

Preliminary communication

**POLY(METHALLYL ALCOHOL)-SUPPORTED RHODIUM
HYDROGENATION CATALYSTS**

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Summary

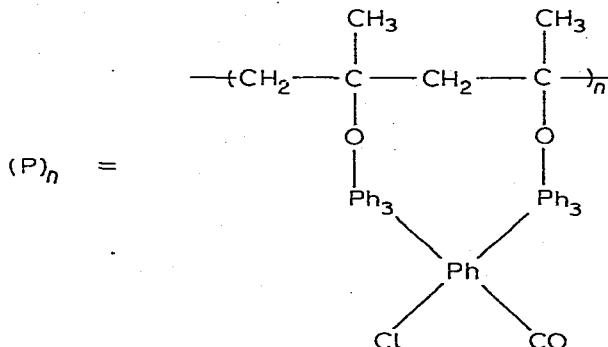
A polyphosphite obtained from poly(methallyl alcohol), when treated with rhodium(I) derivatives, affords soluble and insoluble complexes, some of which are hydrogenation catalysts for olefins in toluene suspension.

There is much current interest in the problem of "heterogenizing" homogeneous catalysts [1,2]. A number of workers have approached this goal by chemical modification of polystyrene-based polymers to produce polymeric phosphines which in turn were used to form insoluble complexes of, for example, rhodium(I) [3-10]. It has been established that the polymer can play an important part in modifying the activity of the catalyst [3,9,10] and with this in mind we have initiated a programme to study a variety of polymer back-bones as supports. In this communication we describe some results using poly(methallyl alcohol) which is readily available from poly(methyl methacrylate).

Atactic poly(methallyl alcohol) reacts with chlorodiphenylphosphine in THF in the presence of pyridine to give the polyphosphite $(P)_n$ which is soluble in most solvents. $(P)_n$ interacts with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in THF to give a yellow precipitate of formula $(P)_n[\text{Rh}(\text{CO})\text{Cl}]_{n/2}$ (I). A second soluble complex II of identical formula can be isolated from the filtrate. When I is suspended in toluene containing octene-1 in contact with H_2 , the complex becomes darker and after an induction period hydrogenation of the olefin proceeds at 25°C ($0.04 \text{ mmol min}^{-1}$ of H_2 using 0.2 mol l^{-1} octene-1 in toluene (3 ml) and 0.1 meq. of I).

Both H_2 and olefin are necessary for the conditioning process; once

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this has been completed, the catalyst can be used repeatedly and reproducibly without loss of activity. Microanalysis of the conditioned polymer for C, H, and Cl shows the stoichiometry to be unaltered (We have not yet checked for the presence of rhodium(II) [3]).

The uptake of H₂ by octene is linear with time until about 70% completion. Hexene-1 is reduced about 3 times as fast as hexene-2, and 20 times as fast as cyclooctene. Unfortunately, the absolute rates cannot be reproduced using fresh samples of I. Compound II is a less active catalyst under the same conditions. Presumably, I and II differ in the amount of cross-linking. The polymeric alcohol produced from syndiotactic poly(methyl methacrylate) does not yield an active analogue of I.

When (P)_n is treated with [NBDRhCl]₂ in THF solution (2:1 molar ratio) a yellow-orange precipitate is obtained. This turns dark brown in toluene suspension in contact with H₂ and the resulting compound III is a very active catalyst for the hydrogenation of a variety of terminal olefins at an essentially uniform rate (e.g. octene-1 and styrene (0.173 mol l⁻¹) in toluene (3 ml) are hydrogenated at rates of 0.282 and 0.228 mmol min⁻¹ respectively in the presence of a standard amount of III) but the rates for hexene-2 and cyclooctene are lower by a factor of 20. The rate of hydrogenation of octene-1 is linearly dependent on catalyst "concentration" in the range 0.23 and 0.0024 eq. l⁻¹ of catalyst using 0.125 mol l⁻¹ olefin solutions; the rate is proportional to [olefin]^{1/2} up to a concentration of 0.3 mol l⁻¹.

The reaction of (P)_n with norbornadienerhodium acetic acid followed by HClO₄, or with [(cyclooctene)₂RhCl]₂ in THF solution gives precipitates which are not hydrogenation catalysts.

These studies raise interesting questions regarding the nature of the catalytic species. We are also concerned with the effects of polymer tacticity and molecular weight on the selectivity of the catalyzed reactions. It is worth noting that analogues of I obtained from phosphites (C₆H₅)₂POR with bulky R groups are not hydrogenation catalysts.

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