JOURNAL OF CATALYSIS 43, 322–330 (1976)

Supported Transition Metal Complexes

IV. Rhodium Catalysts for the Liquid Phase Hydroformylation of Hexene-1

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Received October 14, 1975; revised February 6, 1976

Rhodium complexes have been chemically linked to organic polymers via oxygen and phosphorus ligands, and to silica via nitrogen, oxygen, phosphorus and sulfur ligands. These macromolecular complexes catalyze the liquid phase hydroformylation of hexene-1 at 80–150°C and 42 atm carbon monoxide–hydrogen (1:1) in batch and flow tests.

A species of the type $RhH(CO)(PR_3)_3$ chemically linked to silica showed no loss of activity and no detectable loss of rhodium when tested for 75 hr under continuous flow conditions.

INTRODUCTION

The hydroformylation or "Oxo" reaction involves the conversion of an olefin into an aldehyde or an alcohol by reaction with carbon monoxide and hydrogen in the presence of a suitable catalyst. The discovery by Slaugh and Mullineaux (*1, 2*) that rhodium complexes containing tertiary phosphine and carbon monoxide ligands were particularly adept for this reaction established a new class of hydroformylation catalysts that functioned under milder conditions than the previously employed simple carbonyl derivatives of cobalt. Since this initial discovery, the hydroformylation of olefins by coordination complexes of rhodium containing a variety of ligands such as phosphines, phosphites, β-diketones, amines, in addition to carbon monoxide has been extensively studied (*3*).

As in the case of hydroformylation catalyzed by cobalt complexes, virtually all the studies have been performed using homogeneous liquid phase systems. Although the use of soluble transition metal complexes often gives rise to highly active and selective catalysts, their use in commercial processes may result in certain operational problems. Catalyst recovery and corrosion of equipment are two such problems, the former being of particular importance when expensive metal complexes are employed. The use of a heterogeneous catalyst would largely overcome these difficulties.

Haag and Whitehurst (*4*) recently reported a new class of heterogeneous catalysts that combine the high activity and product selectivity associated with soluble catalysts, yet maintain the advantages associated with the use of a heterogeneous catalyst. These catalysts were derived from transition metal species and macromolecular support materials containing liganding groups in an analogous manner to the formation of metal complexes by ligands in solution.

In this paper we report on the results of our investigations on the use of rhodium complexes chemically bonded to organic polymers via oxygen and phosphorus ligands, and to silica via nitrogen, oxygen, phosphorus and sulfur ligands for the liquid phase hydroformylation of hexene-1.

METHODS

1. Support Materials

The preparation and characterization of organic polymers and silica functionalized with nitrogen, oxygen, phosphorus and sulfur ligands has previously been reported (*5*, *6*).

2. Catalysts

The catalysts were prepared according to previously described procedures (*5*, *6*).

3. Reagents

Hexene-1 (ex Phillips Petroleum) was purified by percolation through activated silica gel followed by distillation from sodium wire under an atmosphere of dry deoxygenated nitrogen, and stored under dry nitrogen. Solvents were redistilled and subsequently dried either by sodium wire or activated 13X molecular sieve. Carbon monoxide–hydrogen mixture (1:1) (ex British Oxygen) was used as received except in specific instances when the gas mixture was deoxygenated by manganous oxide. (The average oxygen content of the carbon monoxide–hydrogen mixture as received was 20–30 ppm.)

4. Apparatus and Procedures

Batch tests were performed in stainless steel autoclaves of 500 ml capacity. In tests without the total exclusion of oxygen, catalyst, olefin and solvent were charged to the autoclave in the atmosphere and subsequently "degassed" with carbon monoxide–hydrogen. Under a positive carbon monoxide–hydrogen pressure the temperature was raised to that required and further carbon monoxide–hydrogen was added to produce the desired total pressure, and the reaction commenced. In tests where oxygen was excluded the catalyst was charged to the autoclave in a sealed ampoule containing a nitrogen atmosphere, while the olefin and solvent were charged with the minimum exposure to the atmosphere. After careful "degassing" with oxygen-free carbon monoxide–hydrogen, the ampoule was shattered either by agitation or pressure, and the heating commenced.

