Ruthenium-catalyzed homogeneous hydrogenolysis of esters to alcohols

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This thesis describes the research executed within the IOP-catalysis project IKA 97001 entitled “The development of industrially applicable catalysts for the homogeneous hydrogenolysis of esters and aminoesters to the corresponding alcohols”. The project was initiated out of the desire to develop an improved and environmentally benign catalyst for this conversion, because currently employed (heterogeneous) systems sometimes suffer from over-reduction of the substrate and depend on the use of environmentally unfriendly supported metal catalysts, e.g. those based on copper and chromium.

Since many hydrogenations are effectively catalyzed by ruthenium compounds in homogeneous solution, our research within the IOP project has been directed to compounds based on this metal and a number of mono- di-, tri- and tetradeutate phosphine ligands as the activating and stabilizing ligands. As a result, suitable ruthenium catalysts were obtained that enable the hydrogenolysis of esters to alcohols in good to excellent yields and high turnover frequencies using mild conditions. The catalysts presented are applicable under mild reaction conditions (e.g. relatively low temperatures (120 °C) and low hydrogen pressures (80-100 bar), in contrast to the catalytic systems known, which often require much higher temperatures and pressures. The ruthenium catalysts employed were either prepared in situ from ruthenium(III) precursors such as Ru(acac)_3, or well-defined precursors such as the complexes [Ru(acac)_2(κ²-triphos)] and [(triphos)Ru(μ-Cl)_3Ru(triphos)]Cl) were synthesized and used. The most active catalysts contained the facially coordinating tripodal phosphine ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) that proved to be essential for the catalysts to work properly. The hydrogenolysis was carried out in classic organic solvents under hydrogen pressure. But polar, protic solvents, preferably polar alcohols, were found to be the solvents of choice for the desired hydrogenolysis. Full conversion of benzyl benzoate, one of the benchmark substrates, could be obtained with over 99.5 % selectivity to benzyl alcohol with turn-over-
Homogeneous Ruthenium-catalyzed Hydrogenolysis of Esters

numbers of up to 2500 and turn-over-frequencies up to 140 per hour in 1,1,1,3,3,3-hexafluoro-2-propanol.

The new catalyst system has proven its capabilities in the hydrogenolysis of a wide range of esters. Activated esters as well as non-activated esters are cleanly and smoothly converted into the corresponding alcohols. The catalyst can also be applied in the hydrogenation of alkenes, aldehydes, ketones and nitriles, which are all reduced in excellent yields and selectivities and at good rates.

Despite its success on laboratory scale, the catalyst is not yet interesting for industrial application; a major restriction being that industrially required rates (space-time constraints) should involve the need to operate in polar solvents such as the expensive and toxic 1,1,1,3,3,3-hexafloro-2-propanol.