GAS PHASE HYDROFORMYLATION OF PROPYLENE AND ALLYL ALCOHOL WITH IMMOBILIZED RHODIUM COMPLEXES

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STELLINGEN

1 Bij de bestudering van de ethaanhydrogenolyse over nikkel/koper alliages, als functie van het kopergehalte, is het Sinfelt *et al.* ontgaan dat de hydrogenolysesnelheid aanvankelijk logaritmisch afneemt met stijgend kopergehalte, terwijl het aantal vrije nikkelplaatsen slechts lineair afneemt. De logaritmische daling van de hydrogenolysesnelheid kan verklaard worden door aan te nemen dat de hydrogenolyse bij voorkeur verloopt op randen en hoekpunten, en op vlakken met hoge Miller indices.

J.H. Sinfelt, J.L. Carter, D.J.C. Yates, *J. Catal.*, 24 (1972) 283.

2 De door Laī en Ucciani beschreven hydroformyleringen van gesubstitueerde styrenen met Rh/Al_2O_3 als katalysator, zijn in werkelijkheid door rhodiumclusters homogeen gekatalyseerde reacties.

R. Laī, E. Ucciani, *J. Mol. Catal.*, 4 (1978) 401.

3 Het door Arai waargenomen katalytisch gedrag van zijn geïmmobiliseerde rhodiumkatalysatoren is niet in overeenstemming met het gedrag dat verwacht mag worden van het door hem veronderstelde actieve rhodiumcomplex.

H. Arai, *J. Catal.*, 51 (1978) 135.

4 Hjortkjaer *et al.* beschouwen hun katalysatoren, die niet-poreuze silica als drager bevatten, ten onrechte als SLP katalysatoren.

J. Hjortkjaer, M.S. Scurrell, P. Simonsen, *J. Mol. Catal.*, 6 (1979) 405.

5 Hoewel de aanwezigheid van basische actieve plaatsen in het dragermateriaal van SLP hydroformyleringskatalysatoren ongewenst is, moet toch ook aandacht besteed worden aan een minimalisering van het aluminiumgehalte, speciaal bij het gebruik van silicadragers, teneinde ongewenste nevenreacties, zoals aldolcondensatie en isomerisatie, te onderdrukken.

L.A. Gerritsen, *proefschrift TH Delft*, (1979).

6 Het door de Cetus Corp. geoctrooieerde proces voor de bereiding van epoxyden met behulp van enzymen biedt geen wezenlijke voordelen boven moderne, reeds in de industriële praktijk getoetste, oxydatieprocessen.

Cetus Corp., *Eur. octrooiaanvrage* 7-176 (1980).

7 De uitsluitend statische beproeving van katalysatoren, bijvoorbeeld in geroerde autoclaven, geeft slechts een uiterst beperkt beeld van hun potentiële toepasbaarheid, en in het geheel geen inzicht in de katalysatorstabiliteit.

8 Het is verbazingwekkend dat in de bibliotheek van de Afdeling der Scheikundige Technologie van de Technische Hogeschool Delft de meest recente belangrijkste octrooien op chemisch-technologisch gebied niet ter inzage liggen.

9 In de zogeheten brede maatschappelijke discussie over het gebruik van kerncentrales wordt ten onrechte weinig aandacht besteed aan het probleem van het (radioactieve) afval, dat bij toepassing van kolencentrales geproduceerd wordt.

10 Het tijdens wedstrijden dragen van een mondbeschermer door basketballspelers voorkomt niet alleen gebitsbeschadigingen, maar ook onnodige irritatie bij de scheidsrechter.

11 De katalyticus zou men de hartspecialist in de chemische technologie kunnen noemen.

N.A. de Munck 24 september 1980

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CONTENTS

CHAPTER 1

INTRODUCTION

1.1 CARBON MONOXIDE AS A CHEMICAL FEEDSTOCK

In the past carbon monoxide was a substance of great industrial interest. It was widely used as a source of energy for various purposes and it is still the reducing agent in the manufacture of iron from ore. However, during the past thirty years the application of carbon monoxide has shifted from a source of energy to chemical feedstock. Carbon monoxide, and especially its combination with various amounts of hydrogen (synthesis gas), will be the key chemical of the future. It has the advantage that it can be produced from almost all carbon containing materials. So the selection of this material will be mainly determined by the price level and less by the availability.

The processes for the manufacture of synthesis gas were originally based on the gasification of coke from hard coal or low temperature coke from brown coal by means of air and steam. During the past thirty years the easy-to-handle and cheap liquid and gaseous fossil fuels - oil and natural gas - have also been used as feedstocks. An additional advantage of the latter fuels is their hydrogen content, the H/C-ratio being 4:1 for methane, 2.4:1 for gasoline and 2:1 for oil, whereas for coal a ratio of 1:1 is found [1]. In future however, only the traditional coal gasification processes will be used for the production of synthesis gas, although in a modern technological form. Processes like the Winkler gasification, the Kopper-Totzek gasification and the Lurgi pressure gasification originated from the 1930's and are now established industrial processes. Besides improving the technology of gasification an effort must be made as regards purification technology in order to obtain a clean synthesis gas ready for chemical processing.

Synthesis gas is currently used for several important industrial processes. One of the most important is the manufacture of methanol, which was developed in Germany in 1923. Despite several technological and catalytic improvements the basic process is still used [2]. Later on in the thirties synthesis gas was applied in the Fischer-Tropsch synthesis of hydrocarbons, a process designed to produce petrochemical feedstocks from coal. In 1938 in his research on the Fischer-Tropsch synthesis Roelen discovered the reaction of unsaturated hydrocarbons with synthesis gas to give aldehydes and alcohols, currently known as the *hydroformylation or OXO process* [3].

In the sixties a large number of transition-metal complexes were found to be catalytically active in the conversion of carbon monoxide. The charateristic property of these complexes is their high selectivity in combination with a high reactivity. Several new or improved processes like the Union Carbide process for the hydroformylation of alkenes [4], the Monsanto process for the carbonylation of methanol [5] and the Shell process for the homologation of methanol to higher alcohols [6] were developed. A more recent development is the synthesis of ethylene glycol from synthesis gas with rhodium cluster catalyst systems. Because of the high pressure required and the low selectivity towards glycol (50%) this process needs to be improved considerably before commercial operation will be realized [7].

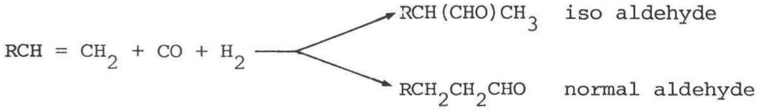
A more promising development in the use of synthesis gas is the conversion of methanol into a synthetic gasoline using a H-ZSM molecular sieve catalyst developed by Mobil Oil Co. This catalyst system has the advantage of converting methanol into mainly aromatics and iso-alkanes. This is much more favourable than what happens in the Fischer-Tropsch process where predominantly aliphatics are produced. By combining a methanol synthesis catalyst system with the H-ZSM catalyst it is possible to produce gasoline from synthesis gas with a high octane number [8,9]. Further modification and improvement of this process and its catalyst are likely to lead to the selective production of basic chemicals such as ethylene, propylene, benzene, toluene and xylene [10]. By combining the Mobil Oil process with processes like hydroformylation and carbonylation it will be possible to produce a whole variety of chemicals from synthesis gas.

The scenario outlined above means a large shift in the way of thinking in the chemical industry. Instead of getting basic chemicals by the traditional cracking of oil, they will be formed by synthesis from small molecules like carbon monoxide and hydrogen. It also means a shift from the non-selective energy wasting processes towards the high-selective energy efficient processes. In order to accomodate this change in philosophy catalyst development, modification and improvement will be required.

In future, alkenes and substituted alkenes, produced from synthesis gas, will be converted into aldehydes and alcohols by reaction with carbon monoxide and hydrogen (hydroformylation). Modern metal-organic complexes will be used in such processes as a catalyst. A study of such a process will be the main theme of this thesis.

1.2 HYDROFORMYLATION OF ALKENES

Hydroformylation is the reaction of an alkene with an equimolar amount of carbon monoxide and of hydrogen to yield an aldehyde.



$$RCH=CH_2 + CO + H_2 \rightarrow \begin{cases} RCH(CHO)CH_3 & \text{iso aldehyde} \\ RCH_2CH_2CHO & \text{normal aldehyde} \end{cases}$$

This reaction was discovered in 1938 by Roelen of Ruhrchemie when he was exploring Fischer-Tropsch reactions [3]. Roelen himself was the first to assume that cobalt hydrocarbonyls are the active catalytic species in the hydroformylation [11]. Later Orchin showed that cobalt metal or salts are converted into cobalt hydrocarbonyls under the conditions of the OXO reaction [12].

The reaction proceeds only in the presence of catalysts. It is exothermic: the heat of reaction being 125.5 kJ/mol with propylene and 117-146 kJ/mol with other alkenes, varying with alkene structure and molecular weight [13]. The reaction takes place homogeneously in the liquid phase with cobalt hydrocarbonyl dissolved in the reaction mixture, containing solvent alkene and products. Depending on temperature, cobalt concentration, added ligand and solvent, carbon monoxide pressures of 4-10 MPa are needed in order to prevent the complex from decomposition.

A reaction mechanism of the cobalt catalysed hydroformylation was first described by Heck and Breslow [14,15]. Their mechanism is still considered to be the most accepted according to a review by Orchin and Rupilius [16]. Pino extensively reviewed cobalt catalysed hydroformylations with respect to substrates, selectivity, kinetics and reaction mechanisms [17]. Other authors also gave excellent reviews on this subject [18-20]; therefore, the application of cobalt catalysts in hydroformylation reactions will not be expatiated on in this thesis.

Other group VIII-metals than cobalt are also active as hydroformylation catalysts. Pt-Sn-phosphine complexes for instance show a good catalytic activity in combination with a high selectivity towards straight-chain aldehydes [21]. By far the most frequently applied noble metal is rhodium, showing the highest activity in hydroformylation. The rhodium catalysed hydroformylation of alkenes occurs under much milder conditions than the corresponding reaction with cobalt (10^2-10^4 times more active). The reaction can be carried out at total pressures of 100 kPa or lower at 25°C [22], but temperatures between 50 and 150°C and total pressures of 2.5-7.5 MPa are generally used [23].

The first applications of rhodium carbonyl complexes appeared between 1950 and 1960 in the patent literature [24-26]. They proved to be extremely active and selective for aldehyde formation, but they also showed a high activity in isomerising the double bond of the *n*-alkene giving iso-alkenes [27]. Therefore unmodified rhodium complexes are giving much more branched-chain aldehydes compared to similar cobalt catalysts. Due to this low n/i-ratio and the high price of rhodium,unmodified rhodium carbonyl complexes are not used in commercial operation.

Research by Wilkinson [28] and by Slaugh and Mullineaux [29] led to the modification of rhodium carbonyl by tertiary phosphines, complexes which do not show double bond isomerisation activity. Besides being active and selective for *n*-aldehyde formation these catalysts are also capable to hydroformylate alkynes, dienes and alkenes containing functional groups [30-32]. Usually an excess of phosphine is used. An increase of the ligand/rhodium ratio increases the n/i-ratio, but decreases the reaction rate [33]. Due to these excellent properties rhodium phosphine complexes are finding wide-spread industrial application [4,34].

Hydroformylation by rhodium phosphine complexes has been thoroughly investigated and has been reviewed by various authors [7,17,20,35]. The reaction mechanism and the influence of many reaction parameters have been carefully investigated by Wilkinson and his co-workers [28,36-38]. The industrial applications of rhodium phosphine complexes in hydroformylation have been published in a large number of patents and have been reviewed by Pruett [7,20].

1.3 IMMOBILIZATION OF HOMOGENEOUS CATALYSTS

As mentioned before, a fast growing interest in organo-metallic complexes became apparent during the past decades [39]. Processes like the Wacker synthesis of acetaldehyde, the Monsanto carbonylation of methanol and the Union Carbide hydroformylation of propylene are based on the successful application of homogeneous noble metal catalysts. Although expensive, their great advantage of possessing a high activity and selectivity more than counterbalanced the disadvantage of a difficult catalyst-reactant separation and the risk of unwanted catalyst losses.

In various applications of homogeneous catalysts the separation of the highly expensive catalyst from the products at the end of the reaction is causing serious problems. Unless the separation is efficient, it will result in some catalyst loss, which may render the process uneconomic and/or contaminate the product. Furthermore, thermal degradation of the product and the catalyst and corrosion of the equipment calls for a cheap and less cumbersome recovery of the catalyst.

The problems around recovery, thermal stability, contamination and corrosion may be solved by *immobilization or heterogenizing* the homogeneous catalyst. This means that the homogeneous catalyst is transferred into a phase differing from that of the reactants and the products. By using a fixed bed reactor or by filtration of the catalyst, a less complicated separation can be realized then.

During the past ten years the immobilization of homogeneous catalysts has been the subject of intensive research. At first sight it was generally thought, that immobilization was an easy problem to solve. However, difficulties with stability and complex elution proved to be a serious disadvantage for technical application of these catalysts. So, much of the current research effort is now concentrated on solving these problems.

Various methods of immobilizing homogeneous catalysts have been developed. Methods *a* and *b* are only applicable in solid-gas reactions, whereas method *c*, *d* and *e* can be used in solid-gas as well as in solid-liquid reactions:

a) Strong physical adsorption on a support [40-42].

b) Capillary condensation of a catalyst solution in a porous support [43, 44,64].

c) Immobilization of the catalyst by ion exchange on resins or zeolites [45-47].

d) Chemical anchoring of the organometallic complex to modified silicas [48,49].

e) Chemical anchoring of the organometallic complex to functionalised organic polymers [50-53].

The preparation and application of immobilized homogeneous catalysts is discussed in a number of reviews [58-61]. The application of polymers in heterogeneous catalysis has been extensively reviewed by Dawydoff [54-56]. Other authors gave more specific reviews on the polymer-supported catalysts [57-63], while Murrell presented a review on the immobilization of transition metal complexes on inorganic supports [49].

1.4 SYNTHESIS OF 1,4-BUTANEDIOL

1,4-Butanediol (1,4-BDO) is a saturated C_4-diol having a pair of primary-alcoholic hydroxyl groups. It is a stable, viscous, colourless and odourless liquid. Its main chemical properties are effected by the hydroxyl groups, just like other saturated diols. However, polymers such as polyurethane and polyesters based on 1,4-BDO do have properties different from those prepared from other glycols. Particularly polybutylene terephtalate (PBT) resin, produced by polycondensation of 1,4-BDO and terephtalic acid is known to be an engineering plastic having attractive properties, such as a good moldability and a high modulus of elasticity, compared with competitive engineering plastics.

1,4-BDO has been initially produced as intermediate raw material for butadiene and later on for tetrahydrofuran (THF). THF is mainly used in solvents and polyurethane elastomers, but 1,4-BDO has found a wider industrial usage. Chemicals other than THF now produced from 1,4-BDO are 2-butyrolactone, 2-pyrrolidone and *N*-vinylpyrrolidone. At present, the consumption of 1,4-BDO is sharply increasing. This causes a strong demand for large quantities of 1,4-BDO. This strong demand cannot be fulfilled yet because of a limited production capacity.

The standard commercial process for 1,4-BDO is based on the so-called Reppe chemistry, which is the basis for processes operated by Du Pont, BASF and GAF, the main producers of 1,4-BDO, with a total production capacity of 280,000 tons per year [65]. It is based on the reactions given in Figure 1.

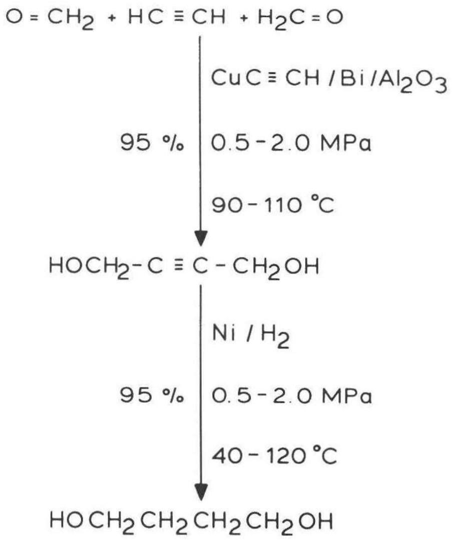


Figure 1 Synthesis of 1,4-butanediol by the Reppe-process [66].

In the first reaction 1,4-butynediol is produced from acetylene and 10-20% aqueous formaldehyde with a copper acetylide catalyst at 90-110°C and 0.5-2.0 MPa total pressure with a maximum yield of 95%. In the next steps a Raney nickel catalyst is used at 40-120°C and 0.5-2.0 MPa hydrogen pressure to hydrogenate 1,4-butynediol to 1,4-BDO. The overall yield of this process is given to be 85-90% [66].

The operation of this process is a rare instance of large-scale industrial activity which uses acetylene as a raw material. The main disadvantage of such a process is its high capital costs due to acetylene processing at high pressures. Moreover, in several countries acetylene cannot be supplied at low cost. In the U.S. acetylene is traditionally obtained from low priced natural gas. However, after the first oil-crisis (1974) the cost of natural gas has rapidly increased. In Japan, where mainly the carbide process is used, acetylene is not available in large quantities, but also its cost, mainly power fees, has increased. Acetylene can be extracted in naphta cracking, but the yield will be about 6,000-8,000 tons only against an annual production of 400,000 tons of ethylene.

Obviously, the supply of acetylene is limited and its cost, because of rapidly increasing energy prices, is rising to a less economical level for 1,4-BDO production. This cloudy forecast for 1,4-BDO-production initiated an intensive research for alternative processes.

1.5 NEW PROCESSES FOR SYNTHESIS OF 1,4-BUTANEDIOL

During the past ten years several new chemical processes have been developed for the production of 1,4-BDO and related substances. These processes have in common that they are based on oil-derived feedstocks, such as propylene, butane, 1- and 2-butene and butadiene. The first compound needs a hydroformylation reaction to convert a propylene derivative into a C_4-precursor of 1,4-BDO. C_4-feedstock can be converted into 1,4-BDO by chlorination of butadiene or by oxidation of butane, 1- and 2-butene or butadiene, as shown in Figure 2.