A single pass trickle flow reactor was used to assess catalytic activity under continuous flow conditions. Facilities were available for loading the catalyst under dry, deoxygenated nitrogen, while both the liquid and gaseous feedstocks could be deoxygenated if required. The liquid and gaseous feeds were blended at the top of the reactor and allowed to pass over the fixed catalyst bed at controlled flow rates. Separation of the liquid and gaseous products was achieved by a series of product receivers which also enabled samples to be removed for analysis.

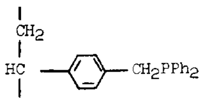
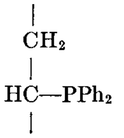
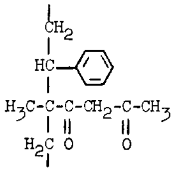
Liquid products were analyzed using a Perkin-Elmer 452 gas–liquid chromatograph with thermistor detectors. A 12 ft column of 25% dimethyl sulfolane/5% dinonyl phthalate on chromosorb W was used to determine hexane/hexenes concentration, while oxygenated products were analyzed using an 8 ft column of Apiezon L supported on Chromosorb W. The rhodium content of product solutions was determined by X-ray fluorescence spectrometry. The lower limit of rhodium detection using this technique was 2 ppm; however, the rhodium content of products found to contain less than 2 ppm was determined by evaporating a known volume of product to a known small bulk.

RESULTS

The hydroformylation activity and product distribution were examined with respect to the nature of the ligand bonding the rhodium center to the macromolecular support. The factors affecting the loss of

TABLE 1

Surface Groups Expected to be Present on Functionalized Organic Polymers

Polymer	Surface group expected to be present	Origin
A		Cross-linked chloromethylated polystyrene beads and potassium diphenyl phosphide
B	 $-CH_2-HC(PPh_2)-$	Polyvinyl chloride and potassium diphenyl phosphide
C		Copolymer of styrene and methacroyl acetone

rhodium from the support in continuous flow operations using a fixed bed of catalyst were also investigated.

1. RHODIUM COMPLEXES CHEMICALLY LINKED TO ORGANIC POLYMERS

Table 1 illustrates the surface groups expected to be present on the functionalized organic polymers used to produce heterogeneous rhodium hydroformylation catalysts.

Macromolecular rhodium complexes of polymers A and B were prepared by reaction with $Rh(acac)(CO)_2$ and that of polymer C by reaction with $[Rh(C_2H_5CO_2)(CO)_2]_2$. In batch autoclave tests all were active for the hydroformylation of hexene-1 at 80–90°C and 42 atm carbon monoxide–hydrogen (1:1). The only other products detected apart from heptaldehydes were isomeric hexenes resulting from the isomerization of the

TABLE 2

Hydroformylation of Hexene-1 by Rhodium Complexes Chemically Linked to Organic Polymers[a]

Polymer type[b]	Rhodium content (% wt)	[Rh] ($\times 10^{-5}$ g atoms)	[Hexene-1] (mol)	Hexene-1 conversion (% wt)	Heptaldehydes yield (% wt)	Normal:iso heptaldehydes ratio	Rhodium in products (ppm)
A	2.2	10.1	1.00	58	40	2.5:1	8
A[c]	2.2	13.2	1.00	60	42	2.5:1	<2
B	7.3	35.4	0.24	87	86	1.5:1	98
B	7.3	15.6	0.81	43	43	2.5:1	30
C	2.3	4.4	0.81	98	93	0.8:1	12
C + n-Bu_3P	1.1	5.3	0.81	77	76	2.3:1	21

[a] Reaction time (hr): 4; temp. (°C): 80–90; pressure (atm): 42 CO/H_2 (1:1); solvent: *n*-heptane.

