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Liquid Phase Polymer-based Catalysis for Stereo- and Regio-selective Hydrogenation

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The preparation and operation cycle of new homogeneous catalyst systems based on linear polymers (liquid phase catalysis, LPC) for ligand-directed regio- and stereo-selective hydrogenations are described.

The immobilisation of homogeneous catalysts on crosslinked functionalised polymers to give 'heterogenized homogeneous catalysts' has afforded catalyst systems whose disadvantages include diffusion-controlled mass transfer, non-uniform reaction rates, and difficult functionalization. This has led us to suggest the binding of catalytic groups to linear, non crosslinked, soluble polymers.^{1,2} The separation of such soluble polymer catalysts from low molecular weight products is readily performed using differences in physical properties. Ultrafiltration of low from high molecular weight compounds is now widely accepted and other techniques, e.g. precipitation, extraction, can also be used for standardized separation. Recently liquid phase metal retention (LPM) has been introduced for the separation and enrichment of metals in homogeneous solution by selective binding to chelating polymers, followed by ultrafiltration.^{3,4} In the course of this work, a variety of linear, soluble polychelatogens became available^{5,6} and catalytically active groups have been incorporated into these polymers, yielding new catalysts for liquid phase catalysis (LPC).

In order to maintain a strictly linear polymer structure and avoid crosslinking during functionalization and complex formation, polymer backbones which are more stable towards crosslinking have been chosen and only *ca*. 5-20% of the available functional groups of the polymer are used for chelating. A smaller loading is also favourable for site isolation of the catalytically active centres in the polymer. Investigations have also revealed that it is advantageous not to use very strong complexing groups in the polychelatogens to achieve high activities. Ligand exchange during the catalytic process is faster if the stability constants are smaller, and it can be visualized that mass transfer in the polymer coil also



Figure 1. Working cycle of liquid phase polymer-based hydrogenation and catalyst preparation.

becomes faster with both decreasing ligand strength and loading of the active centre. The co-ordination of the metal to the polychelatogen does not result in a fixed position of a certain active centre to a certain ligand. Moreover a steady ligand exchange occurs in the polymer. As long as all chelating groups in a polyfunctional polymer are completely equal, an active centre can statistically be present in any position in the polymer coil, including those positions where an uptake of substrate and a release of product is favourable. The polymeric metal catalysts can be prepared by liquid exchange or by substitution and active site isolation achieved by binding additionally spacious low molecular weight ligands. The possible variation of polymers, metal atoms, and low molecular weight ligands has enabled a large number of catalysts to be synthesised and tailored to specific types of catalysis. We now report examples of this for several hydrogenation reactions which pose more or less severe problems with known catalysts.

Several catalyst systems and their possible application are given in Table 1. Soluble polychelatogens preferentially used are poly(vinylpyrrolidinone), poly(ethyleneimine), poly-(acrylonitrile), poly(ethyleneiminodiacetic acid). The choice of the basic polymer is dependent upon the required solubility and activity. To these polychelatogens, metal ions are chelated with or without additional ligands. If no special selectivity is necessary, low molecular weight ligands are omitted as with LPC systems 1 and 2 in Table 1, which are general purpose catalysts for hydrogenation of aromatics and double bonds respectively. Even for standard hydrogenations of double bonds, these LPC systems are superior to presently used heterogeneous hydrogenation catalysts considering their



Figure 2. Hydrogenation and ultrafiltration cell: 1, membrane; 2, filtrate; 3, low molecular weight products and starting material; 4, polymeric catalyst (retentate); 5, gas burette; 6, three way valve; 7 and 8, magnetic stirrer; 9, stopcock (closed during hydrogenation reaction); 10, filling tube.

fast turn-over. In addition, repeated recycling of the catalysts is possible without loss of activity. A preactivation of the catalyst is only necessary before the first hydrogenation, and the activated form can be stored. Steering by ligands now enables certain hydrogenation problems to be solved as demonstrated by the following examples.

Since the introduction of the partial hydrogenation of fats and oils by Norman,⁷ a ubiquitous problem has been the avoidance of *cis-trans* isomerisation, double-bond migration, and, in many cases, production of saturated fatty acids. An LPC system has been used in the partial hydrogenation of soya-bean oil. 10 ml 1% aqueous solution of Pd catalyst 3 (Table 1) is activated under H_2 . The solution is stirred vigorously at 60 °C and 50 g of soya oil, prewarmed to 60 °C, is added. 1 I H_2 is consumed within 13 min at normal pressure, after which the solution is cooled. The oil separates from the aqueous solution of catalyst which can be reused without further reactivation. The composition of the starting material is then compared with that of the hydrogenated oil (% fatty acid in the latter given in parentheses): palmitic acid 12% (12), stearic 4 (5), oleic 24 (36), linoleic 53 (46), linolenic 7 (1). High stereospecificity is found (97% cis), and the formation of saturated fatty acids (e.g. stearic acid) is negligible. The low concentration of catalyst with respect to the metal atom, the short reaction time, and the mild reaction conditions are noteworthy. The metal concentration lies in the p.p.m. range: 1 g Pd is sufficient for the hydrogenation of 100 kg oil or fat.

The selective hydrogenation of alkynes to alkenes without further reaction to alkanes is still a preparative problem, in particular if stereoselective hydrogenation of internal triple bonds to *cis*- or *trans*-alkenes is desired. The Lindlar catalysts widely employed for this reaction are relatively slow, and often gave unsatisfactory yields and selectivity.^{8,9} In LPC stereoselectivity can be steered either to *cis*- or *trans*-alkenes, and fast hydrogenation is achieved at room temperature and normal pressure.