The chlorination of butadiene to 1,4-dichloro-2-butene and the subsequent hydrolysis and hydrogenation to 1,4-BDO has been developed and commercialized by Toyo Soda in 1971 with a production capacity of 6,000 tons/year [67]. Disadvantages of this process are its low selectivity towards the desired product (65%) and the inherent conversion of valuable chlorine into sodium chloride, reasons why this process has not found wider application. The acetoxylation of butadiene lacks these disadvantages and yields about 85% of the 1,4-

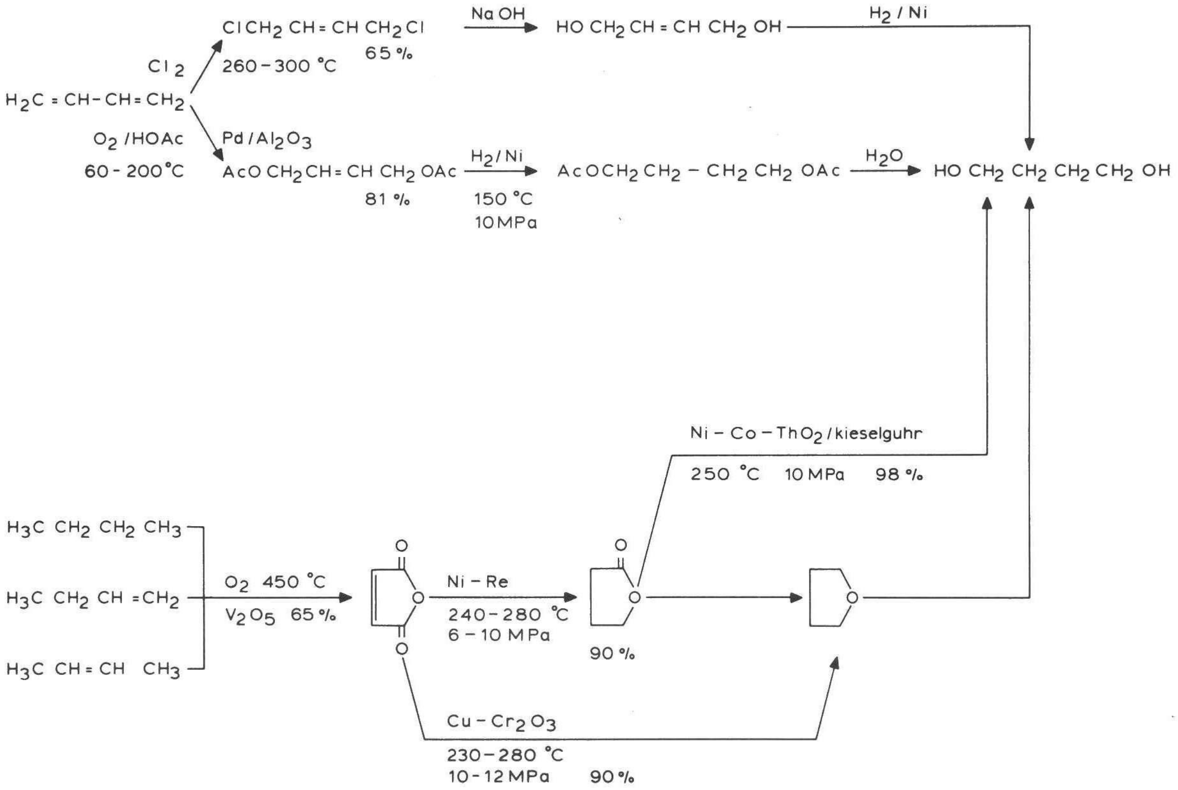


Figure 2 Synthesis of 1,4-BDO based on C_4-feedstock.

disubstituted product and no waste products, because it is possible to convert the 1,2-product into the 1,4-product [68-73].

The hydrogenation of maleic acid anhydride or γ-butyrolactone probably offers the best perspectives of the C_4-feedstock. Maleic acid anhydride can be produced by partial oxidation of 1- or 2-butene, and subsequent hydrogenation to γ-butyrolactone, tetrahydrofuran or 1,4-BDO [74-76]. By choosing a particular catalyst and the right reaction conditions it is possible to produce one single product or a mixture of products. A more recent development is a process for the oxidation of butane to maleic acid anhydride [77]. Butane will be a cheap feedstock available from LPG.

Several processes have been developed for the hydroformylation of propylene derivatives, such as acrolein acetal, allyl acetate or allyl alcohol. They all have in common that they are homogeneous and batch wise. After the hydroformylation reaction one or more reactions are required to convert the hydroformylation products to 1,4-BDO (Figure 3).

The homogeneous hydroformylation of acrolein acetal with rhodium phosphites has been developed by Du Pont. It is possible to obtain a high selectivity of 95% to the *n*-product at almost complete conversion [78]. After hydrogenation the iso-product is used in the acetalization reaction with acrolein. In the final hydrolysis and hydrogenation reaction it is possible, by choosing the appropriate hydrogen pressure and space velocity, to produce either 1,4-BDO or THF [79]. Commercial drawbacks of this process are that it needs at least four reaction steps to get 1,4-BDO and a very complicated rhodium recovery because of the low volatility of the reactants. Recently a similar process has been developed by Celanese [80].

The hydroformylation of allyl acetate has been developed by General Electric. This company uses the classical cobalt catalyst. Therefore a low selectivity towards the *n*-product (65%) is obtained and the iso-products have to be regenerated to allyl acetate [81-83]. Analogous processes have been developed by BASF and Mitsubishi [84-86]. Although the General Electric process is less complicated than Du Pont's the low selectivity in the hydroformylation reaction does not favour commercialization, but the corrosivity of allyl acetate might also be an important drawback.

Of all hydroformylation processes for the production of 1,4-BDO the homogeneous hydroformylation of allyl alcohol attracted most attention. Several chemical companies concentrated their research on this reaction. By far the most developed process is from Kuraray [87-89], but other companies such as General Electric [90,91], Celanese [92] and Firestone [93] are also developing homogeneous allyl alcohol hydroformylation processes. They all have

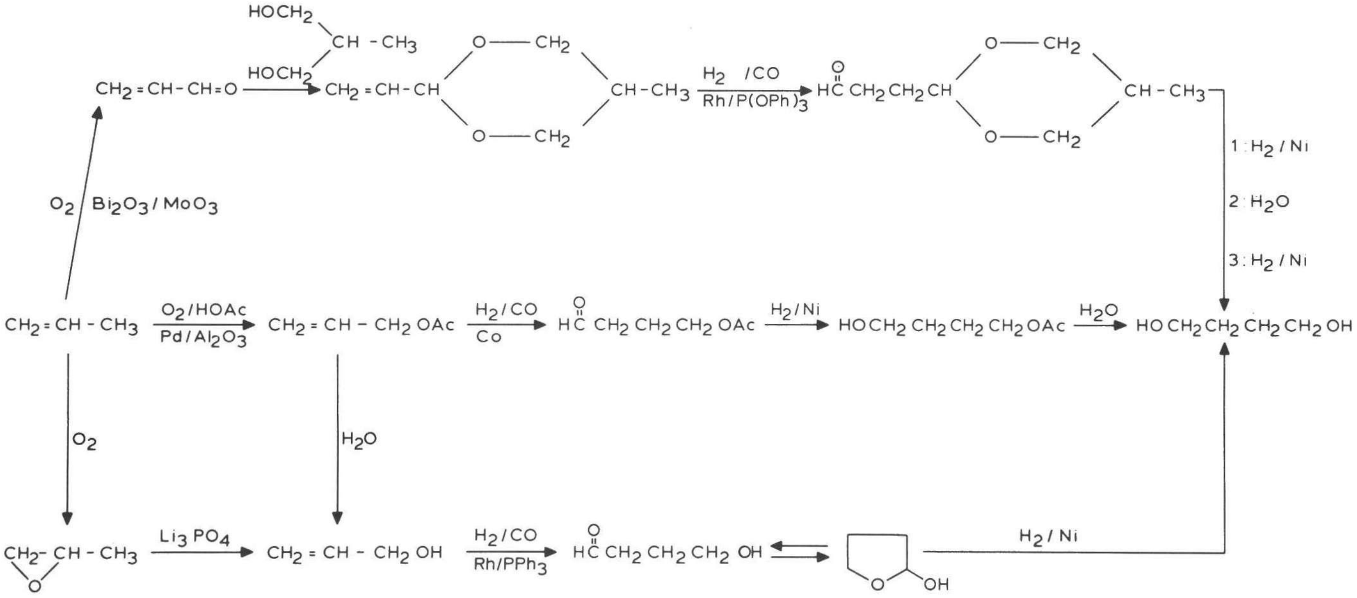


Figure 3 Synthesis of 1,4-BDO from propylene derivatives.

in common catalysis by rhodium complexes and an excess of triphenylphosphine and giving 4-hydroxybutyraldehyde or 2-hydroxytetrahydrofuran as the main product. The relatively low boiling point of the hydroformylation product favours an easy recovery of the rhodium by distillation, which makes this process the most attractive one.

Apart from the chlorination of butadiene none of the processes have been commercialized. Commercialization of one of these processes will depend on future developments in the oil price situation. In Western Europe the oxidation of butane, because of the availability of LPG from the North Sea, and the hydroformylation of allyl alcohol will have the best prospects.

1.6 SCOPE OF THIS THESIS

Previous studies by Spek and Tjan [40,41] on the heterogeneous gas-phase hydroformylation of alkenes with physisorbed rhodium complexes showed such catalysts to be only stable at low pressure (30 kPa) and small conversions (0.1%). At higher pressures such catalysts are not stable due to thermal degradation of the complex to rhodium metal crystallites. One of their conclusions was that stabilization of the catalyst could be achieved by chemical anchoring of the complex to a support, which would also enable the use of the catalyst in the liquid phase. Another method of stabilizing the complex is the use of supported liquid phase catalysts, which have been extensively studied by Gerritsen [43].

One of the subjects of the present study is the immobilization of rhodium complexes on porous supports by chemical anchoring and testing of these catalysts in a continuous flow-system at the solid-gas phase boundary for the hydroformylation of alkenes. As a support we selected macroporous polystyrene-divinylbenzene; its surface could easily be functionalized with ligands. The stability of this polymer is going beyond the stability of the rhodium complexes; so, degradation of the support will not be a drawback in the use of these catalysts in hydroformylation reactions.

A number of papers dealing with the use of polymer anchored rhodium complexes in hydroformylation reactions have been published. Except for one, they all deal with reactions at the liquid-solid phase boundary and are usually tested in a batch type operation. Arai published a study on the continuous gas phase hydroformylation of alkenes with rhodium phosphine complexes chemically anchored to polymer-coated silica [50]. Our study presents the results of various immobilization methods, in particular the performance of the catalyst in the continuous hydroformylation of propylene at the solid-gas phase boundary, with respect to stability, activity and selectivity.

The second part of this thesis describes the application of an immobilized catalyst in the hydroformylation of a substituted alkene. As mentioned in section 1.5 the hydroformylation of allyl alcohol could be an attractive process for the production of 1,4-BDO and of tetrahydrofuran. At present the supported liquid phase catalysts developed by Gerritsen [43] have the best prospects for commercial application. Therefore the SLP catalyst system was selected for the continuous gas phase hydroformylation of allyl alcohol. All published hydroformylations of allyl alcohol deal with homogeneously catalysed reactions in a batch type operation. Our study will give the results of the hydroformylation of allyl alcohol in a flow system with SLP catalysts.

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CHAPTER 2

GAS PHASE HYDROFORMYLATION OF PROPYLENE WITH POROUS RESIN ANCHORED RHODIUM COMPLEXES

Part I. Methods of catalyst preparation and characterization*)

by

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2.1 SUMMARY

Hydridocarbonyltris(triphenylphosphine)rhodium(I) anchored to the surface of macroreticular polystyrene-divinylbenzene is applied in the heterogeneous hydroformylation of propylene at 90°C and 0.1 MPa total pressure. The performance of the catalyst depends on the method of preparation. We finally succeeded in preparing highly stable, active and selective catalysts.

The methods of functionalization of the support with phosphine and phosphite ligands by means of chloromethylation and chlorophosphonation are studied and correlated with the performance of the catalyst. The method of coupling of the rhodium complex to the functionalized support influences the activity and selectivity of the catalyst.

Laser-Raman spectroscopy showed the presence of a high content of unpolymerized vinyl groups. Functionalization of the resin lowers the amount of vinyl groups substantially, which is supported by the results of a specific reaction with iodine chloride.

The texture of the catalyst was studied by physical adsorption and capillary condensation of nitrogen and is discussed in relation to the preparation of the catalyst.

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2.2 INTRODUCTION

During the past few years a number of papers dealing with the use of polymer anchored rhodium complexes in hydroformylation reactions have been published [1-9]. Except for one [3], they all deal with reactions at the *liquid-solid phase boundary* and the catalysts are usually tested batch-wise. However, application of these catalysts in a liquid phase flow system is hampered by a slow leaching-out of the rhodium complex, which makes the catalysts unattractive for industrial use [5,7,9].

The advantages of applying chemically anchored rhodium complexes in *gas phase* hydroformylation are the ease of separation of the catalyst from the reactants and the absence of rhodium elution. However, because of the absence of solvent stabilization there is a greater danger of catalyst deactivation due to thermal degradation or poisoning. Another advantage of chemically anchored rhodium complexes is the suppression of migration of the rhodium complex over the surface of the support, which was found by Spek in his study on rhodium complexes physically adsorbed on γ-alumina [12].

To prevent diffusional retardation of the rate of reaction we need a support with a large surface area, and nevertheless with wide pores; therefore we selected macroporous polystyrenedivinylbenzene (XAD-2 and XAD-4).

Though heterogeneous gas phase hydroformylation has been studied before [3,10-16], hardly any work has been done with chemically anchored rhodium complexes. Arai published a study on the heterogeneous gas phase hydroformylation of several alkenes with rhodium phosphine complexes chemically anchored to a polymer coated silica [3]. He found an extremely low hydroformylation activity accompanied by an appreciable alkane byproduct formation, and no information is given about the stability of his catalyst.

For immobilization of rhodium phosphine complexes on macroporous resins it is necessary first to functionalize the surface with phosphine ligands in order to accomplish a fairly strong complex anchoring to the support. Most methods of immobilization deal with low-crosslinked, swelling polymers, highly accessible to the reagent. Macroreticular polystyrene-divinylbenzene resins do not swell at all, which makes functionalization much more difficult, despite their high porosity.

This study presents the results of various functionalization methods (Figure 1) for immobilization of $RhHCO(PPh_3)_3$ on macroreticular polystyrene-divinylbenzene. They will be discussed with respect to the stability, activity and selectivity of the catalysts in the gas phase hydroformylation of propylene in a continuous flow system.

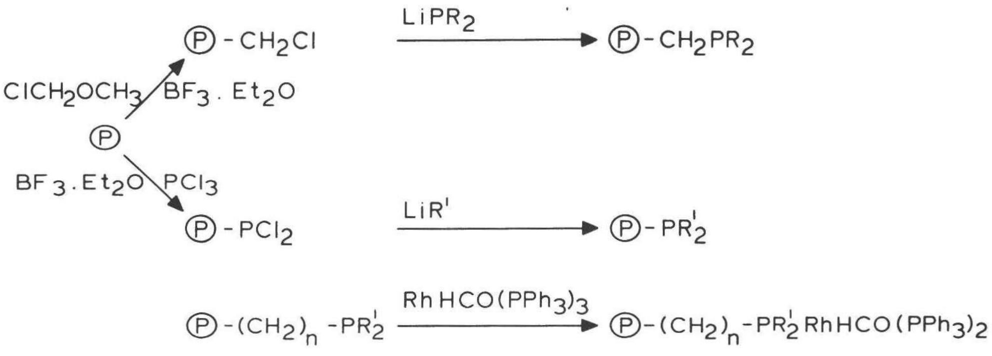

Figure 1 Schematic representation of the functionalization of the support.
R = Ph, OPh; R' = Ph, OPh, OMe; Ⓟ = XAD-2 or XAD-4 polymer surface; n = 0 or 1.

2.3 EXPERIMENTAL

2.3.1 Materials

$RhHCO(PPh_3)_3$ was prepared by the method of Ahmad [17]. Triphenylphosphine (Fluka, Switzerland, 99.5%) and diphenylphosphine (Strem Chemicals, USA, 99.5%) were used as received. Phosphorus trichloride (Aldrich, Belgium, 98%) was distilled prior to use. Toluene (Baker, The Netherlands, 99%), tetrahydrofuran (Baker, The Netherlands, 99%), n-hexane (Merck, German, 99%), diethyl ether (Merck, Germany, 99.5%) and 1,1,2,2-tetrachloroethane (Lamers & Indemans, The Netherlands, 96%) were dried over molecular sieve 3A (Union Carbide, USA). Aluminium trichloride (Baker, The Netherlands, 99.5%), boron trifluoride etherate (Aldrich, Belgium, 96%), butyllithium (Aldrich, Belgium, 1.6 M solution in hexane), chloromethyl methyl ether (Merck, Germany, 90%) and phenyllithium (Aldrich, Belgium, 1.8 M solution 70:30 benzene/ether) were used as received. Nitrogen (99.98%), carbon monoxide (99.5%) and propylene (99.5%) were all obtained from Air Products, USA, and were freed of traces of oxygen and water over BASF catalyst R3-11 and molecular sieve 3A, respectively. Moreover, carbon monoxide and propylene were freed from carbon dioxide over "Ascarite" (A.H. Thomas, USA). Hydrogen (Air Products, USA, 99.99%) was freed from oxygen and water over a Pd/Al_2O_3 catalyst (Engelhard, U.K.) and molecular sieve 3A. Polystyrene-divinylbenzene "Amberlite" XAD-2 and XAD-4 (Serva, Germany), with a particle size from 0.1 to 1.0 mm, were dried at 100°C for 48 hours to remove water and styrene.

2.3.2 Catalyst preparation

Extraction of XAD-2

Dried XAD-2 (0.3 kg) is subsequently boiled for 25 hrs with 800 ml of the following solvents: water, methanol, Et_2O and *n*-pentane. After each solvent extraction the polymer is washed with clean solvent and dried. After completing the extraction the polymer is dried at 90°C for 48 hrs.

Chloromethylation [18]

Dried support material (50 g) was stirred with 125 ml of chloromethyl methyl ether in 500 ml *n*-hexane for 0.5 hr under N_2. 25 ml $BF_3.Et_2O$ were added and stirred at 35°C for 4 hrs. After standing overnight the support was collected by filtration and washed with 3 x 200 ml *n*-hexane, 3 x 200 ml methanol, 3 x 200 ml water, 3 x 200 ml methanol and 3 x 200 ml dichloromethane. After suction to dryness the chloromethylated support was further dried at 85°C for 24 hrs. By variation of the amount of $BF_3.Et_2O$ and the reaction time the degree of chloromethylation of the polymer could be varied.