[b] Phosphorus content of polymer type A (% wt): 2.0; phosphorus content of polymer type B (% wt): 4.8.

[c] Test performed under oxygen-free conditions.

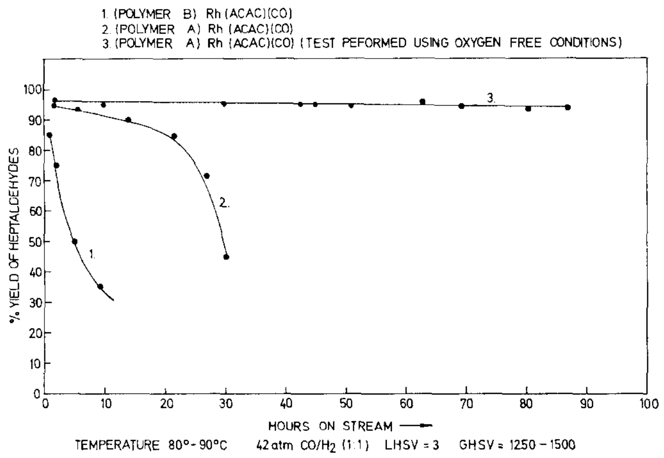


FIG. 1. Continuous flow liquid phase hydroformylation of hexene-1 by rhodium species linked to organic polymers.

hexene-1 feed. The results are summarized in Table 2.

An indication that trace quantities of oxygen in the reaction mixture facilitated the loss of rhodium from the support was shown by the results produced by the catalyst based on polymer A. Although the rhodium concentration, rate of reaction and product distribution are of the same order, there is a distinct difference in the rhodium content of the products. Exclusion of oxygen lowered the rhodium concentration in the products from 8 ppm to below the limit of detectability (2 ppm).

Homogeneous hydroformylation using simple carbonyl derivatives of rhodium has been found to produce a lower normal: isoaldehydes ratio than with complexes containing tertiary phosphine ligands in addition to carbon monoxide coordinated to the metal center (7). A similar observation was made when the heterogeneous catalyst based on polymer C was tested, a normal:isoheptaldehydes ratio of 0.8:1 being produced. However, when this catalyst was treated with tri-*n*-butyl phosphine a normal:isoheptaldehydes ratio of 2.3:1 was obtained under the same experimental conditions.

Continuous flow pilot plant tests were performed using catalysts based on polymers A and B. A comparison of heptaldehyde yields is given in Fig. 1.

A liquid feed of hexene-1 in *n*-heptane (1:2 v/v) and a gaseous feed of carbon monoxide–hydrogen (1:1) were used throughout the tests. Conditions were standardized at 80–90°C and 42 atm carbon monoxide–hydrogen (1:1) with a total liquid hourly space velocity of 3 and a gas hourly space velocity of 1250–1500.