Catalyst† 1	Polychelatogen Poly(vinylpyrrolidinone)	Low molecular weight ligand —	Central metal atom Rh	% Metal/ polymer 5	Application Hydrogenation of aromatics and heteroaromatics; cyclohexanone from phenol. Sugar alcohols from sugars.
2	Poly(vinylpyrrolidinone)	_	Pd or Pt	1	General purpose hydrogenation catalyst for double bonds, nitro groups, nitriles, benzyl protective groups, C=N bonds.
3	Poly(vinylpyrrolidinone)	Alanine	Pd	0.5	Partial hydrogenation of fats and fatty acids.
4	Poly(ethyleneimine)	_	Pd	1	Internal alkynes to cis-alkenes.
5	Poly(ethyleneimine)	Benzonitrile	Pd	1	Internal alkynes to trans-alkenes.
6	Poly(ethyleneimine)	Alanine	Ni	2	Alkynes to cis-alkenes.

Table 1.	Catalyst systems	based on p	polychelatogens	for various	hydrogenations.
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Using the preactivated catalyst 4 (Table 1), pent-2-yne can be hydrogenated (20 °C, 1 bar) in ca. 40 min in 98% stereoselectivity to cis-pent-2-ene. Recycling of the catalyst after separation from products is possible without loss in rate of reaction. The molar ratio of chelated palladium to alkyne is 10^{-4} . With Lindlar catalysts, the concentration of the noble metal catalyst required is two orders of magnitude higher.8 A dramatic change in the stereoselectivity occurs, however, if a spacious low molecular weight ligand such as benzonitrile is bound to the Pd catalyst (5, Table 1). In this case 100% trans-pent-2-ene is formed, and neither cis-alkene nor further hydrogenation to pentane is observed. Nickel catalysts (6, Table 1) can also be used and recycled for stereoselective hydrogenation of alkynes to alkenes. The extremely high activity of the polymer-bound nickel (molar ratio nickel: alkyne 10^{-4}) is remarkable in comparison with e.g. Raney nickel. Despite the high activity and hence dispersion of the nickel, the shielding of the metal by the polymer leads to high stability even in preactivated form, which is neither deactivated nor inflammable even on standing in air. Recycling without loss of activity or loss of the alanine ligands demonstrates the dispersion of the nickel in the Ni⁰ state.

In the hydrogenation of aromatic compounds such as phenols to give cyclohexanones, the latter are usually obtained by hydrogenation followed by oxidation of the resulting cyclohexanols to give the ketones, since the yields of the direct hydrogenation are poor.¹⁰ Employment of the Rh catalyst 1 allows the direct hydrogenation of phenol to give cyclohexanone in almost 90% yield at 20 °C and atmospheric pressure. A noteworthy aspect of the reaction is the decrease in the rate of hydrogenation of the third double bond of the benzene ring, apparently as a result of stabilisation of the tautomeric intermediary cyclohexenol by hydrogen-bonding to the polymer and complexation with rhodium.

Together with the highly active Ziegler–Natta catalysts, this new class of homogeneous polymeric catalyst belongs to the most reactive synthetic group of catalysts known, with activities (reacted substrate molecules/metal atom/min) at 25 °C approaching those typical of slow enzymes: catalyst 3 (Table 1) in the hydrogenation of linoleic acid to give oleic acid, 12 000; chymotrypsin, 6 000; ¹¹ catalase, 4 800 000; HCo in the hydroformylation of propene, 1.44×10^{-4} ;¹¹ catalyst (C₅H₅)₂TiMe₂/AlMe₃/H₂O in the Ziegler polymerisation of ethene 24 000.¹² Their reactivities are orders of magnitude greater than many classical heterogeneous catalysts, *e.g.* Pd on active carbon has an activity of 1 at 25 °C in the hydrogenation of cinnamic acid to give phenylpropionic acid.¹³ These homogeneous polymeric catalysts are thus of interest for all types of hydrogenation owing to the milder reaction conditions required, lower consumption of noble metals, and their direct reusability without the need for regeneration or loss of activity.

Figure 1 shows the catalyst preparation and reaction sequence in the hydrogenation of linolenic to linoleic acid ester. Special care is required during preactivation, which should not be done in the presence of substrate. The high activity and the stoicheiometric bonding of low molecular weight ligands indicate monomeric or dimeric active centres.

Two standard techniques for the use of these catalysts in the laboratory have proved especially suitable: (i) ultrafiltration to separate catalyst from products in homogeneous solution. The products, together with unreacted starting material if still present, pass through the membrane, whereas the polymeric catalyst is retained and can be reused. Since these liquid phase hydrogenations were performed under atmospheric pressure, the reaction and subsequent ultrafiltration were carried out in the ultrafiltration cell[†] shown in Figure 2 equipped with a burette to observe the hydrogen uptake. The solvent feed and drain were kept closed during the hydrogenation. After completion of the reaction, hydrogen was displaced by nitrogen for diafiltration. (ii) The emulsion method is a technique for functionalised water-soluble polymers such as poly(oxypoly(vinylpyrrolidinone), poly(vinylalcohol), ethylene), or poly(ethylenimine) which are used in aqueous solution. The substrate is added in a water-immiscible solvent, and the mixture stirred vigorously. Compared with hydrogenation in homogeneous solution, the reaction times are 30-50% longer, an acceptable value considering the extremely high activity of these catalysts. After completion of the reaction, the phases are allowed to separate and the aqueous catalyst solution can generally be reused directly. The fast hydrogenation rates also enable a continuous process,

[†] Ultrafiltration cells and catalysts were obtained from Chemische Fabrik Heyl, D-1000 Berlin 37, Goerzallee 253.

where the two immiscible phases move in a counter current mode.

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