Phosphination

A solution of lithium diphenylphosphine was prepared by reaction of 40 g diphenylphosphine with 7.6 g lithium in 500 ml of dry tetrahydrofuran under nitrogen for 24 hrs. After removing the excess lithium by filtration the solution was added to 50 g of chloromethylated support and boiled under reflux of 6 hrs under nitrogen. After filtration the support was washed with 500 ml water, 500 ml acetone/water, 200 ml acetone and 5 x 100 ml THF, and finally dried. The reaction with lithium diphenylphosphite was performed in a similar fashion.

Chlorophosphonation

Dried support material (10 g) was stirred for 0.5 hr with 60 ml of freshly distilled PCl_3 under N_2. 22 ml of $BF_3.Et_2O$ was added and the temperature was raised to 50°C. After 2 hrs the support was collected by filtration under N_2 and washed with 3 x 100 ml *n*-hexane and 3 x 100 ml Et_2O.

The chlorophosphonated polymer was then reacted with 60 ml of a phenyllithium solution and 60 ml toluene for 3 hrs at 70°C under N_2. After filtration it was washed with 3 x 100 ml toluene, 3 x 100 ml methanol, 3 x 100 ml water, 3 x 75 ml methanol, 3 x 75 ml Et_2O and finally dried under N_2.

Other phosphines or phosphites are prepared in a similar fashion by reacting the chlorophosphonated polymer with the corresponding lithium compound. Analysis proved that no chlorine is left in the polymer after reaction with the lithium compound.

Coupling of the complex

The functionalized polymer is stirred with the desired amount of $RhHCO(PPh_3)_3$ and an excess of PPh_3 (3 mol PPh_3/mol Rh) in 80 ml toluene saturated with hydrogen. The temperature is raised slowly to 65°C in 1 hr and the mixture is kept under H_2 at 65°C for 2 hrs. The polymer is separated from the solution and carefully washed with 3 x 100 ml toluene and 2 x 100 ml Et_2O in order to remove excess rhodium complex and PPh_3. In some cases the catalyst is now contacted for 0.5 hr with a solution of PPh_3 in Et_2O to add additional PPh_3 to the surface. In all cases the catalyst is dried under H_2.

2.3.3 Catalyst characterization

Chlorine analysis of the catalyst was performed by the standard method of Schöniger [19].

The phosphorus content of the catalyst was determined by digestion of the sample, followed by a colorimetric titration. The digestion of the sample was carried out with a solution of sodium sulfate/mercury oxide in 95-98% sulfuric acid at a temperature of 370°C for 24 hrs. In a Technicon autoanalyzer a blue colour is formed on addition of orthophosphate, molybdate ion and antimony ion followed by a reduction with ascorbic acid at pH 7 [20]. The phosphomolybdenum complex concentration was measured at $\lambda = 660$ nm.

The rhodium content of the catalyst was determined by neutron activation analysis, based on the detection of the isotope ^{104}Rh. The "single comparator" method was used with Ti as a reference material [21].

The texture of the pure supports and the catalysts was determined by physical adsorption and capillary condensation of nitrogen at -196°C using a Carlo Erba 1800 "Sorptomatic", or by mercury porosimetry in the pressure range of 0.1 - 200 MPa using a Carlo Erba porosimeter type 70 H.

2.3.4 Method of determining the catalytic performance

The catalytic performance in the gas phase hydroformylation of propylene was studied in a continuous flow apparatus at a total pressure of 0.1 MPa and temperatures up to 140°C (Figure 2). Hydrogen, carbon monoxide, propylene and nitrogen were purified from oxygen, water and carbon dioxide by passing them subsequently over BASF catalyst R3-11, molecular sieve 3A and sodium hydroxide on asbestos (Ascarite) as mentioned in section 2.3.1. The gases were each metered with a Porter VCD 1000 flowcontroller and measured with a differential pressure indicator.

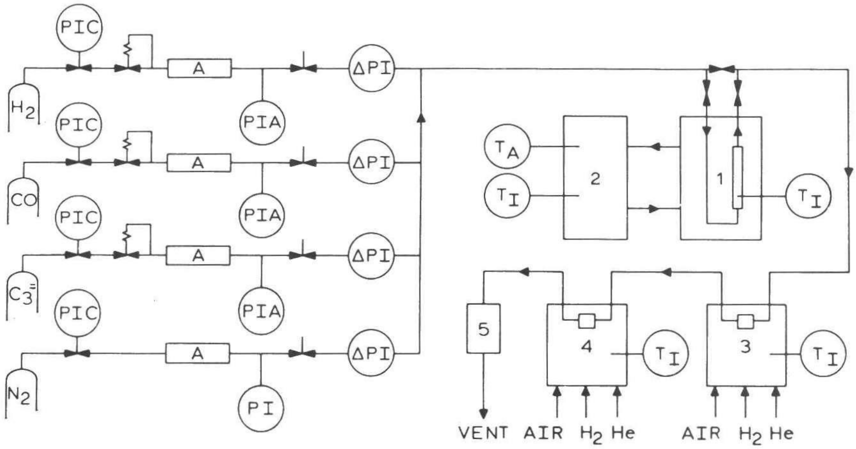

Figure 2 Continuous flow apparatus.
A = purification, PI = Pressure indicator, PIA = Pressure indicator and alarm, PIC = Pressure indicator and controller, ΔPI = Differential pressure indicator, TI = Temperature indicator, TA = Temperature alarm. Items 1-5 are mentioned in the text.

After thoroughly mixing at room temperature the reactants were passed through a 0.15 m long pyrex glass fixed bed reactor (inner diameter 0.010 m) ① , in which the catalyst is placed between two porous plugs of 1 cm of glass wool. Reactor ① is heated with oil and a Tamson thermostatic heater was used, permitting isothermal operation to within ± 1°C. The operating conditions were chosen as to assure ideal plug flow. The reaction mixture was periodically sampled via Carle sampling valves (in ③ and ④) and analyzed gaschromatographically with helium as a carrier gas: in ③ on a Porapak-QS column (3 m, 0.004 m Ø) at a temperature of 120°C, for the separation of aldehydes and propylene, and in ④ on a Porapak Q column (1.5 m, 0.002 m Ø) at 35°C to check if any hydrogenation of propylene to propane had occurred. The detection proceeded with flame ionisation using a Hewlett Packard 5704A electrometer. The peak areas were recorded and integrated on a digital integrator (Infotronics CRS 309). After measurement of the total gas flow in a soap film meter ⑤ , the gases were vented.

Aldehydes being the only products observed, the conversion of propylene (ξ) was calculated as follows:

$$\xi = \frac{A_1R + A_2R}{A_0 + A_1R + A_2R}$$

where A_0, A_1 and A_2 are the integrated peak areas for propylene, *n*-butyraldehyde and isobutyraldehyde, respectively, and R is a response factor correcting for the difference in sensitivity between propylene and the aldehydes. The response factors of *n*-butyraldehyde and isobutyraldehyde are equal.

The selectivity for the formation of *n*-butyraldehyde (S) is calculated as the ratio of *n*-butyraldehyde to isobutyraldehyde:

$$S = \frac{A_1}{A_2}$$

The reactor was operated differentially, so that the initial rate of hydroformylation (r) could be expressed as:

$$r = \frac{\xi}{(W/F)}$$

where W is the weight of rhodium in the reactor, F is the flow rate of propylene; r is expressed in cm^3 propylene at 0.1 MPa and 25^oC per gram of rhodium metal and per second.

On starting the experiment first the reactor temperature is raised stepwise from room temperature to the desired temperature level in a period of one hour, while hydrogen flows over the catalyst. When the final temperature level is reached and after total removal of residual solvent from the catalyst, a 1/1/1 mixture of hydrogen, carbon monoxide and propylene is fed to the catalyst to start the hydroformylation of propylene.

2.3.5 Laser-Raman spectroscopy

Laser-Raman spectra were recorded with a Jobin-Yvon (France), type HG 2 S spectrometer. The krypton-ion 647.1 nm type 500 K laser was from Coherent

Radiation (USA).

2.3.6 Determination of vinyl groups in the resins

The determination of vinyl groups in the resins proceeded after a modified method of Wijs [22]. The sample was evacuated at room temperature and 0.8 kPa for 48 hrs. 1 g of the polymer was reacted for 6 hrs with 10 ml of a 0.2 *N* Wijs-solution (16.2 g ICl in 1 l acetic acid). After the reaction was completed 10 ml of a solution of 20% KI in water was added to the sample. After decantation the sample was washed 5 times with 15 ml acetic acid, 5 times with 15 ml water and transferred to a glass filter. Next the sample was rinsed with 50 ml ethanol, 50 ml tetrachloromethane and 50 ml acetone, and dried by suction. After drying it was evacuated at room temperature and at 13.3 kPA for 12 hrs and to a final pressure of 0.07 mPa for 5 hrs.

The iodine and chlorine content of the samples were determined by neutron activation analysis, using KI as a reference material. The contents are converted to a bromine number, which is a measure of the amount of unsaturates at the surface of the polymer.

2.4 RESULTS AND DISCUSSION

2.4.1 Functionalization by chloromethylation

Chloromethylation of polystyrene-divinylbenzene resins, originally developed by Merrifield [23], followed by a reaction with a lithium phosphorus compound is now a common procedure. A serious problem is the removal of Zn [23] or Sn [24] compounds from the macroporous polymers. An undesired side reaction is substitution in the backbone of the polymer or at the ortho positions of the phenyl group in the polymer at higher substitution ratios [25].

We selected a modified functionalization procedure by using $BF_3.Et_2O$ as catalyst, which can be easily removed from the polymer after the reaction, and moreover gives less undesired substitutions [18].

Initially, hydroformylation experiments with catalysts prepared via chloromethylation exhibited a very rapid deactivation of the catalysts. Comparative experiments with physically adsorbed rhodium complexes, both on XAD-2 and on chloromethylated XAD-2 proved the chloromethyl group to be responsible for the rapid deactivation, which can be ascribed to a reaction between the chloromethyl and a phosphine group, resulting in the formation of a phosphonium compound (Figure 3). The occurrence of such a reaction is known for low cross-

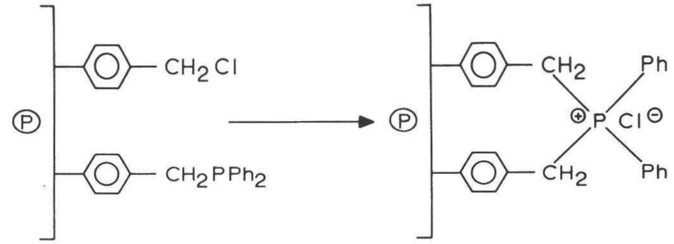

Figure 3 Phosphonium compound formation of anchored ligand (also possible for PPh_3).

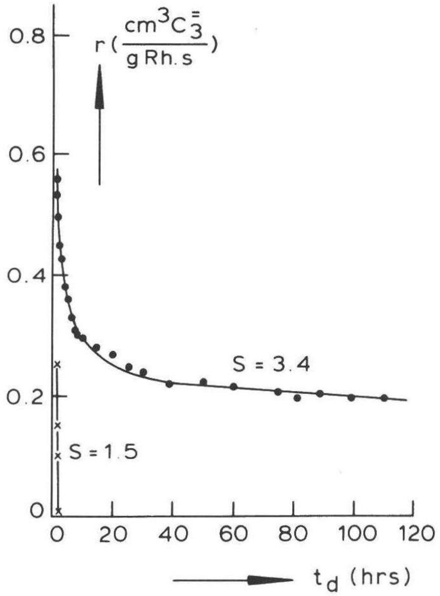

Figure 4 Influence of treatment with phenyl lithium of chloromethylated catalyst, before (x) and after (●) refluxing with PhLi for 3 hrs.
$t = 90^{o}C$; $C_3^{=}/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; XAD-2 as a support. x : W/F = 40.9 mg Rh.s/cm^3 $C_3^{=}$; P = 2.10%; Rh = 0.081%; Cl = 1.67%. ● : W/F = 88.6 mg Rh.s/cm^3 $C_3^{=}$; P = 2.10%; Rh = 0.165%; Cl = 0.67%.

linked polymers applied in the liquid phase [26].

Despite a low chlorine substitution and an excess of $LiPPh_2$ we were not able to convert the chlorine totally during the functionalization.

After functionalization the remaining chlorine could be removed by treatment with PhLi or BuLi. We refluxed a polymer containing chloromethyl and diphenylphosphine groups with a solution of PhLi for 3 hrs. Figure 4 shows that the stability of the catalyst is dramatically improved by this treatment. The slow deactivation is due to a small amount of chlorine still left in the polymer. Besides an improvement in stability an improvement in selectivity has been noticed.

2.4.2 Functionalization by chlorophosphonation

Attempts to functionalize XAD-2 with other phosphines and phosphites than diphenylphosphine resulted in a lower substitution of the chloromethyl group. The lithium phosphorus compounds used are prepared from the corresponding chloro phosphorus compounds, which are prepared from phosphorus trichloride. In order to immobilize a variety of phosphorus compounds we decided to first immobilize phosphorus trichloride on the polymer and subsequently substitute the chlorines for phenyl, phenoxy or methoxy groups.

All published procedures to immobilize PCl_3 on polystyrene resins are based on Friedel-Crafts reactions with aluminium trichloride as a catalyst [6,26-30]. Following Haag and Whitehurst's procedure we obtained an unstable catalyst [6]. The catalyst is prepared by first reacting $PCl_3/AlCl_3$ at 97°C with XAD-2 and then, after extraction of the aluminium compounds, reacting with PhLi. Analysis of the brown coloured catalyst showed a high amount of aluminium left in the polymer (0.75%). Therefore $AlCl_3$ was replaced by $BF_3.Et_2O$. Figure 5 shows that now a stable highly active catalyst is obtained, although with a lower selectivity. Remarkably, the PPh_2 coverage is in the $BF_3.Et_2O$ prepared catalyst lower than in the $AlCl_3$ prepared catalyst. In general a higher phosphine coverage stabilizes the catalyst [4,31]; apparently this is not true for the $AlCl_3$ prepared catalyst, the phosphines are not able to stabilize the catalyst.

The PPh_2 coverage of all of our $BF_3.Et_2O$ prepared catalysts is rather low. The highest coverage is obtained for extracted XAD-2 resins treated with $BF_3.Et_2O$ at 50°C for 2 hrs. Other conditions result in a much lower PPh_2 coverage, which is due to an important side reaction of the chlorophosphonated polymer [32].

$$2\ \text{Ⓟ}\text{-PCl}_2 \longrightarrow \text{Ⓟ}_2\text{-PCl} \quad + \quad \text{PCl}_3$$

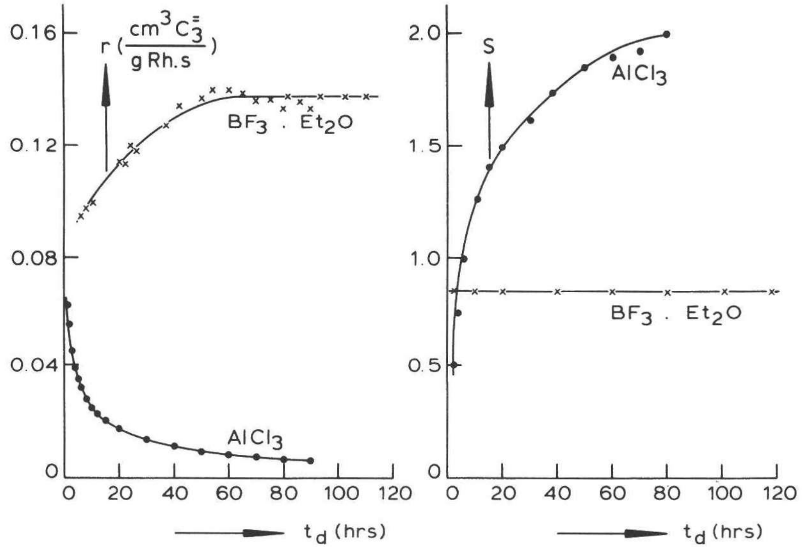

Figure 5 Influence of the type of Friedel-Crafts catalyst ($AlCl_3$ (●) and $BF_3.Et_2O$ (x)) in the chlorophosphonation of XAD-2 on the catalytic performance.
t = 90°C; $C_3^=/H_2/CO = 1/1/1$; P_t = 0.1 MPa; XAD-2 (extracted) as a support with anchored PPh_2.
●: W/F = 176.3 mg Rh.s/cm^3 $C_3^=$; P = 3.73%; Rh = 0.32%; Al = 0.75%; P/Rh = 38.7.
x: W/F = 15.0 mg Rh.s/cm^3 $C_3^=$; P = 0.38%; Rh = 295 ppm; P/Rh = 42.8.

2.4.3 Coupling of the rhodium complex to the support

$RhHCO(PPh_3)_3$, dissolved in toluene, is anchored to the support by exchange of one of its PPh_3 ligands for the immobilized PPh_2 ligand (Figure 6) [4]. From EXAFS studies we know that the rhodium coordinates with one anchored ligand only [33]. Furthermore, Wilkinson and coworkers showed that, especially in the absence of PPh_3, we run the risk of dimerization of the complex under evolution of hydrogen [34].

Generally, nitrogen is applied as the shelter gas during the exchange reaction, but in doing so we observed a colour change of the complex solution from yellow to red, which is, according to Wilkinson [34], the result of

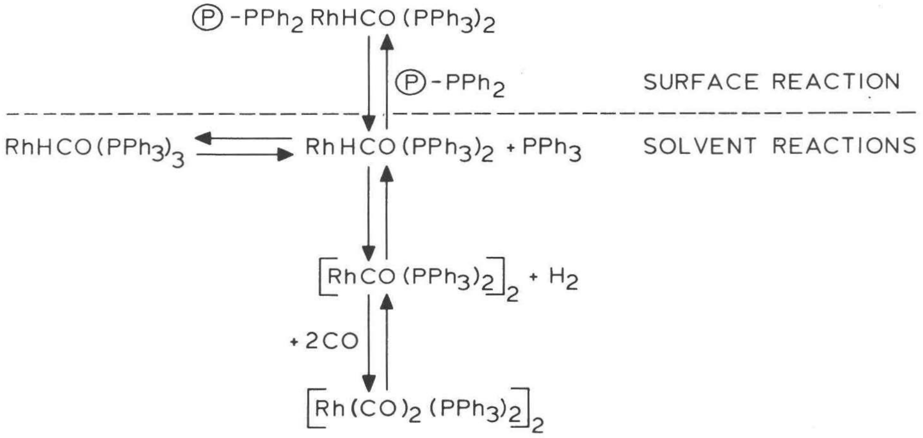

Figure 6 Equilibria occurring in the exchange reaction of $RhHCO(PPh_3)_3$, dissolved in toluene, with the functionalized polymer.