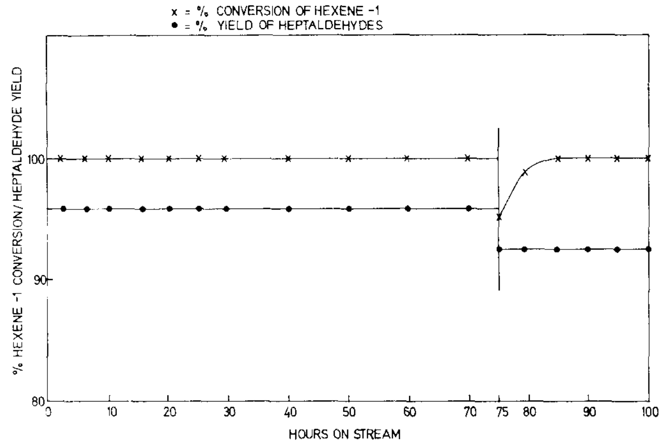
A catalyst based on polymer B and containing 7.3% wt rhodium was tested under conditions where no precautions were taken to exclude oxygen from the gaseous feed, but the liquid feed was deoxygenated prior to use. For this test the catalyst (2 ml) was dispersed in silica to give a total volume of 25 ml. The dispersion of the catalyst in silica was a precaution against the possibility of polymer swelling to such a degree that a blockage in the reactor would result. (Previous evidence suggested that polymer B based catalysts were prone to swelling when contacted with liquid hydrocarbons for long periods.) During the 9 hr on stream the hexene-1 conversion fell from 86 to 36% wt, and yield of heptaldehydes fell from 85 to 35% wt. The normal:isoheptaldehydes ratio remained constant at 2.0:1 as did the selectivity to aldehydes at 99%, the only other products detected being isomeric hexenes. The steady decline in hexene-1 conversion was related to the high loss of rhodium from the reactor, up to 78 ppm being detected in product samples. Solubility tests showed that this catalyst, although insoluble in the hydrocarbon feedstock, had a significant solubility in heptaldehydes which was facilitating the loss of the catalyst from the reactor. However, the use of the analogous rhodium species chemically bonded to polymer A, which was found to be insoluble in both reactants and products, showed that there were further mechanisms by which rhodium was lost from the macromolecular support. A test on this catalyst performed under similar conditions to that previously described for the polymer B based catalyst, was continued for 34 hr on stream. The catalyst (25 ml) containing 2.2% wt rhodium, initially showed 99% hexene-1 conversion with greater than a 90% yield of heptaldehydes. However, up to 90 ppm of rhodium was detected in the products and consequently, as the total quantity of eluted rhodium increased, the hexene-1 conversion fell to 72% wt and the yield of heptaldehydes fell to 45% wt by the end of the test. The normal:isoheptaldehydes ratio was within the range 2.2 to 2.5:1 for the total duration of the test and no products other than isomeric hexenes were detected.

Since autoclave tests had indicated that the presence of traces of oxygen may be promoting the elution of rhodium, the test using the polymer A based catalyst was repeated under oxygen-free conditions. In this test, performed for 87 hr on stream, a consistently high conversion of hexene-1 (>97% wt) was recorded. The yield of heptaldehydes remained greater than 90% wt, the only other products detected being isomeric hexenes. The normal:isoheptaldehydes ratio was constant at 2.2:1. The rhodium content of the products rapidly fell to 1 ppm and remained below this value for the duration of the test. It was also shown that rhodium losses to the products could be reduced still further by incorporating a bed of polymer A beneath the catalyst. The tertiary phosphine groups on the polymer coordinated to the solubilized rhodium in the product stream, thereby removing it from solution.

Factors Influencing the Dissociation of the Rhodium–Phosphorus Bond

Autoclave and pilot plant studies had shown that oxygen in the reaction mixture resulted in cleavage of the rhodium–phosphorus bond and the subsequent loss of rhodium to the products. The effects of deoxygenated reagents and products were also examined in short (10 hr on stream) pilot plant tests using the catalyst based on polymer A. The catalyst (20 ml) containing 2.2% wt rhodium was charged to the reactor under an atmosphere of dry, deoxygenated nitrogen. Conditions were standardized at 80–85°C and 42 atm pressure. Initially, with dry, deoxygenated *n*-heptane as the liquid feed, three tests were performed using pure carbon monoxide, pure hydrogen and a carbon monoxide–hydrogen mixture (1:1). In no case was rhodium detected in the liquid eluate. A further test using redistilled, deoxygenated *n*-heptaldehyde in *n*-heptane (1:2 v/v) as the liquid feed and carbon monoxide–hydrogen (1:1) as the gaseous feed did yield a small amount of rhodium (7 ppm) in the liquid eluate.

