer ratio of 1:3 and a Rh content of 1.95 mg of Rh/g of catalyst. The synthesis route for this Rh-polymer catalyst is reproducible.