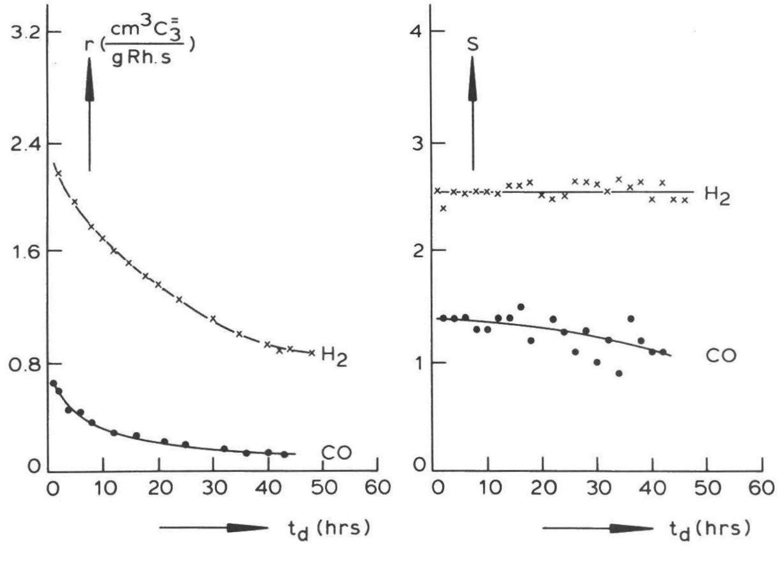

Figure 7 The influence of the choice of the shelter gas during the exchange of $RhHCO(PPh_3)_3$ with the functionalized XAD-2 resin. (x) under hydrogen, (●) under carbon monoxide. $t = 75^{\circ}C$; $C_3^{=}/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; x: $W/F = 13.51$ mg $Rh.s/cm^3$ $C_3^{=}$; $P = 0.19\%$; $Rh = 0.089\%$. ●: $W/F = 16.36$ mg $Rh.s/cm^3$ $C_3^{=}$; $P = 0.22\%$; $Rh = 0.067\%$.

rhodium dimer formation. Figure 7 shows that the choice of the shelter gas has a great influence indeed; with catalysts produced under hydrogen a much higher activity and selectivity level is arrived at than on applying carbon monoxide. In part II we will show that with this type of catalysts a perfect stable behaviour is arrived at. With nitrogen a similar behaviour as with carbon monoxide is observed.

In the preparation of our catalysts, dimerization was further suppressed by adding excess PPh_3 to the complex solution; a $PPh_3/RhHCO(PPh_3)_3$ ratio of three was chosen.

2.4.4 Laser-Raman spectroscopy

The laser-Raman spectrum of extracted XAD-2 (Figure 8) shows a very intense band at 1636 cm^{-1}, which can be ascribed to a vinyl group in the polymer [35]. Figure 8 shows a lowering of the 1636 cm^{-1} band intensity on functionalization of XAD-2 with PPh_2 ligands (-40%, calculated with the 1006 cm^{-1} band as a reference). This must be due to the partial disappearance of vinyl groups after chlorophosphonation. The assignment of the other bands in the spectrum is given in Table I [35].

Table I Assignment of bands in laser-Raman spectrum of XAD-2.

Band (cm^{-1})	Assignment
645, 800	para disubstitution
1006	breathing vibration of benzene ring
1190, 1240	para disubstitution
1320	bend vibrations of CH_2 and CH_3
1410, 1450	disubstitution
1590, 1612	C-C stretch vibrations of benzene ring
1636	C=C stretch vibration of vinyl group
2910	C-H stretch vibrations
3006, 3060	C-H stretch vibrations of benzene ring

In the synthesis of XAD-2 and XAD-4, 20 mol % *p*-divinylbenzene (a 50% solution in *p*-ethylstyrene) is mixed with styrene in a 1:3 ratio and polymerized [36]. Hence the polymer contains *p*-ethylphenyl groups, not available

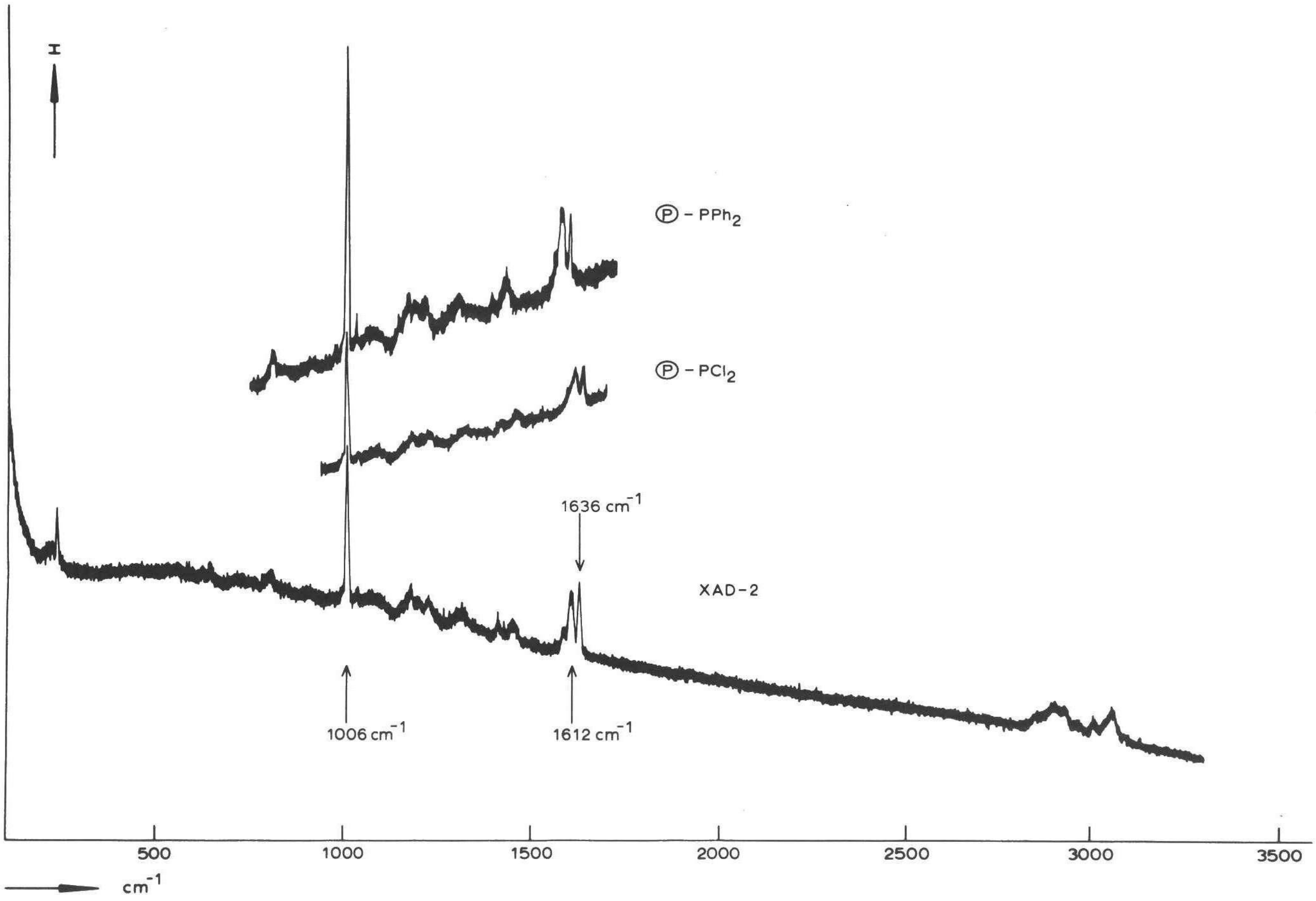

Figure 8 Laser-Raman spectra of XAD-2 (extracted) and XAD-2 functionalized with PCl_2 and PPh_2.

for functionalization. The bands at 645 cm^{-1} and between 1150 cm^{-1} and 1500 cm^{-1} prove the presence of these ethyl groups in the polymer. The strong vinyl band at 1636 cm^{-1} implies that part of the *p*-divinylbenzene did not polymerize completely. It is likely, for steric reasons, that one out of two vinyls did not polymerize due to the high percentage of crosslinking agent.

Figure 9 represents the functional groups at the surface of the resin; it is conceivable that, on functionalization of the polymer, the functionalization agent will not only react with the phenyl, but also with the vinyl and/or the ethyl group and/or with the polymer backbone. Under rigorous conditions substitution will even take place at the ortho positions of the phenyls. The degree of substitution will depend on the reactivity of the functionalization agent.

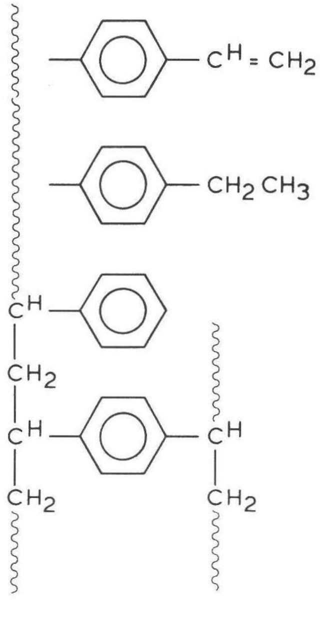

Figure 9 Functional groups in XAD-2.

In order to quantify the amount of unsaturates (vinyls) in the polymer we calculated the bromine number of the polymers XAD-2 and XAD-4, of a chloromethylated and of a chlorophosphonated XAD-2 and of two spent catalysts prepared via the above mentioned procedures. A modified method of Wijs [22] was used, with ICl as a reagent; the calculated bromine numbers are presented in Table II.

Table II Bromine numbers obtained by reaction with ICl.

Sample		I (w%)	Cl (w%)	bromine number	$\frac{\text{mmol } Br_2}{\text{g polymer}}$
XAD-2		8.89	2.12	10.4	0.65
XAD-2 (extracted)		9.76	2.42	11.6	0.73
XAD-4		4.76	0.97	5.1	0.32
XAD-2 CH_2PPh_2	(2.71%P)	4.86	1.39	6.2	0.39
XAD-2 PPh_2	(0.09%P)	4.95	1.52	6.6	0.41
XAD-2 CH_2PPh_2 cat.	(2.10%P)	5.46	1.40	6.6	0.41
XAD-2 PPh_2 cat.	(0.54%P)	4.73	1.75	6.9	0.43

The theoretical bromine number of XAD-2 will be 27.7 assuming that of each *p*-divinylbenzene molecule only one vinyl group has polymerized. Hence, we may conclude from Table II that either 40% of the *p*-divinylbenzene did not polymerize completely or dehydrogenation of the ethylstyrene has occurred during the radical polymerization reaction. Functionalization affects the vinyl groups and lowers the bromine number by 40%, in accordance with our laser-Raman results. Obviously, in both functionalization methods $BF_3.Et_2O$ reacts with the vinyl groups to hitherto undefined products. We also notice that after anchoring a rhodium complex to the support and using such a catalyst in the hydroformylation of propylene the bromine number does not change. As a result the vinyl group does not react with any species during hydroformylation.

It should be noted that the rhodium phosphine complex can coordinate to the vinyl group as well as to the functionalized ligands. It is also possible to anchor a rhodium complex to nonfunctionalized XAD resins; despite the absence of anchored ligands stable catalysts are obtained in such case [37].

2.4.5 Texture of supports and catalysts

BET surface areas and pore size distributions were determined from the physical adsorption and capillary condensation of nitrogen at -196°C. The analysis of the adsorption and desorption isotherms is performed according to the methods of Broekhoff [38,39]. In the determination of the pore shape we use the classification of pore shapes introduced by De Boer [40]. Mercury penetration was used to determine macropore size distributions.

Figure 10 shows the adsorption and desorption isotherm of nitrogen at

$-196^{o}C$ for XAD-4 after a pretreatment of the powdered sample at $90^{o}C$ *in vacuo* for 16 hrs. From the adsorption part of the isotherm (up to $p/p_o = 0.3$) a BET surface area of 788 m^2/g is calculated, taking for the cross-sectional area of a N_2 molecule 0.162 nm^2. The observed hysteresis loop in Figure 10 points to the presence of ink-bottle type cavaties, according to De Boer's classification. From electron microscopy [41] we know, that in reality we are dealing with a loose packing of polymer spheres. It is known that such porous substances behave like spherical cavaties interconnected by small channels, and hence they can roughly be compared with the idealized ink-bottle shaped pores.

The pore size distribution in the range of pores from 3 to 30 nm was calculated from the adsorption branch of the isotherm. Figure 11 gives the cumulative pore volume of the ink-bottles as a function of the radii of the bottles. Likewise the pore size distribution was calculated from the desorption branch, and this distribution is related to the radii of the necks of the ink-bottles [38,40].

Figure 11 shows, that the pore size distribution of the necks is much smaller and at lower values of radii than the distribution of the radii of the bottles. This is in accordance with electron microscopic observations.

The adsorption branch of the isotherm is represented in Figure 12 in the form of a so-called *t*-plot [38]. It is interesting to note that this plot is not in accordance with what might be expected of materials obeying the "common *t*-curve", like most other support materials (oxides, graphite, activated carbon). The non-linearity of the *t*-plot together with the negative intercept with the V_{ads}-axis is characteristic for materials with non-polar surfaces like polyethylene and PTFE [38], on which the adsorbability of nitrogen is relatively low.

Interesting additional information is obtained from the mercury penetration curve of XAD-2 (Figure 13). This result reveals that at radii above 30 nm a macroporous system is present with a pore volume of about 0.30 cm^3/g, which makes the support easily accessible for the reactants and the functionalization agents.

The influence which the catalyst preparation has on the texture of the support was studied for samples functionalized via chloromethylation of XAD-2. Figure 14 gives the pore size distributions of XAD-2 and functionalized XAD-2 in the different stages of the catalyst preparation. The distributions are calculated from the adsorption branch of the nitrogen capillary condensation isotherms and they relate, in the same way as XAD-4, to the bottle radius of the ink-bottles.

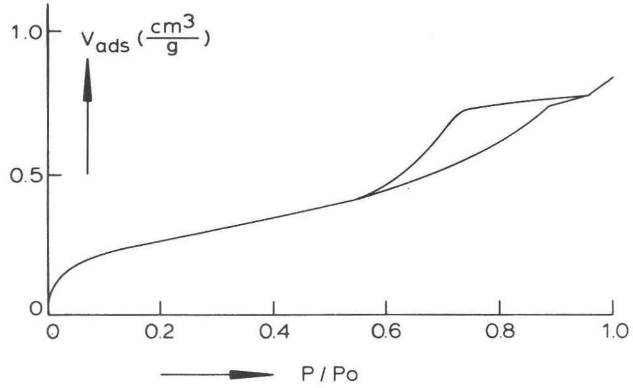

Figure 10 The adsorption and desorption isotherm of nitrogen at -196°C for XAD-4.

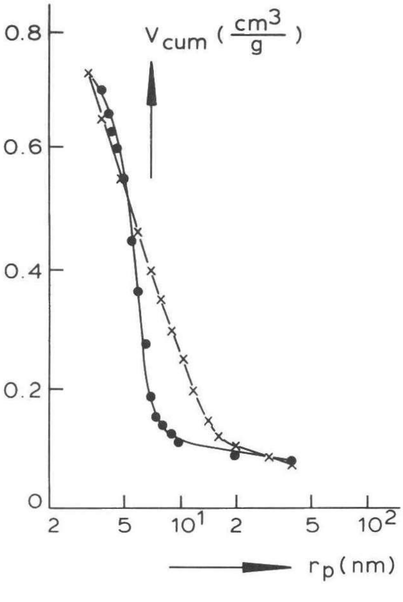

Figure 11 Pore size distribution of XAD-4 as determined by nitrogen capillary condensation at -196°C.
x: adsorption branch; ●: desorption branch.

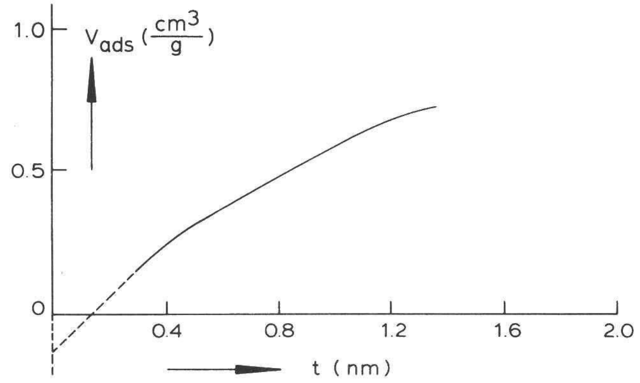

Figure 12 Total volume adsorbed vs. layer thickness for XAD-4 (*t*-plot).

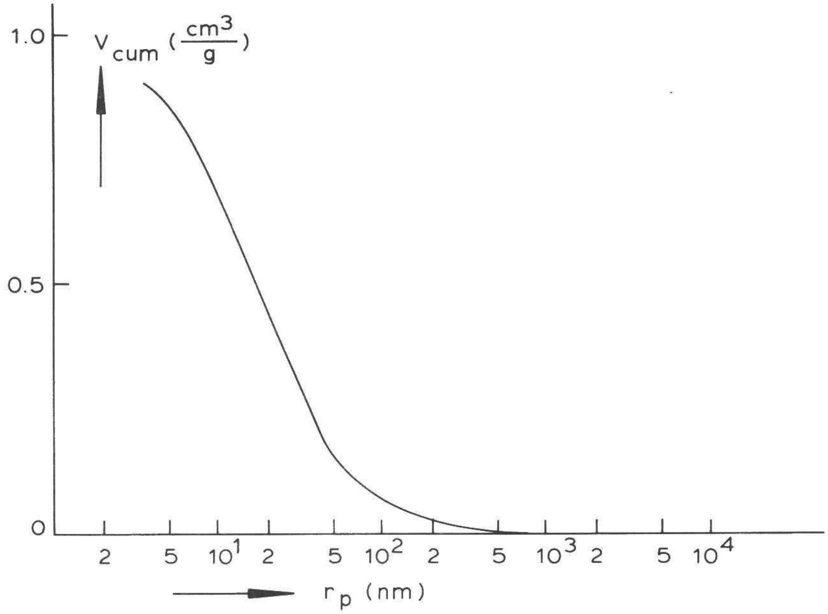

Figure 13 Pore size distribution of XAD-2 as determined by mercury porosimetry.

Figure 14 shows that by chloromethylation of XAD-2 the pore volume is reduced to about the same extent over the whole range of pores. This means, that the chloromethyl groups are homogeneously distributed over the support surface. Subsequent reaction with lithium diphenylphosphine, giving bulky anchored diphenylphosphine groups, further reduces the pore volume to about the same extent, also quite homogeneously. Coupling a relatively small amount of rhodium complex to the functionalized support hardly further changes the pore size distribution. In Table III the BET surface areas of these samples are given. The results support the conclusions obtained from the pore size distributions.