The desirability of excluding oxygen from the reaction mixture was further shown in a test in which the catalyst was oxidized in air for 6.5 hr at 85°C and 42 atm using *n*-heptane as the liquid phase. During this oxidation stage, less than 2 ppm of rhodium was detected in the eluate. However, on changing the gas to carbon monoxide–hydrogen (1:1), rhodium elution increased to 8 ppm. When the *n*-heptane was replaced by hexene-1 in *n*-heptane (1:2 v/v), rhodium elution increased further to 30 ppm. During the 9 hr



TEMPERATURE 100 - 120 °C 43 atm CO/H_2 (1:1)
LHSV = 3 (0-75 HOURS ON STREAM), LHSV = 6 (75-100 HOURS ON STREAM)

FIG. 2. Continuous flow liquid phase hydroformylation of hexene-1 using the complex RhH(CO)-$[Ph_2PCH_2CH_2Si(OEt)_3]_3$ linked to silica.

of this final stage of the test, the hexene-1 conversion fell from 75 to 24% wt. The yield of heptaldehydes fell from 56 to 18% wt, and, as in all the previous hydroformylation tests using this catalyst, the only other products detected were isomeric hexenes. The recovered catalyst which had changed color from yellow to blue had a metallic luster and contained only 0.5% wt rhodium.

2. RHODIUM COMPLEXES CHEMICALLY LINKED TO SILICA

The preparation of rhodium complexes chemically linked to silica via nitrogen, oxygen, phosphorus and sulfur ligands has been reported previously (*6*).

a. Rhodium Complexes Chemically Linked to Silica via Phosphorus Ligands

Results of autoclave studies using rhodium complexes chemically linked to silica via the phosphorus ligand–silane $(EtO)_3SiCH_2CH_2PPh_2$ have previously been reported (*8*). These results showed that the best species for combining high activity with low rhodium elution was the complex

$$RhH(CO)[Ph_2PCH_2CH_2Si(OEt)_3]_3$$

linked to silica. This catalyst (20 ml) containing 1.2% wt rhodium was tested in the continuous flow pilot plant for 100 hr on stream at 100–120°C and 43 atm carbon monoxide–hydrogen (1:1). The liquid feed was hexene-1 in *n*-heptane (1:2 v/v), and no precautions were taken to exclude oxygen from the gaseous or liquid feeds.

During the initial 75 hr on stream at a total liquid hourly space velocity of 3 and a gas hourly space velocity of 1250, a high conversion of hexene-1 and a high yield of heptaldehydes were obtained, see Fig. 2. The only other products detected were isomeric hexenes. The normal:isoheptaldehydes ratio remained constant at 2.2:1 and, after the elution of small amounts of rhodium during the first few hours on stream, no further rhodium was detected in the products (<0.07 ppm). Increasing the total liquid hourly space velocity to 6 for the remaining 25 hr on stream had no effect on the hexene-1 conversion, nor on the normal:isoheptaldehydes ratio, but a small decrease in the yield of heptaldehydes was observed.

b. Rhodium Complexes Chemically Linked to Silica via Nitrogen Ligands

The results of autoclave tests performed at 80–90°C, 45 atm carbon monoxide–

hydrogen (1:1) using complexes prepared from $[RhCl(CO)_2]_2$ and a variety of nitrogen ligand–silanes linked to silica has been reported previously (*8*).

In order to assess the oxidative stability of the rhodium–nitrogen bond, no precautions were taken to exclude traces of oxygen from the system. All the catalysts eluted rhodium, between 4 and 45 ppm being detected in the products. Generally, the nitrogen based catalysts were of lower activity than the phosphorus based species when tested under similar experimental conditions and, although heptaldehydes were the major products, low yields of heptanols were also detected in certain instances.

c. A Rhodium Complex Chemically Linked to Silica via an Oxygen Ligand

The supported complex formed by reaction of silica with $Rh[(EtO)_3SiCH_2CH_2CH_2CH(COCH_3)_2](CO)_2$, was tested in an autoclave for the hydroformylation of hexene-1 in *n*-heptane at 140°C, 42 atm carbon monoxide–hydrogen (1:1). The hexene-1:rhodium molar ratio was 10,000:1. After 4 hr, total conversion of the hexene-1 with a 90% yield of heptaldehydes was recorded. The normal:isoheptaldehydes ratio was low at 0.65:1 and 15 ppm rhodium were detected in the products. No special precautions were taken to exclude oxygen from the reactor during the test.

