

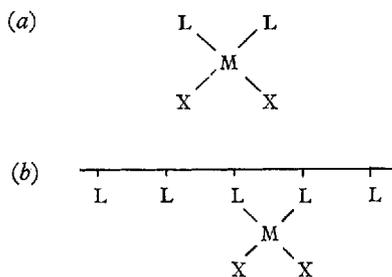
# Homogeneous Catalysis with Macromolecular Ligands

By J. Manassen

Weizmann Institute of Science, Rehovot, Israel

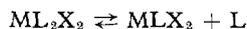
Homogeneous and heterogeneous catalysis have hitherto been regarded and treated as separate, although related aspects of the whole field of catalysis. The boundary between them, previously thought to be well defined, is now becoming blurred as a result of research carried out on the behaviour of ligands in selected systems.

In a conventional homogeneous catalyst a metal ion is surrounded by ligands (a); it is possible, however, to replace some ligands by a polymeric chain carrying the same functional group (b).



Such complexes, where the simple ligand is wholly or partially replaced by a polymeric ligand, can show important advantages over conventional homogeneous systems in certain systems. First, they are generally insoluble in the reaction medium and if their catalytic activity has been preserved the homogeneous catalyst has been converted into a heterogeneous catalyst. This enables conventional technology to be employed with catalysts having the high selectivity of homogeneous catalysts. Some possible applications have been recently described (1). Secondly, an advantageous change in catalytic activity may

be observed. This may result from certain preferred conformations of the polymeric chain in solution, a changed stereochemistry around the metal ion imposed by the chain, or by simple steric crowding. It is known, for example, that the activity of many homogeneous catalysts depends on dissociation taking place in solution:



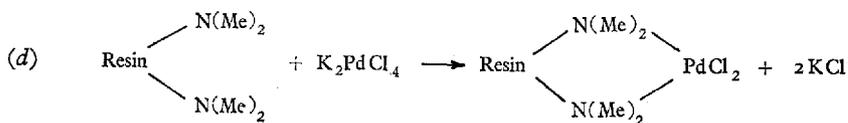
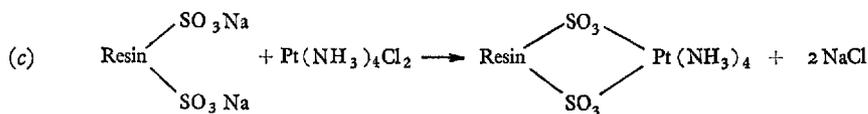
If the ligand molecules L are part of a polymeric chain the dissociation equilibrium, and consequently the catalytic activity, will be affected. The possibilities opened up by this approach have only recently started to be explored.

The easiest way to render a metal salt insoluble is to bind it to an ion exchange resin. This may be achieved either by an ionic linkage where the anion of the salt is reacted with that of the resin (c) or by a coordinative linkage as in (d).

The accompanying table illustrates reactions that have been catalysed by resin-bound platinum metal salts. In all except the last example commercially available or modified ion exchange resins were used. The poly-(p-diphenyl phosphine)styrene employed in the hydroformylation reactions using rhodium and ruthenium chloride, however, was specially synthesised and polymerised (3).

## Change of Catalytic Activity by a Polymeric Ligand

If a linear polymer of p-diphenylphosphinostyrene or its copolymer with styrene is reacted in dimethylacetamide solution with certain rhodium compounds a soluble rho-



dium-polymer complex can be obtained that is an excellent hydrogenation catalyst, giving higher rates than tris(triphenylphosphine) rhodium chloride under the same conditions. For example, the hydrogenation of camphene results in the formation of a mixture of endo- and exo-isocamphanes. The isomer distribution has been found to vary according to the nature of the ligand (monomeric triphenylphosphine, a copolymer of p-diphenylphosphinostyrene or its homopolymer). Effects are small, however, and experiments

are proceeding in our laboratory to investigate this effect in greater detail.

The field of polymeric ligands is still in its infancy but it is clear, however, that by the use of polymers a new dimension can be added in the search for ligand effects in catalysts.

#### References

- 1 W. O. Haag and D. D. Whitehurst, *Belgian Patent* 721, 686
- 2 P. Legzdins, G. L. Rempel, and G. Wilkinson, *Chem. Commun.*, 1969, 825
- 3 J. Manassen, *Israeli Patent Appl.* 30505

Reactions Catalysed by Resin-bound Platinum Metal Salts			
Reaction	Metal salt	Resin	Ref.
Carbonylation	$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	Amberlyst 15	1
"	$\text{K}_2\text{PdCl}_4$	Amberlyst A21	1
"	bis(benzonitrile)-dichloropalladium(II)	Chloromethylated polystyrene resin reacted with chlorodiphenylphosphine	1
"	Rh or Ru acetate in $\text{HBF}_4$ -phosphine	Not specified	2
Hydrogenation	"	"	2
"	bis(benzonitrile)-dichloropalladium(II)	Amberlyst 15	1
"	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	Amberlyst A21	1
Double bond shift	"	"	1
Transesterification	$\text{K}_2\text{PdCl}_4$	"	1
Vinyl acetate synthesis	"	"	1
Hydroformylation	tristriphenyl rhodium(I) chloride	Chloromethylated polystyrene resin reacted with chlorodiphenylphosphine	1
"	hexachlororhodate(III)	Jonac XaX-1393	1
"	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	Amberlyst A21	1
"	Rh or Ru chloride	Poly-(p-diphenylphosphino)styrene	3