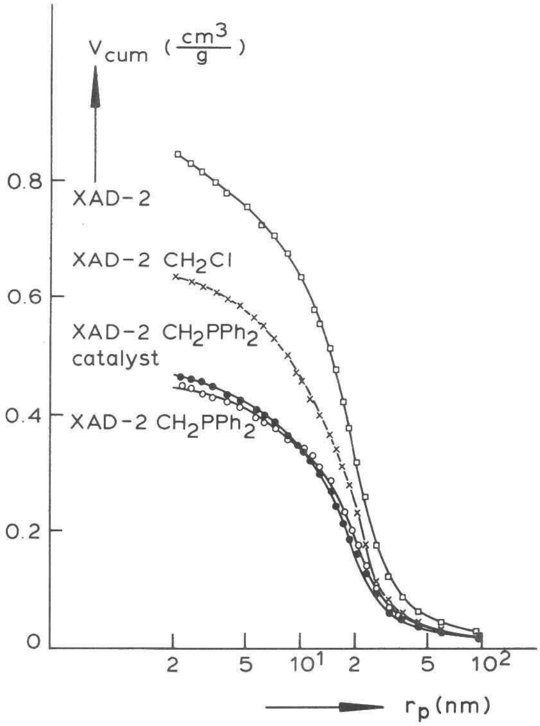

Figure 14 The influence of functionalization via chloromethylation on the pore size distribution of XAD-2, as determined from nitrogen capillary condensation at -196°C.
□: XAD-2; x: XAD-2 CH_2Cl, 4.17% Cl; o: XAD-2 CH_2PPh_2, 2.71% P;
●: XAD-2 CH_2PPh_2 catalyst, 2.10% P, 0.081% Rh.

Table III reveals that there is a relation between the phosphorous content of the polymer and the lowering of the surface area. The catalysts prepared via chloromethylation have a lower surface area than comparable catalysts prepared via chlorophosphonation.

Because of the similarities in the functionalization reaction there are reasons to believe that diphenylphosphine ligands anchored via chlorophosphonation, are also homogeneously distributed over the support surface. It is also seen that catalysts with physically adsorbed PPh_3 have a much lower surface area than catalysts with chemically anchored phosphines.

Table III BET surface area of various supports and catalysts.

Sample[a]	S_{BET} (m^2/g)[b]
XAD-4	788
XAD-4 PPh_2 catalyst (0.31% P, $BF_3.Et_2O$)	712
XAD-2	345
XAD-2 CH_2Cl (4.17% Cl)	284
XAD-2 CH_2PPh_2 (2.17% P)	159
XAD-2 CH_2PPh_2 catalyst (2.10% P, 0.081% Rh)	168
XAD-2 PPh_2 catalyst (0.38% P, $BF_3.Et_2O$)	338
XAD-2 PPh_2 catalyst (3.73% P, $AlCl_3$)	250
XAD-2 PPh_3 catalyst (0.063% P)[c]	322
XAD-2 PPh_3 catalyst (0.166% P)[c]	243
XAD-2 PPh_3 catalyst (0.52 % P)[c]	182

[a] All samples evacuated at 150°C for 3 hrs.

[b] Corrected if necessary for weight increase due to functionalization.

[c] Prepared by immobilization of $RhHCO(PPh_3)_3$ on XAD-2 and after addition of PPh_3, which is physically adsorbed.

2.5 CONCLUSIONS

Macroreticular resins, functionalized via chloromethylation and especially those functionalized via chlorophosphonation, are very well suited as supports for chemically anchored rhodium complexes in the hydroformylation of alkenes at the solid/gas phase boundary.

The method of preparation of the catalyst particularly influences the total catalytic performance. In the preparation of the catalysts it is of importance that remaining chlorine is thoroughly removed. With $BF_3.Et_2O$ as the Friedel-Crafts catalyst much better results are arrived at as with $AlCl_3$, especially with respect to the stability of the catalyst.

Laser-Raman spectroscopy, and also the reaction with ICl, show that the surface of macroreticular polystyrene-divinylbenzene resins is partly covered with unpolymerized vinyl groups, which may take part in the functionalization reactions.

From the study of the texture of the various intermediate forms leading to the finaly catalyst it follows that the original support texture is not affected during the catalyst preparation. The changes in BET surface area and pore size distribution observed can be ascribed to expected volume reductions.

In the second part of this series a more detailed study of the catalytic performance will be presented. Special attention will be given to aspects such as stability, activity per g of rhodium, and selectivity for the formation of *n*-butyraldehyde in the hydroformylation of propylene. Also the influence of the anchored ligand coverage and of the addition of excess PPh_3 will be dealt with.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

A_i	peak area of component i	a.u.
Cl	chlorine content	w%
F	flow of propylene at 0.1 MPa and 25°C	cm^3/s
P	phosphorus content	w%
P/Rh	molar phosphorus to rhodium ratio	mol/mol
P_t	total pressure	MPa
R	response factor	----
Rh	rhodium content	w%
r	reaction rate	cm^3/g Rh.s
r_p	pore radius	nm
S	selectivity n/iso ratio	mol/mol

S_{BET}	BET surface area	m^2/g
t	reaction temperature	^oC
t_d	streamtime	hrs
V_{ads}	adsorbed volume of liquid N_2 at -196^oC	cm^3/g
V_{cum}	cumulative pore volume	cm^3/g
W	weight of rhodium metal in the reactor	g

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CHAPTER 3

GAS PHASE HYDROFORMYLATION OF PROPYLENE WITH POROUS RESIN ANCHORED RHODIUM COMPLEXES

Part II. The catalytic performance*)

by

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3.1 SUMMARY

Hydridocarbonyltris(triphenylphosphine)rhodium(I) chemically anchored via phosphine or phosphite ligands to the surface of macroreticular polystyrene-divinylbenzene is successfully applied in the heterogeneous gas phase hydroformylation of propylene at 90°C and 0.1 MPa total pressure.

Catalysts prepared via chlorophosphonation are stable; at a conversion of 0.9% no deactivation is observed over a period of more than 500 hrs. Catalysts prepared via chloromethylation deactivate slightly, but have a higher selectivity for *n*-butyraldehyde than those prepared via chlorophosphonation. The hydroformylation activity per unit weight of rhodium, for catalysts with anchored diphenylphosphines prepared via chlorophosphonation, decreases with increasing phosphorus ligand coverage.

Addition of a small amount of triphenylphosphine to a catalyst with chemically anchored ligands raises the selectivity for *n*-butyraldehyde formation. The influence of the type of the anchored ligand on the catalytic performance will be discussed.

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3.2 INTRODUCTION

In part I of this series [1] the preparation and characterization of porous resin anchored rhodium complexes are discussed. Moreover, the methods of functionalization of macroreticular polystyrene-divinylbenzene with phosphine and phosphite ligands through chloromethylation and chlorophosphonation are presented and correlated with the performance of the catalyst in the heterogeneous gas phase hydroformylation of propylene.

Hardly any work has been published on the heterogeneous gas phase hydroformylation of alkenes with polymer anchored rhodium complexes. Arai studied the hydroformylation of several alkenes with rhodium phosphine complexes chemically anchored to a polymer coated silica [2]. He found a very low hydroformylation activity, accompanied by an appreciable alkane byproduct formation, and no information is given on the stability of the catalyst.

Most other publications on the heterogeneous gas phase hydroformylation of alkenes deal with the application of supported liquid phase catalysts [3-7] and of physically adsorbed catalysts [8-10]. Only in the case of supported liquid phase catalysts with e.g. triphenylphosphine as the solvent, highly stable, active and selective catalysts were obtained [5-7]. A possible drawback of such a system in high temperature applications is the gradual evaporation of the solvent, and chemical anchoring of the ligand to the support might prevent this. Another advantage of chemical anchoring of one of the ligands to a support is the suppression of migration of the rhodium complex over the support surface. The difficulty of migration was encountered by Spek in his study of physically adsorbed catalysts [8].

In the present paper a study is presented on the catalytic performance of polymer anchored rhodium complexes at 90°C and 0.1 MPa in the gas phase hydroformylation of propylene. The effect of the addition of triphenylphosphine to the catalysts will also be discussed.

3.3 EXPERIMENTAL

The preparation and characterization of the catalysts as well as the method of determining their catalytic performance and the chemicals used are given in part I of this series [1]. The relevant data characteristic for the catalysts are summarized in Table 1.

Table I The catalysts

Catalyst[a]	Anchored ligand	θ[b]	Anchored P (w %)	Total P[c] (w %)	[Rh] (ppm)	P/Rh[d] (mol/mol)	
PS-6	PPh_2	0.14	0.30	0.30	289	25.4	
PS-13	$P(OMe)_2$	0.05	0.12	0.19	1290	3.1	(4.9)
PS-14	$P(OPh)_2$	0.06	0.13	0.19	893	4.8	(7.3)
PS-15	PPh_2	0.09	0.19	0.23	496	12.7	(15.4)
PS-18	PPh_2	0.09	0.19	0.89	273	23.1	(108.3)
PS-20	PPh_2	0.03	0.07	0.84	265	8.8	(105.3)
PS-25*	PPh_2	0.05	0.12	0.12	172	21.9	
PS-27*	PPh_2	0.17	0.38	0.38	295	42.8	
PS-30*	PPh_2	0.12	0.26	0.26	297	26.4	
PS-31*	PPh_2	0.23	0.52	0.52	575	30.0	
PS-37*	PPh_2	0.17	0.37	0.37	339	36.3	
PS-40	CH_2PPh_2	0.51	1.14	1.14	775	48.9	
PS-41	CH_2PPh_2	0.95	2.10	2.10	1650	42.3	
PS-41II	CH_2PPh_2	0.95	2.10	2.19	1500	46.5	(48.5)

[a] All catalysts have XAD-2 as the support. The catalysts marked with an asterisk are prepared from XAD-2 resin, purified by extraction [1].

[b] θ, the estimated surface coverage with anchored ligands is calculated from:

$$\theta = \frac{(\text{mol P/g support})\cdot N_{av}\cdot S_{ligand}}{S_{BET}\text{ of XAD-2}}$$

S_{ligand} = cross-sectional surface area of a PPh_2 or CH_2PPh_2 anchored ligand, $0.80\ 10^{-18}\ m^2$.

S_{BET} = BET surface area of XAD-2, $345\ m^2/g$.

N_{av} = Avogrado's number, $6.02\ 10^{23}$ molecules/mol.

[c] A difference between "total P" and "anchored P" in the table is due to additional PPh_3, added by wet impregnation after coupling of the rhodium complex.

[d] The chemically anchored phosphorus/rhodium ratio, which is also the total phosphorus/rhodium ratio without the addition of PPh_3. Between brackets the *total* phosphorus/rhodium ratio is given in case of additional PPh_3.

3.4 RESULTS AND DISCUSSION

3.4.1 Comparison with other immobilized catalysts

The catalytic performance in the hydroformylation of propylene, as a function of streamtime (t_d), for two typical anchored rhodium complexes, viz. a catalyst prepared via chlorophosphonation and a catalyst prepared via chloromethylation, is shown in Figure 1. By way of comparison the activity and selectivity of XAD-2 supported liquid phase catalyst (SLP-catalyst) with PPh_3 as the "solvent ligand" are also given (liquid loading = 0.66, 3.78% P, 0.15% Rh, P/Rh = 81.4, particle diameter 0.42-0.50 mm). The latter catalyst has been prepared after the method of Gerritsen [6,7].

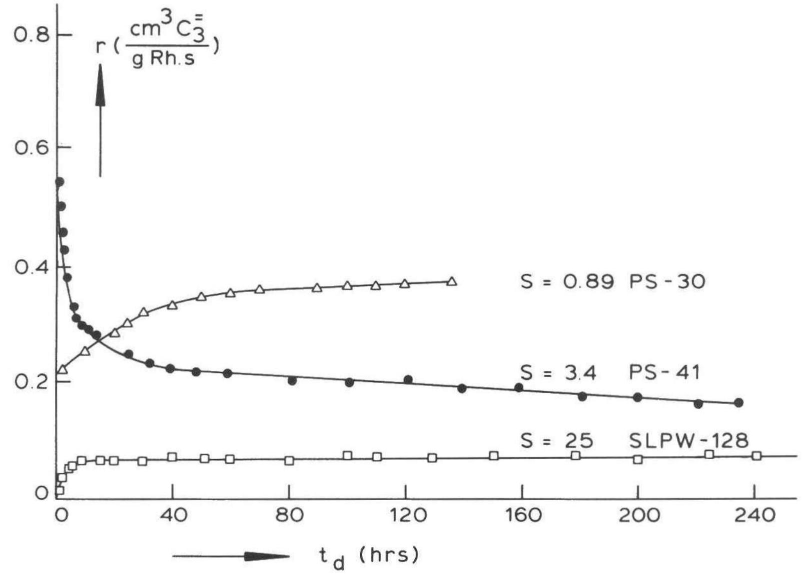


Figure 1 Catalytic performance in hydroformylation of propylene of PS-30 (prepared via chlorophosphonation, Δ), of PS-41 (prepared via chloromethylation, ●) and of SLPW-128 (supported liquid phase system, □).
$t = 90^oC$; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; W/F = 14.35 (Δ), 88.56 (●) and 29.95 (□) mg $Rh.s/cm^3\ C_3^=$.

Figure 1 shows that after 135 hrs streamtime catalyst PS-30 is, per gram of rhodium, five times as active as the SLP-catalyst (SLPW-128) and has twice the activity of PS-41. The time-dependency of the activity of the catalysts is remarkable: SLPW-128 is stable during the whole testperiod and the activation time is short; PS-30 shows an activation of 60% during the first 40 hrs and later on an additional slow activation of 10%; PS-41 on the other hand deactivates to 40% of its original activity over the first 40 hrs and further to 30% during the next 200 hrs. The deactivation of PS-41 is thought to be due to a quaternization reaction of excess chloromethyl groups with phosphine ligands of the complex, as explained in part I of this series [1]. This poisoning side-reaction proceeds gradually under the reaction conditions during hydroformylation.

The selectivity of the three catalysts is time-independent, and aldehydes are formed exclusively. Generally speaking, with increasing phosphine ligand coverage and with increasing amounts of free PPh_3 added, the selectivity for *n*-butyraldehyde formation increases. The very high selectivity of the SLP catalyst is due to the presence of excess liquid PPh_3; otherwise, this excess also partly explains its lower activity. Another reason for the lower activity is the low rhodium efficiency of the SLP catalyst; the rhodium complexes active in hydroformylation are mainly located in the liquid PPh_3-gas phase boundary. The gradual rise in activity with time of catalyst PS-30 cannot be ascribed to a change in the nature of the rhodium complex, as the selectivity is constant. Probably it should be attributed to a gradual improvement of the accessibility of the active sites through surface migration.

In Table II we compare our anchored systems with various other immobilized rhodium complexes as to activity and selectivity in propylene hydroformylation. Except for catalyst A all measurements are performed at the same temperature and total pressure and data as provided by the authors are tabulated. Catalyst A is studied under deviating conditions at 130°C and at a feed composition of $C_3/H_2/CO = 3/3/1$. Under these conditions Arai observed a substantial alkane formation.

In general the activity per g of rhodium is much higher for our catalysts than for the other immobilized systems. Especially Arai's anchored catalyst A [2] shows a much lower activity; after correction for the difference in temperature and in feed composition the activity is even lower than indicated in Table II. The activity of the physically adsorbed catalyst B, studied by Spek [8,11], is 2-4 times lower, but its selectivity is about equal.

It is of interest to note that rhodium clusters on ZnO (Table II C and D) [12] show an activity 15-80 times lower than that of our systems, but a selectivity of the same order, despite the absence of phosphine ligands. Little can be said on the *stability* of the various systems; most authors do not provide any information on this important aspect.

The higher activity level of our chemically anchored catalysts is first of all due to the better rhodium dispersion. By anchoring phosphine ligands to the support, which, as appears from our texture study [1], are molecularly dispersed over the surface, all rhodium sites are available for catalytic action. However, anchored phosphine ligands are not able to improve the selectivity for *n*-butyraldehyde formation to the same high level as free physically adsorbed PPh_3 does, the anchored ligands are localized and unable to coordinate to the rhodium centre.

3.4.2 Catalysts prepared via chloromethylation

In Figure 2 the catalytic performance of three catalysts with anchored diphenylphosphine ligands prepared via chloromethylation (see also Table I) is shown. In the preparation catalyst PS-40 is refluxed with *n*-butyllithium, whereas PS-41 is refluxed with phenyllithium. Despite a higher chlorine content left in PS-41 (0.67% Cl against 0.43% Cl), this catalyst shows a slower rate of deactivation than PS-40. Obviously, treatment with phenyllithium is much more effective than treatment with *n*-butyllithium in preventing chloromethyl groups to react with rhodium phosphine complexes. The more bulky character of the phenyl group might be responsible for this effect. For PS-41 the selectivity is higher than for PS-40, which may be ascribed to the higher phosphorus content of PS-41 (2.10% against 1.14%).

After a test period of 400 hrs (final activity 0.10 cm^3 $C_3^=$/g Rh.s) catalyst PS-41 was taken from the reactor and treated with a solution of PPh_3 in diethyl ether (1.2 g in 100 ml) for 0.5 hr, in order to enrich the catalyst with a known amount of PPh_3. After collection by filtration the catalyst (now indicated as PS-41 II) was dried for 1 hr at 90°C in a hydrogen atmosphere. An amount of 0.09% P in the form of PPh_3 was added. Then PS-41 II was tested in hydroformylation. An initial raise in activity due to PPh_3 addition from 0.1 (final activity of PS-41) to 0.25 cm^3 $C_3^=$/g Rh.s is found, but the deactivation again proceeds in the same manner as for PS-41 (Figure 2). After 40 hrs the rate of deactivation is the same for both catalysts. The advantage of addition of PPh_3 lies in an increase in selectivity (from 3.4 to 5.7), on addition of 2 mol PPh_3/mol Rh (see Table I, last column).

Table II Comparison of our anchored rhodium complexes with other immobilized rhodium complexes with respect to the catalytic performance in hydroformylation of propylene.

Catalyst[a]	P/Rh ($\frac{mol}{mol}$)	P_t (MPa)	Temp. °C	r ($\frac{cm^3 C_3^=}{g\ Rh.s}$)	*n*-Bu[b] (mol %)	Stability[c]
PS-30	26.4[e]	0.1	90	0.37	47.1	+
PS-41	42.3[e]	0.1	90	0.19	77.3	±
SLPW-128	81.4	0.1	90	0.075	96.1	+
A	?	0.1	130	0.0065	22.4	?
B	2	0.1	90	0.0825	60.4	+[d]
C	0	0.1	90	0.0124	60	?
D	0	0.1	90	0.0047	72	?