d. A Rhodium Complex Chemically Linked to Silica via a Sulfur Ligand

The results of hydroformylation studies using a rhodium complex linked to silica via the sulfur containing ligand–silane $(EtO)_3SiCH_2CH_2CH_2SH$ has been reported previously (*8*). The silica linked complex failed to show any hydroformylation activity at 80–90°C, 45 atm carbon monoxide–hydrogen (1:1) and only low activity at 140–150°C (heptaldehydes yield 8% wt). Although no precautions were taken to exclude traces of oxygen from the system, rhodium elution was low, less than 0.3 ppm being detected in the products.

DISCUSSION

The results of a number of studies on the use of macromolecular heterogeneous analogues of soluble rhodium complexes for the liquid phase hydroformylation of α-olefins have recently been published (*4*, *9*). The majority of these studies have used, as the support material, organic polymers to which groups capable of coordinating to the rhodium center have been chemically attached. In most cases these studies were performed in batch-type equipment, and, by contrast, only very few tests with a fixed bed of catalyst under continuous liquid flow conditions have been described. Furthermore, relatively few data on the ease of elution of rhodium from the support and the factors affecting this have yet appeared. However, total retention of rhodium on the catalyst under reaction conditions is essential if these catalysts are to offer viable heterogeneous alternatives to the homogeneous systems currently known.

In our studies, we have:

i. Examined rhodium complexes bound to organic polymers via phosphorus and oxygen ligand groups.

ii. Extended this concept to the use of inorganic oxides (principally silica) to which rhodium complexes have been bonded via nitrogen, oxygen, phosphorus and sulfur ligand groups.

iii. Investigated some of the factors influencing the loss of rhodium from the catalyst bed under liquid-phase continuous flow operating conditions.

The rhodium complexes linked to phosphorus ligand–polymers were prepared by reaction of the polymer with $Rh(acac)(CO)_2$. This leads to the evolution of carbon monoxide and the formation of species of the type $Rh(acac)(CO)PR_3$ in which the rhodium center is linked to the polymer via a single phosphorus–metal bond. Normal:isoaldehydes ratios in the product (about 2:1) suggest that the active species does contain a phosphorus–rhodium bond since under comparable conditions phosphine-free complexes give rise to much lower normal:iso ratios (~1:1). During continuous flow tests, appreciable amounts of rhodium were often detected in the products. In the case of the PVC based polymer (B), solubility of the polymer complex in the aldehyde product contributed significantly to rhodium losses. However, even with an insoluble highly cross-linked polystyrene polymer (A), rhodium elution was still significant. Cleavage of the tertiary phosphine groups from the polymer structure under reaction conditions seems extremely unlikely, and the most probable cause of rhodium elution is cleavage of the rhodium–phosphorus bond. This could arise in a number of ways:

i. Via an equilibrium of the form:

$$\textcircled{P}\text{—}CH_2PPh_2Rh(CO)(acac) + CO \rightleftharpoons \textcircled{P}\text{—}CH_2PPh_2 + Rh(CO)_2(acac).$$

It appears that the effect of this equilibrium is very small, as applying a higher pressure of carbon monoxide gave no increase in rhodium elution.

ii. Via thermal decomposition due to the heat of reaction liberated and subsequent formation of a soluble rhodium species. This does not seem likely since experiments at higher temperatures did not give rise to higher rhodium elutions.

iii. Via oxidation caused by traces of oxygen in the feedstocks. Our data recorded above point to this as a major source of rhodium elution.