[a] PS-30 = anchored $RhHCO(PPh_3)_3$ prepared via chlorophosphonation (see Table 1 of this paper).

PS-41 = anchored $RhHCO(PPh_3)_3$ prepared via chloromethylation (see Table 1 of this paper).

SLPW-128 = supported liquid phase catalyst with XAD-2 as a support and PPh_3 as the ligand solvent (Figure 1 of this paper).

A = $RhCl(CO)_2$ anchored to polystyrene coated silica through phosphine ligands [2].

B = $Rh(\pi\text{-allyl})CO(PPh_3)_2$ physically adsorbed on γ-alumina 000-3P [8,11].

C = $Rh_4(CO)_{12}$ cluster supported on ZnO [12].

D = $Rh_6(CO)_{16}$ cluster supported on ZnO [12].

[b] *n*-Bu: mol % *n*-butyraldehyde in the converted part of propylene.

[c] Stability: + = stable; ± = slightly deactivating; ? = unknown.

[d] At the higher total pressures of 1.2 and 1.6 MPa this catalyst deactivates [9,13].

[e] Note that PS-30 and PS-41 contain chemically anchored PPh_2, whereas SLPW-128 only contains physically adsorbed and capillary condensed PPh_3.

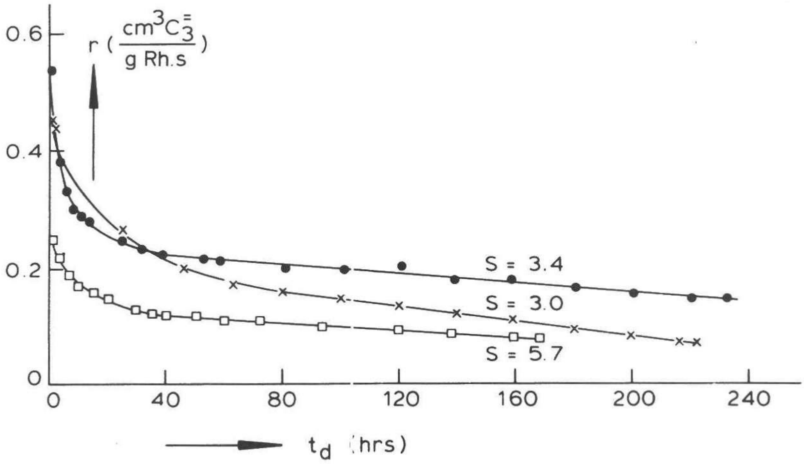


Figure 2 Catalytic performance of catalysts prepared via chloromethylation.
x: PS-40 (0.43% Cl); ● = PS-41 (0.67% Cl); □ : PS-41 II (0.66% Cl); t = 90°C; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; W/F = 25.92 (x), 88.56 (●) and 78.80 (□) mg Rh.s/cm^3 $C_3^=$.

3.4.3 Catalysts prepared via chlorophosphonation

Six catalysts with anchored diphenylphosphine ligands were prepared via chlorophosphonation [1], with $BF_3.Et_2O$ as a Friedel-Crafts catalyst, and again these systems were tested in propylene hydroformylation. Results are shown in Figure 3 and listed in Table III (see also Table I for the analytical data of these catalysts). PS-6 (not shown in Figure 3), tested for 20 hrs, shows a stable activity of 0.24 cm^3 $C_3^=$/g Rh.s and a selectivity of 1.0.

The stability of all catalysts, prepared via chlorophosphonation, is high; catalyst PS-27 for instance, shows no sign of deactivation at a conversion of 0.9% over a period of more than 200 hrs (see Figure 3), but even after 500 hrs testing the activity was still at the same level and this holds for all other catalysts in Figure 3. PS-27 was tested in the temperature range from 70 to 100°C and from the results an apparent activation energy of 33.0 kJ/mol is calculated.

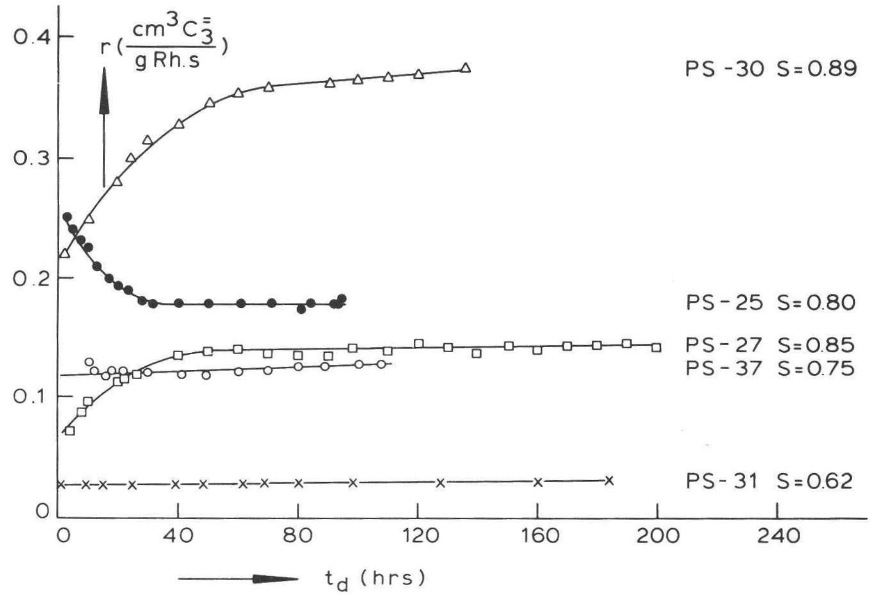


Figure 3 Performance of catalysts prepared via chlorophosphonation. $t = 90^{o}C$; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa.

Table III Results of the test of the catalytic performance of catalysts prepared via chlorophosphonation.

Catalyst[a]	θ[b]	Anchored P (w %)	r ($\frac{cm^3 C_3^=}{g\ Rh.s}$)	S ($\frac{mol}{mol}$)	P/Rh ($\frac{mol}{mol}$)	W/F ($\frac{mg\ Rh.s}{cm^3\ C_3^=}$)
PS-25	0.05	0.12	0.18	0.80	21.9	7.53
PS-30	0.12	0.26	0.37	0.89	26.4	14.35
PS-6	0.14	0.30	0.24	1.0	34.5	12.8
PS-37	0.17	0.37	0.13	0.75	36.3	20.4
PS-27	0.17	0.38	0.14	0.85	42.8	15.03
PS-31	0.23	0.52	0.033	0.62	30.0	26.04

[a] see also Table I.

[b] θ = estimated PPh_2 coverage.

Figure 4 shows that above $\theta = 0.1$ the final activity per g of rhodium decreases with increasing coverage θ, whereas the selectivity (Table III) is low and decreases slightly with increasing θ (only the activity of PS-25 does not show a clear correlation with θ. The phosphorus content of PS-25 is too low for an immediate stabilization of the catalyst; it deactivates in 30 hrs to a stable level).

For the decrease in activity with increasing θ no direct explanation is at hand. However, in Table III we see, that the selectivity decreases slightly with increasing θ, whereas the phosphorus to rhodium ratio does not influence the activity nor the selectivity. The rhodium complex is bound to one anchored ligand [1]; the decrease in activity with increasing θ cannot be due to a change in the number of anchored phosphine ligands coordinated to the rhodium complex, but must be due to a change in the nature of the anchored ligand as a function of θ_{PPh_2}. At low θ the more accessible phenyl groups in the surface of the resin have reacted with phosphorus trichloride and hence more accessible diphenylphosphine groups are available for coordination to rhodium. At higher values of θ less accessible anchored ligands are formed, which cannot have an ideal coordination to the rhodium, resulting in a lower activity for the hydroformylation reaction. This also explains the slightly lower selectivities observed at higher values of θ.

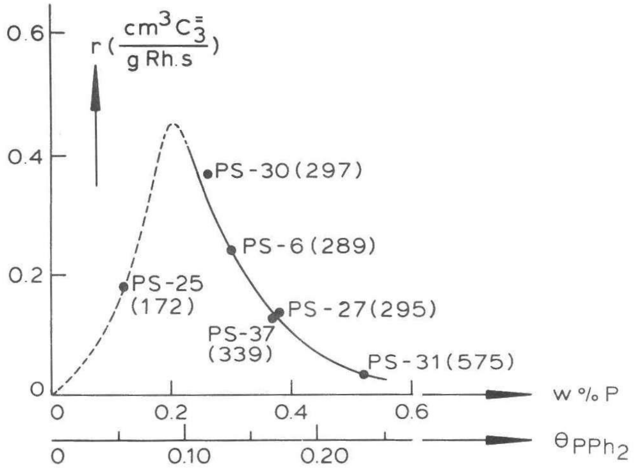
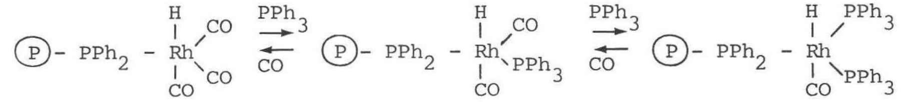


Figure 4 The final hydroformylation activity per unit weight of rhodium of catalysts prepared via chlorophosphonation, as a function of θ_{PPh_2}.
Dashed part: not measured; expected behaviour. The rhodium concentrations in ppm are indicated in the figure between parenthesis for each catalyst.

In order to test our catalyst system for a possible application in liquid phase hydroformylation the spent catalyst PS-30 was extracted in a Soxhlet apparatus with allyl alcohol under a 1:1 hydrogen/carbon monoxide atmosphere. In a period of 36 hrs the rhodium content of the catalyst decreased from 297 ppm to 57 ppm, whereas after 96 hrs of extraction the rhodium content was only 45 ppm. Hence, despite the stabilizing action of the anchored ligands in gas phase hydroformylation, they are not able to anchor the rhodium complex in liquid phase applications. Phtalocyanine systems are likely to be much more suitable for this purpose [14], but it is expected that due to stronger anchoring the catalytic activity will be lower.

3.4.4 The influence of additional triphenylphosphine

In part I of this series evidence was presented for the rhodium complex to be bound to one anchored ligand only [1,15]. Under our hydroformylation conditions the same situation will exist and this explains the low selectivities observed for the catalysts mentioned in the previous section. It is to be expected that on addition of PPh_3 a higher number of phosphine ligands is coordinated to the rhodium complex, and that a higher selectivity can be expected:



In section 3.4.2 we already demonstrated that the addition of an amount of PPh_3 molecules twice the number of Rh atoms to a catalyst prepared via chloromethylation improves the selectivity and to a smaller extent also the activity. We now performed the same treatment with two catalysts prepared via chlorophosphonation, though in this case an excess of PPh_3 was added. The performance of these catalysts is shown in Figure 5. PS-18 and PS-20 are freshly prepared catalysts, impregnated with a PPh_3 solution (2.5 g in 100 ml Et_2O) after coupling the complex to the support. In Table 1 the characteristic data of these catalysts are given.

Figure 5 shows that on addition of excess PPh_3 very active and selective catalysts are obtained. Although catalysts PS-18 and PS-20 have almost the same total phosphorus content they differ a factor of three in activity, which is apparently caused by the difference in anchored phosphine coverage (0.19% P for PS-18 and 0.07% P for PS-20). The dashed line in Figure 4 suggests that without addition of PPh_3, similar to PS-25, catalyst PS-20 will have a very low (instable) activity of 0.06, whereas catalyst PS-18 is expected to have an activity of 0.43 $cm^3\ C_3^=/g$ Rh.s. In the case of PS-20 the stability of the catalyst is improved upon addition of PPh_3; for both catalysts a remarkable improvement in activity as well as in selectivity is obtained.

It is of interest to remark, that the addition of two to three PPh_3 molecules per Rh atom (chemically anchored via diphenylphosphine ligands) to catalyst PS-15 also influences activity and selectivity in a positive sense (see hereafter, section 3.4.5).

In part III of this series the improvement in activity and selectivity will be discussed by comparing the performance of the above mentioned catalysts with that of catalysts without anchored phosphine ligands [16].

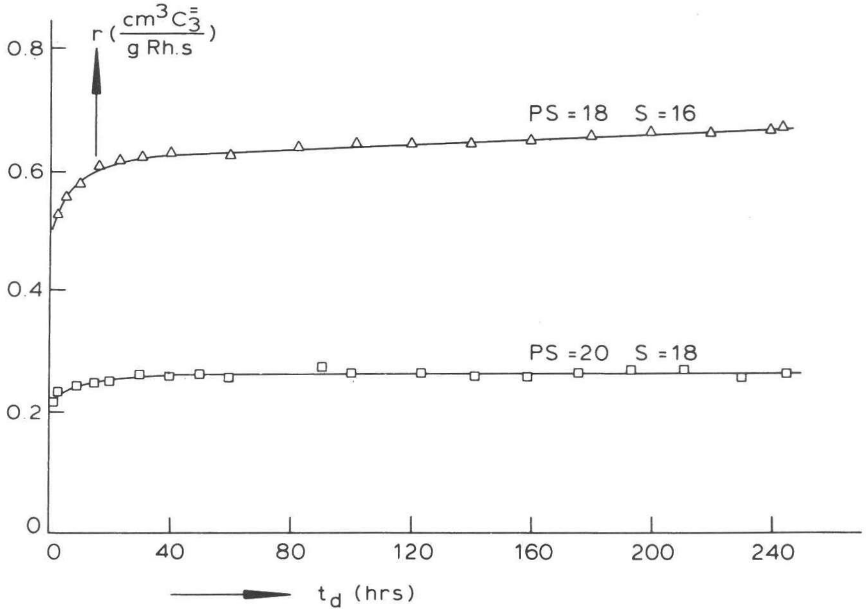


Figure 5 Catalytic performance of catalysts prepared via chlorophosphonation with additional triphenylphosphine.
$t = 90^oC$; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa. Δ: PS-18; □: PS-20; W/F = 13.16 (Δ) and 13.39 (□) mg Rh.s/$cm^3\ C_3^=$.

3.4.5 The influence of the type of anchored ligand

In order to study the influence of the type of anchored ligand we synthesized catalysts with anchored $P(OMe)_2$, $P(OPh)_2$ and PPh_2 (Table I, catalysts PS-13, PS-14 and PS-15). To all catalysts small amounts of extra PPh_3 are added (0.04 - 0.07% P), but these additional amounts did not surpass the amounts which can be liganded by the anchored rhodium complex. Figure 6 shows the activity as a function of time. From this figure we see that both PPh_2 and $P(OMe)_2$ anchored ligand catalysts reach a stable activity level; $P(OPh)_2$ deactivates continuously, which is in our view due to an ortho-metallation reaction of the $P(OPh)_2$ ligand with the rhodium metal centre resulting in a complex inactive for hydroformylation [17]. For $P(OPh)_2$ ortho-metallation goes much easier than for PPh_2, because a less strained complex is obtained (Figure 7).

It follows from Figure 6 that within the framework of this research diphenylphosphine is the preferred anchored ligand giving the highest activity and selectivity. We have also shown that upon addition of a stoichiometric amount of PPh_3 a very active catalyst with a sufficiently high selectivity is obtained.

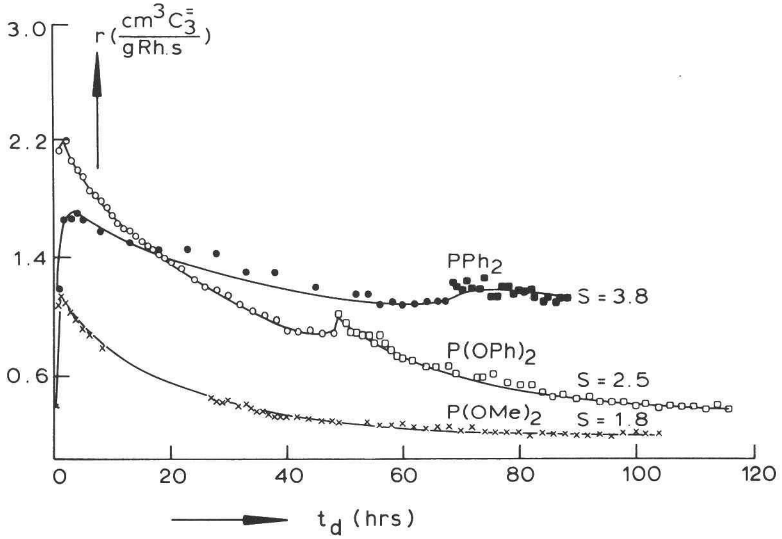


Figure 6 The influence of the type of anchored ligand on stability and activity in hydroformylation of propylene. $t = 75^oC$; $C_3^=/H_2/CO = 1/1/1$ (x,o,●) and 1/1.5/0.5 (□,■); $P_t = 0.1$ MPa. x: PS-13 $P(OMe)_2$, W/F 31.61; o,□ : PS-14 $P(OPh)_2$, W/F 13.80; ●,■ : PS-15 PPh_2, W/F 9.26 mg $Rh.s/cm^3$ $C_3^=$.

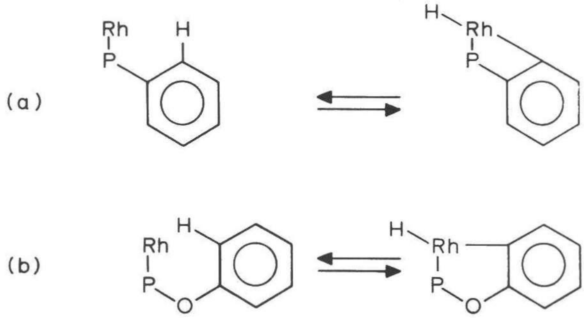


Figure 7 Ortho-metallation of anchored diphenylphosphine (a) and anchored diphenylphosphite (b).

3.5 CONCLUSIONS

Rhodium phosphine complexes chemically anchored via phosphine or phosphite ligands to the surface of XAD-2 macroreticular resins are very attractive as catalysts in the heterogeneous gas phase hydroformylation of propylene at low pressures. They possess a very high activity per gram of rhodium together with a good stability, especially the types prepared by functionalization of XAD-2 via chlorophosphonation. Catalysts prepared by functionalization via chloromethylation will also show a stable behaviour, provided that the remaining chlorine is totally removed.

Additional triphenylphosphine improves the activity as well as the selectivity. Already addition of a small amount of PPh_3 (2-4 mol PPh_3/mol Rh complex) results in a strong increase in activity together with a moderate increase in selectivity.

Our chemically anchored catalysts do not display the extremely high selectivities characteristic for SLP catalysts [6,7]. However, their substantial higher activity per gram of rhodium, due to a molecular dispersion of the rhodium complexes over the support surface is an important feature in relation to the rhodium economy, and may well counterbalance the disadvantage of a lower *n*-aldehyde selectivity.

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LIST OF SYMBOLS

F	flow of propylene at 0.1 MPa and 25 °C	cm^3/s
P/Rh	molar phosphorus to rhodium ratio	mol/mol
P_t	total pressure	MPa
r	reaction rate	cm^3/g Rh.s
S	selectivity = *n*/iso ratio	mol/mol
t	reaction temperature	°C
W	weight of rhodium metal in the reactor	g
θ	surface coverage	----
N_{av}	Avogrado's number	molecules/mol

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CHAPTER 4

GAS PHASE HYDROFORMYLATION OF PROPYLENE WITH IMMOBILIZED RHODIUM COMPLEX MONOLAYER CATALYSTS

4.1 SUMMARY

Mixtures of triphenylphosphine and hydridocarbonyltris(triphenylphosphine)-rhodium(I), monomolecularly dispersed over the surface of macroreticular polystyrene-divinylbenzene resins, are successfully applied in the heterogeneous gas phase hydroformylation of propylene between 58 and 92°C and at 0.1 MPa total pressure.

The addition of physically adsorbed triphenylphosphine is necessary in order to obtain stable catalysts. Under the condition of stable catalytic behaviour, the activity for propylene hydroformylation decreases with increasing triphenylphosphine coverage, whereas the selectivity for *n*-butyraldehyde formation increases.

In the temperature interval from 58 to 75°C an apparent activation energy of 61.6 kJ/mol is found, whereas between 75 and 92°C a value of 32.8 kJ/mol is obtained. The selectivity is constant up to 83°C, but decreases sharply at higher temperatures.

The influence of the texture of the support on the performance of the catalysts is studied, and a comparison is made with the behaviour of catalysts immobilized via chemically anchored diphenylphosphine ligands.

4.2 INTRODUCTION

The presence of a large amount of unpolymerized vinyl groups (0.65 mmol/g) in macroreticular polystyrene-divinylbenzene XAD-2 is proved by laser-Raman spectroscopy as well as by a specific reaction with iodine chloride (see Chapter 2) [1].

In Chapter 3 we described the catalytic performance of $RhHCO(PPh_3)_3$, chemically anchored via phosphine ligands to the surface of macroreticular polystyrene-divinylbenzene, in the gas phase hydroformylation of propylene [2]. The anchored ligands are able to stabilize the rhodium complex, but additional triphenylphosphine is required in order to obtain a catalyst with a sufficiently high selectivity for *n*-butyraldehyde.

In this chapter the catalytic performance of rhodium complexes, adsorbed in a monomolecular layer on the surface of porous *unmodified* polystyrene-divinylbenzene resins is presented. The stabilizing action of PPh_3, and the influence the PPh_3 coverage has on both activity and selectivity, will be discussed. A comparison is made between these catalysts and rhodium complexes chemically anchored via chemically bound phosphine ligands to the surface of XAD-2.

4.3 EXPERIMENTAL

In Chapter 2, section 2.4.4 and 2.4.5, the composition and structure of polystyrene-divinylbenzene XAD-2 and XAD-4 is presented [1]. The surface of these resins consists of vinyl and phenyl groups and therefore a strong physical interaction between $RhHCO(PPh_3)_3$ and the support surface is to be expected. Because of this strong interaction, and due to the low surface coverage with rhodium complexes, an adsorbed monolayer is formed.

Dry XAD-2 or XAD-4 (not extracted) is stirred with a solution of the desired amount of $RhHCO(PPh_3)_3$ and an excess of PPh_3 (3 mol PPh_3/mol Rh) in 80 ml toluene, saturated with hydrogen. The temperature is raised slowly to 65 °C during 1 hr and the mixture is kept under H_2 at 65 °C for 2 hrs. The complex-loaded polymer is separated from the solution and carefully washed with 3 x 100 ml of toluene and 2 x 100 ml of diethyl ether, in order to remove excess rhodium complex and PPh_3. The catalysts (except for PS-1) are contacted with a solution of PPh_3 in Et_2O for 0.5 hr in order to add additional PPh_3 to the surface. All catalysts are dried under H_2. The relevant data characteristic for the catalysts are summarized in Table 1.

For the chemicals used, the characterization of the catalysts and the method of determining the catalytic performance see Chapter 2.

Table I The catalysts.

Catalyst[a]	θ_{PPh_3}[b]	[P] (w %)	[Rh] (ppm)	P/Rh[c] (mol/mol)	$RhHCO(PPh_3)_3$[d] (mg)	PPh_3[d] (g)
PS-1	0.023[e]	0.034	678	1.64	250	---
PS-2	0.041[e]	0.060	594	3.36	250	0.15
PS-3	0.112	0.165	211	25.6	250	0.75
PS-4	0.43	0.64	730	29.1	250	2.5
PS-5	0.48	0.71	480	49.1	250	3.5
PS-7	0.32	0.48	180	88.6	200	2.5
PS-8	0.28	0.41	181	75.3	300	2.5
PS-9	0.31	0.46	109	140.2	150	2.5
PS-10	0.35	0.52	113	153.4	100	2.5
PS-11	0.32	0.48	164	97.2	350	2.5
PS-39	0.16	0.24	145	55.0	250	1.2
X4-1	0.112	0.38	282	44.8	250	1.2

[a] XAD-2 is used as the support. Only X4-1 is XAD-4 supported.

[b] θ_{PPh_3}, the surface coverage with free PPh_3, is calculated from:

$$\theta_{PPh_3} = \frac{(\text{mol P/g support}).N_{av}.S_{PPh_3}}{S_{BET}}$$

S_{PPh_3} = cross-sectional surface area of a PPh_3 ligand, 1.20 10^{-18} m^2.

S_{BET} = BET surface area of the support; for XAD-2 345 m^2/g, for XAD-4 788 m^2/g.

N_{av} = Avogrado's number, 6.02 10^{23} molecules/mol.

[c] P/Rh, total PPh_3 to rhodium ratio. 2-3 PPh_3 molecules are coordinated to the rhodium atom.

[d] Amount of complex contacted with 10 g of support. PPh_3 (last column) is the amount dissolved in 100 ml Et_2O in order to add additional PPh_3 to the surface.

[e] Most of the PPh_3 is coordinated to the rhodium complex.

4.4 RESULTS

4.4.1 The stabilizing action of triphenylphosphine

Our first experiments with catalysts comprising $RhHCO(PPh_3)_3$ immobilized on the surface of XAD-2 showed a deactivating behaviour in the hydroformylation of propylene (Figure 1, PS-1 and PS-2). The phosphorus to rhodium ratio was only 1.64 and 3.36, respectively, which accounts for the low selectivities observed.

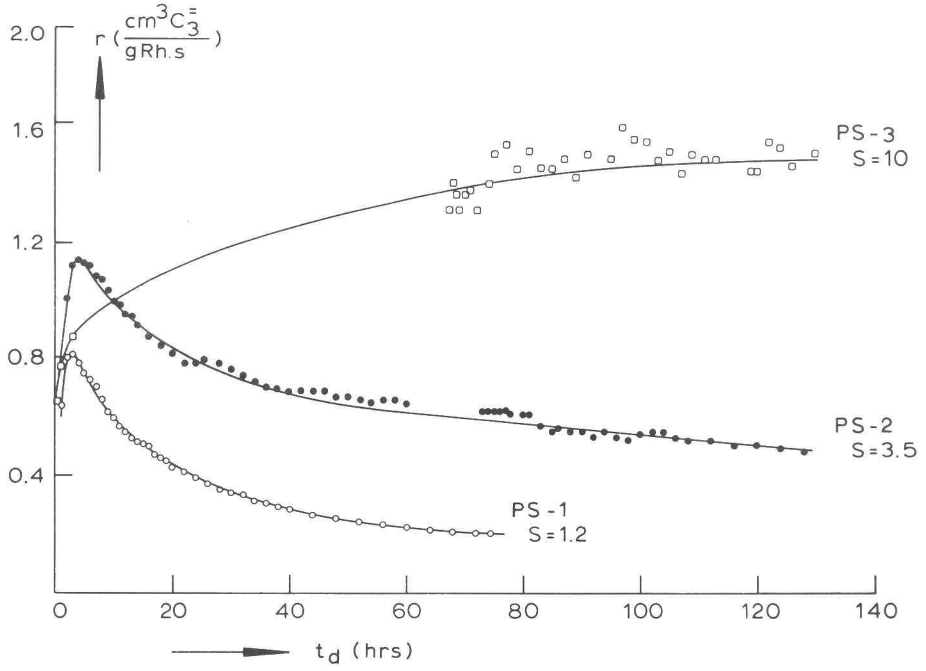

Figure 1 The stabilizing action of PPh_3 on $RhHCO(PPh_3)_3$ immobilized on the surface of XAD-2 in the hydroformylation of propylene. $t = 75^\circ C$; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; W/F = 3.88 (o), 3.66 (●) and 10.22 (□) mg $Rh.s/cm^3\ C_3^=$.

In order to obtain stability, additional PPh_3 was adsorbed by impregnation with PPh_3 dissolved in Et_2O. Figure 1 shows that a stable catalyst is obtained when the PPh_3 coverage is increased from 0.023 (PS-1, all PPh_3 coordinated to the rhodium complex) to 0.112 (PS-3), whereas a strong increase in selectivity for *n*-butyraldehyde formation is observed. The addition of PPh_3 results in an enrichment of the rhodium complexes with PPh_3 ligands as well as in a higher surface coverage with PPh_3.

4.4.2 The influence of triphenylphosphine coverage on the activity and the selectivity

A closer investigation of the catalytic performance is made for PPh_3 coverages from 0.112 up to 0.48, corresponding with phosphorus to rhodium ratios from 25.6 to 153.4. In view of the strong physical interaction between PPh_3 and the surface of the resin PPh_3 is monomolecularly dispersed over the surface, and it is unlikely that below $\theta_{PPh_3} = 0.5$ capillary condensation of PPh_3 in the micropores will occur.

The performance of a number of catalysts is shown in Figure 2. All catalysts show a period of activation before reaching their final stable activity. By way of comparison the performance of an XAD-2 supported SLP catalyst (SLPW-123), prepared after [3], is also given in Figure 2. The final activities and selectivities of the catalysts are listed in Table II.

Table II Final activities and selectivities of rhodium complex monolayer catalysts, and tested in the hydroformylation of propylene at 90°C and 0.1 MPa total pressure.

Catalyst	θ_{PPh_3}	r ($cm^3\ C_3^=/g\ Rh.s$)	S (mol/mol)	$W_{Rh}/F_{C_3^=}$ ($mg\ Rh.s/cm^3\ C_3^=$
PS-3	0.112	2.29	7.7	10.22
PS-39	0.16	1.32	9.6	6.9
PS-8	0.28	0.89	12.6	8.2
PS-9	0.31	0.82	14.5	5.4
PS-7	0.32	0.73	14.4	8.2
PS-11	0.32	0.77	14.2	6.3
PS-10	0.35	0.72	15.0	5.7
PS-4	0.43	0.26	15.5	32.5
PS-5	0.48	0.24	16.5	27.0

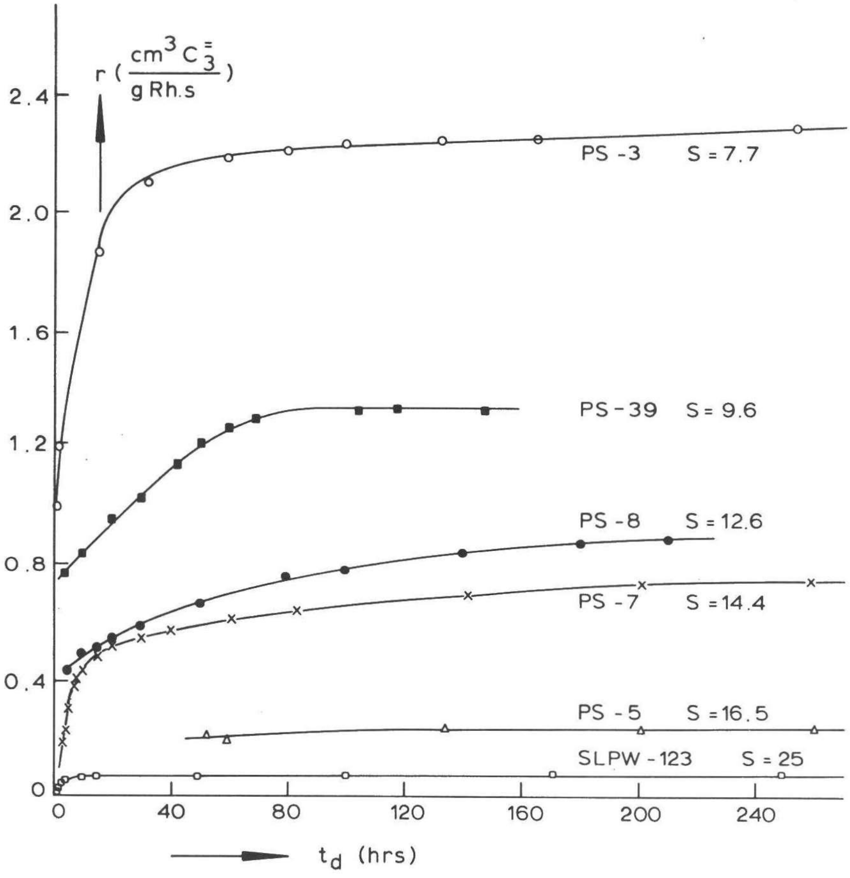

Figure 2 The performance of catalysts with varying PPh_3 coverage (see Table II) in the hydroformylation of propylene at 90°C and 0.1 MPa.

By way of comparison the performance of a SLP catalyst (SLPW-123) is also shown: XAD-2 is the support, and PPh_3 the solvent ligand, liquid loading = 0.66, 3.78% P, 0.15% Rh, P/Rh = 81.4, particle size 0.42 - 0.50 mm.

Figure 3 shows the final activity per unit weight of rhodium as a function of the PPh_3 coverage on the surface of XAD-2, whereas Figure 4 shows the final selectivity as a function of θ_{PPh_3}. From these figures we can conclude that with increasing PPh_3 coverage the activity for the hydroformylation of propylene decreases, whereas the selectivity for *n*-butyraldehyde increases. The results with the SLP catalyst, with a much higher PPh_3 loading (3.8% P), are consistent with this behaviour.

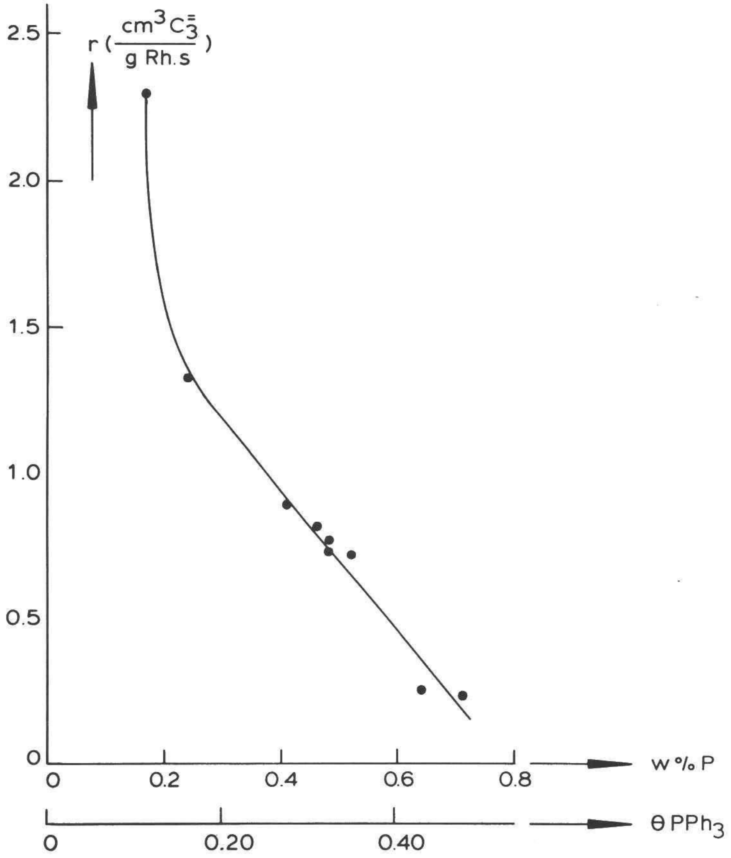

Figure 3 Final activity per unit weight of rhodium of catalysts with a rhodium complex/PPh_3 monolayer, as a function of θ_{PPh_3}.

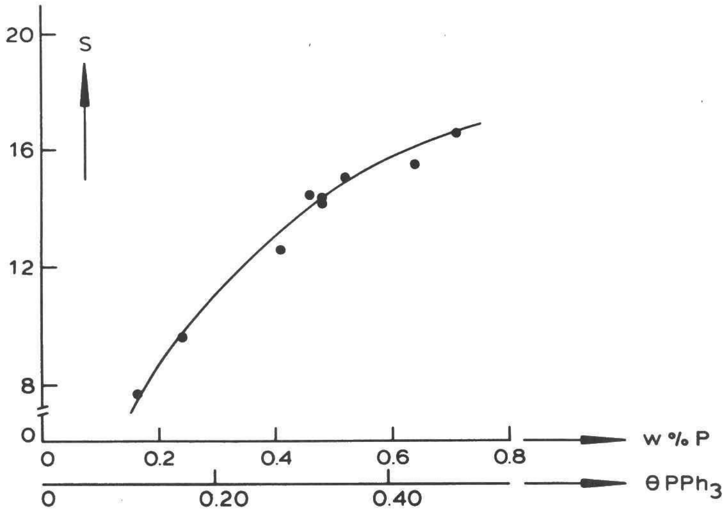

Figure 4 Final selectivity for *n*-butyraldehyde as a function of θ_{PPh_3}.

4.4.3 The temperature dependency of the catalytic performance

The apparent activation energy is determined from an Arrhenius plot (Figure 5), measured with catalyst PS-10. From 58°C up to 75°C an apparent activation energy of 61.6 kJ/mol is found, whereas between 75°C and 92°C this value is 32.8 kJ/mol.

With respect to the selectivity for *n*-butyraldehyde, up to 83°C the temperature has a minor influence, but at higher temperatures the selectivity strongly decreases (Figure 6). This behaviour is opposite to that found by Gerritsen for SLP catalysts; at a total pressure of 1.57 MPa, and above 70°C, the selectivity for *n*-butyraldehyde of his SLP catalyst strongly increases at increasing temperatures [4].