The pilot plant studies using catalysts derived from polymer A clearly indicate that even relatively low levels of oxygen in the feedstocks can give rise to substantial amounts of rhodium elution. The mechanism of this process has not been investigated. It could involve rhodium-catalyzed oxidation of the tertiary phosphine to phosphine oxide, which no longer coordinates to the rhodium center. Alternatively, the dioxygen could react with the aldehyde product to form a per-acid, which then attacks the complex leading again to formation of phosphine oxide. In the case of the polymer based catalysts, there is only one phosphorus–rhodium bond anchoring the catalyst to the support, and any factors leading to the rupture of this bond leads to immediate loss of rhodium from the support.

Although analogues of $RhH(CO)(PPh_3)_3$ have been prepared by a ligand exchange reaction of the complex with a phosphorus ligand–polymer (*10*), our own observations suggest that with highly insoluble cross-linked polymers (needed for use in continuous operation) only a limited number of the total tertiary phosphine groups present on the polymer can take part in complex formation, owing to the steric restrictions of the polymer structure. When silica is used as the support material, complexes cannot only be prepared via direct reaction with a phosphorus ligand–silica (analogous to phosphorus ligand–polymer reactions), but also via intermediate formation of a complex with a phosphorus-containing silane, which is subsequently linked to silica, by a condensation reaction. This latter method overcomes the steric constraints imposed on the formation of complexes of the type $RhH(CO)(PPh_3)_3$ and was used to form the silica based analogue of this species.

This silica-supported complex was shown to have not only high activity for the liquid phase hydroformylation of hexene-1, but to have markedly better resistance to rhodium elution even when traces of oxygen were not rigorously excluded from the feedstocks. The catalyst operated for 75 hr on stream with no decline in the yield of heptaldehydes. It seems likely that the presence of several phosphorus–rhodium links to anchor the catalyst may be responsible for this greater stability.

However, even for this catalyst, the removal of oxygen from the feedstocks is believed to be essential if the catalyst is to be used for prolonged operation.

Tests with rhodium complexes with β-diketone groups on silica or polymer supports showed that this rhodium–ligand bond is readily cleaved under hydroformylation conditions. By contrast, a complex linked to silica via a sulfur ligand showed high retention of rhodium but only very low hydroformylation activity even at elevated temperatures, where extensive isomerization of the olefin was the major reaction observed.

Nitrogen ligand groups on silica generally gave rise to complexes which were less active than silica based species containing phosphorus ligand groups. Rhodium elution from these catalysts was often high, and low normal:isoheptaldehydes ratios suggest that some activity was attributable to species in solution not containing nitrogen ligands. Furthermore, although aldehydes were the major products, low yields of alcohols and paraffins were also produced. This contrasts with the results of Rollman *et al.* (*9*), who reported the formation of high yields of alcohols from rhodium complexes with polymers containing amine ligand groups. The formation of alcohols was said to be related to the presence of cluster complexes of rhodium bonded to the amine polymer, and it is possible that in our studies favorable conditions for formation of these species were not attained.

CONCLUSIONS

Rhodium complexes linked to organic polymers and silica via nitrogen, oxygen, phosphorus and sulfur ligands have been prepared and tested as catalysts for the liquid phase hydroformylation of hexene-1. The complexes containing phosphorus ligands were the most active and a phosphorus ligand–silica based complex gave a 99% conversion of hexene-1 with a 96% yield of heptaldehydes in continuous operation over 75 hr without loss of activity. Complexes containing nitrogen ligands gave low yields of alcohols and paraffins, in addition to aldehydes (and internal hexenes formed by isomerization of the hexene-1).

Factors affecting the loss of rhodium from the catalyst were examined for a complex linked to an organic polymer via a phosphorus ligand. Oxygen in the feedstocks was shown to promote rhodium elution and rigorous exclusion of oxygen is essential for the continuous operation of polymer and silica based catalysts over prolonged periods.

ACKNOWLEDGMENT

Permission to publish this paper has been given by The British Petroleum Co. Ltd.

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