4.4.4 The influence of the texture of the support

In order to study the influence of the texture, a catalyst was prepared with XAD-4 as the support, and its performance is compared with that of an XAD-2 supported catalyst with the same PPh_3 coverage (catalysts X4-1 and PS-3, see

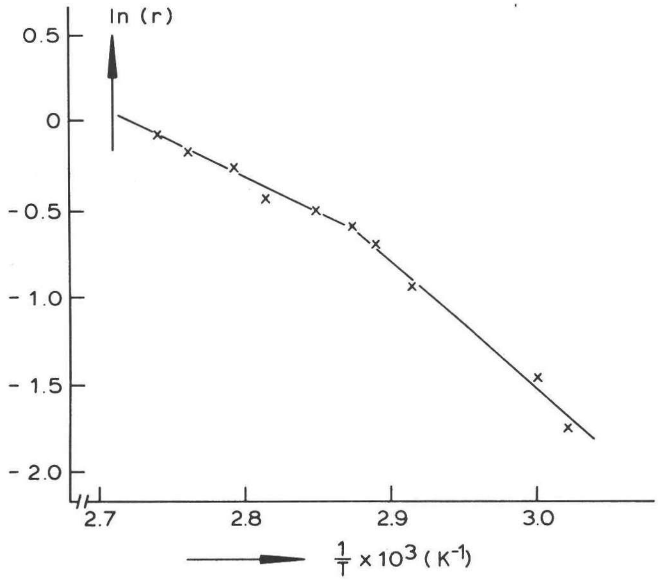

Figure 5 Arrhenius plot for the hydroformylation of propylene (catalyst PS-10). $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; t = 58-92°C; W/F = 5.7 mg Rh.s/cm^3 $C_3^=$.

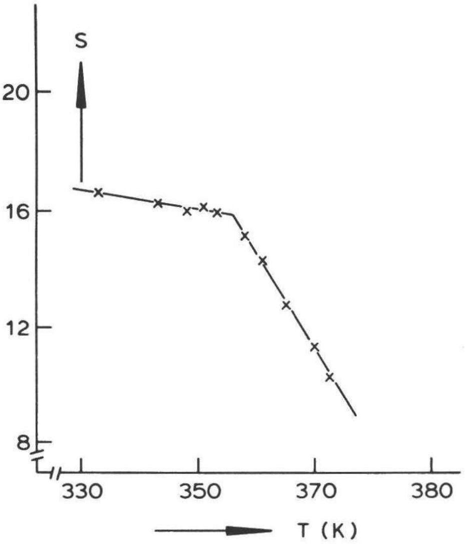

Figure 6 The selectivity as a function of temperature (catalyst PS-10). Conditions as in Figure 5.

Table I). Figure 7 shows the performance of both catalysts as a function of streamtime.

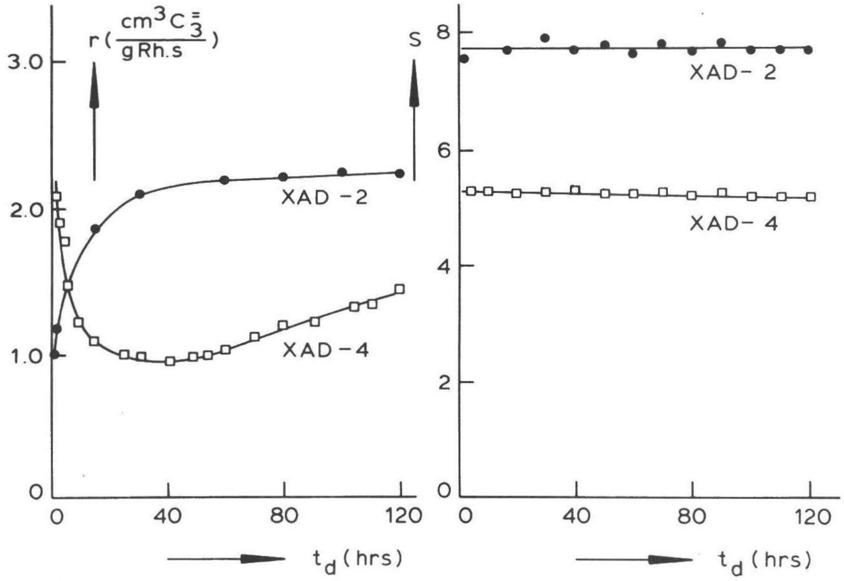

Figure 7 The influence of the texture of the support on the performance of catalysts with a monolayer of rhodium complexes in PPh_3. $t = 90^oC$; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; W/F = 10.22 (PS-3, ●), and 16.23 (X4-1, □) mg Rh.s/cm^3 $C_3^=$.

The activity of PS-3 in the hydroformylation of propylene gradually increases to a stable level, but the activity of X4-1 decreases in the first 40 hrs, and later on it shows an increase in activity. Although the activities of both catalysts are changing with time, the selectivities for *n*-butyraldehyde remain constant. Hence the changes in activity probably are not the result of a change in the nature of the active complex, but more likely of a change in the accessibility of the complexes. The selectivity of PS-3 is higher than that of X4-1, which might be due to a difference in the texture of XAD-2 and XAD-4. XAD-4 has an average pore diameter of 5 nm and a BET surface area of 788 m^2/g, whereas for XAD-2 these values are 10 nm and 345 m^2/g, respectively [1].

By way of comparison Figure 8 shows the performance of catalysts with chemically anchored diphenylphosphine ligands on XAD-2 and XAD-4 (PS-15 and X4-2). For these catalysts the activity also changes, the selectivity remains constant, and again the XAD-4 supported sample has the lower selectivity. PS-15 deactivates to a stable level; X4-2 shows an initial decrease, but later on an increase in activity occurs. PS-15 and X4-2 have the same P/Rh ratio, but X4-2 has a lower coverage with PPh_2 ligands than PS-15 (PS-15 $\theta_{PPh_2} = 0.09$, X4-2 $\theta_{PPh_2} = 0.06$).

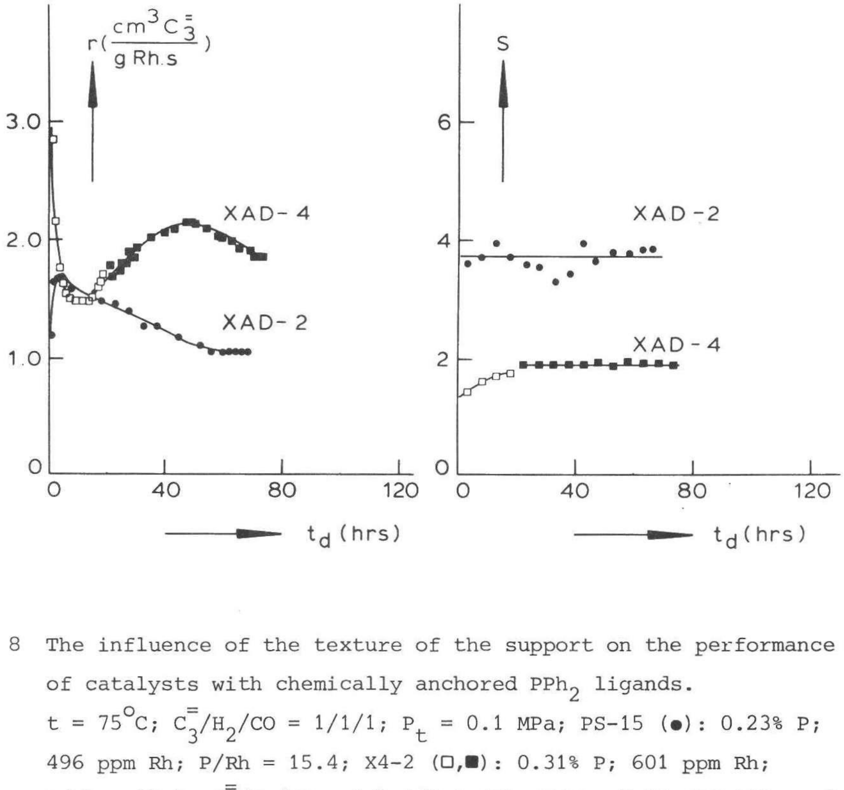

Figure 8 The influence of the texture of the support on the performance of catalysts with chemically anchored PPh_2 ligands.
$t = 75°C$; $C_3^=/H_2/CO = 1/1/1$; $P_t = 0.1$ MPa; PS-15 (●): 0.23% P; 496 ppm Rh; P/Rh = 15.4; X4-2 (□,■): 0.31% P; 601 ppm Rh; P/Rh = 17.1; $C_3^=/H_2/CO = 1/1.5/0.5$ (■); W/F = 9.26 (PS-15), and 9.90 (X4-2) mg $Rh.s/cm^3$ $C_3^=$.

4.4.5 Comparison with catalysts with chemically anchored diphenylphosphine ligands

In Chapter 3 the performance of catalysts with chemically anchored PPh_2 ligands to which additional PPh_3 was added, is discussed [2]; this addition results in an increase in activity as well as in selectivity. We now compare the performance of these catalysts with the rhodium complex monolayer catalysts (Table III).

Table III Comparison of the performance of rhodium complex monolayer catalysts with catalysts with chemically anchored PPh_2 ligands: A, with additional PPh_3; B, without addition of PPh_3

	Catalyst[a]	θ_{PPh_2}	θ_{PPh_3}	r (cm^3 $C_3^=$/g Rh.s)	S (mol/mol)
A	PS-20	0.03	0.52	0.27	18
	---[b]	----	0.52	0.21	18.3
	PS-18	0.09	0.47	0.67	16
	PS-5	----	0.48	0.24	16.5
B	PS-30	0.12	----	0.37	0.89
	PS-3	----	0.11	2.29	7.7
	PS-27	0.17	----	0.14	0.85
	PS-39	----	0.16	1.32	9.6

[a] All catalyst have XAD-2 as support. Catalysts PS-18, PS-20, PS-27, PS-30 are described in [2]. Catalysts PS-3, PS-5 and PS-39 are prepared from non extracted XAD-2 with 0.65 mmol/g vinyl groups. All activities and selectivities are measured at 90°C and 0.1 MPa.

[b] Not measured, activity is calculated by extrapolation of the activities of PS-4 and PS-5. The selectivity is calculated from the results shown in Figure 4.

Table III-A shows that at the same PPh_3 coverage equal selectivities are obtained. However, the catalysts with anchored PPh_2 ligands have a higher activity than those without anchored ligands. Although the PPh_2 coverages are low, PS-20 and PS-18 show that at increasing PPh_2 coverage a higher increase in activity is obtained.

In Table III-B the performance of rhodium complex monolayer catalysts is compared with the performance of catalysts with chemically anchored PPh_2 ligands to which no additional PPh_3 is added. We see that at the same coverage with either PPh_2 or PPh_3 ligands, the catalysts with chemically anchored PPh_2 ligands are much less active than those to which physically bound PPh_3 ligands are added. These PPh_3 ligands are mobile and can coordinate to the rhodium complex, which results in a higher activity and selectivity.

4.5 DISCUSSION

During catalyst preparation it appeared that there is a fairly strong interaction between the rhodium complex and the surface of XAD-2, because careful washing with toluene and diethylether does not remove the rhodium complex from the polymer. The presence of a high content (0.65 mmol/g) of unpolymerized vinyl groups in XAD-2 is probably responsible for this strong interaction [1]. Figure 9 shows a possible exchange reaction of $RhHCO(PPh_3)_3$ with a vinyl group of the polymer surface; this results in an anchored $RhHCO(PPh_3)_2$ complex.

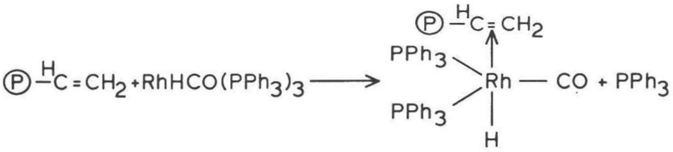

Figure 9 The immobilization of $RhHCO(PPh_3)_3$ on the surface of XAD-2 via coordination to a polymeric vinyl group. Ⓟ = polymer surface.

In the course of a propylene hydroformylation experiment the vinyl groups of the polymer might be hydroformylated to propionaldehyde groups through the catalytic action of the rhodium complex itself, and this results in a mobilization of the $RhHCO(PPh_3)_2$ complex.

The stabilizing action of PPh_3 may be explained by the following equilibria which also hold for non-adsorbed free complexes in solution [5,6].

a $RhHCO(PPh_3)_2 \rightleftarrows RhHCO(PPh_3) + PPh_3$

b $PPh_3 + RhHCO(PPh_3)_2 \rightleftarrows RhHCO(PPh_3)_3$

The addition of PPh_3 hampers the dissociation of $RhHCO(PPh_3)_2$ to complexes with a lower number of coordinated PPh_3 ligands, which are unstable and give a low selectivity for *n*-butyraldehyde (catalysts PS-1 and PS-2). Addition of PPh_3 also favours the formation of $RhHCO(PPh_3)_3$. Hence at increasing coverage with PPh_3 the formation of phosphine-rich complexes leads to a decrease in activity, but to an increase in selectivity as is shown in Figures 3 and 4 [5]. The observed temperature dependence of the selectivity for a catalyst with a high PPh_3 coverage indicates that for temperatures up to 83°C equilibrium *b* is not much affected by change in temperature. For temperatures higher than 83°C the PPh_3 mobility increases and now the selectivity for *n*-butyraldehyde drops, and this corresponds with a dissociation reaction of $RhHCO(PPh_3)_3$ (equilibrium *b* shifts to the left). The observed change in apparent activation energy from 61.6 kJ/mol to 32.8 kJ/mol is in accordance with this behaviour.

The mechanisms for the hydroformylation of propylene catalyzed by $RhHCO(PPh_3)_3$ originate from Wilkinson et al. [5,6]. It is now generally assumed that in the presence of a solvent, $RhH(CO)_2(PPh_3)$ and $RhH(CO)_2(PPh_3)_2$ are the active complexes, and a selectivity for *n*-butyraldehyde of 1-2 is obtained with these complexes [5,7]. Wilkinson also studied $RhHCO(PPh_3)_3$ in molten PPh_3 in the temperature range of 80-160°C and at 0.1 MPa total pressure [6]. He did not observe any reaction between $RhHCO(PPh_3)_3$ dissolved in PPh_3, and CO, although under these conditions, which are similar to ours, hydroformylation of propylene with a selectivity of 19 for *n*-butyraldehyde occurred [6]. Hence, PPh_3 rich complexes such as $RhHCO(PPh_3)_2$ and $RhHCO(PPh_3)_3$ can be active for hydroformylation and give rise to very high selectivities for *n*-butyraldehyde.

In order to describe the catalytic action of $RhHCO(PPh_3)_2$ a reaction scheme similar to those presented by Wilkinson [5] may be postulated. However, for the description of the catalytic action of $RhHCO(PPh_3)_3$ a different approach is needed. Figure 10 shows two possibilities for the first step in the reaction path of the hydroformylation of propylene (in the presence of excess PPh_3). Reaction step I leads to a 6-coordinated 20 electron complex, which is not in accordance with the 18 electron rule. Although the occurrence of such a complex is rather uncommon, the existence of a 20 electron complex is known and proved by n.m.r. [8]. The steric and electronic properties of the three PPh_3 ligands predominantly result in *n*-addition. Reaction step II immediately gives the *n*-

propyl complex; again the high number of PPh_3 ligands favours *n*-addition. After the formation of the *n*-propyl complex as shown in Figure 10, carbonyl insertion and hydrogen addition takes place, which gives *n*-butyraldehyde as the final product. Due to the high number of PPh_3 ligands around the rhodium complex isobutyraldehyde formation will be minor.

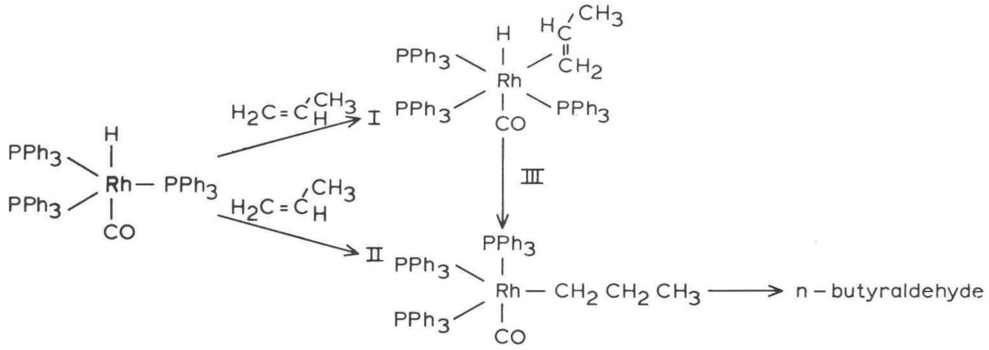

Figure 10 Two proposals for the first step in the hydroformylation of propylene with $RhHCO(PPh_3)_3$ in the presence of excess PPh_3.

At present it is not possible to give further evidence for the suggested reaction mechanism. In order to explain the observed very high selectivity for *n*-butyraldehyde it will be necessary to make a detailed study of the reaction mechanism, applying various analytical methods.

The results presented in this Chapter demonstrate that rhodium phosphine complexes monomolecularly dispersed over the surface of unmodified polystyrene-divinylbenzene resins are very attractive for application in the heterogeneous gas phase hydroformylation of propylene. The catalysts are very active and selective, and they have a high degree of rhodium utilization. Furthermore, the preparation of the catalysts is simple and relatively cheap.

LIST OF SYMBOLS

F	flow of propylene at 0.1 MPa and 25°C	cm^3/s
P/Rh	molar phosphorus to rhodium ratio	mol/mol
P_t	total pressure	MPa
r	reaction rate	cm^3/g Rh.s
S	selectivity = *n*/iso ratio	mol/mol
t	reaction temperature	°C
W	weight of rhodium metal in the reactor	g
θ_{PPh_2}	surface coverage with PPh_2 ligands	----
θ_{PPh_3}	surface coverage with PPh_3 ligands	----
N_{av}	Avogrado's number	molecules/mol

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CHAPTER 5

GAS PHASE HYDROFORMYLATION OF ALLYL ALCOHOL WITH SUPPORTED LIQUID PHASE CATALYSTS*)

by

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5.1 SUMMARY

Hydridocarbonyltris(triphenylphosphine)rhodium(I) dissolved in triphenylphosphine or in tri-*p*-tolylphosphine, and capillary condensed in the pores of a support material is successfully applied in the heterogeneous gas phase hydroformylation of allyl alcohol. Very high selectivities for 4-hydroxybutyraldehyde are obtained. No sign of catalyst deactivation was observed even after 250 hrs of testing.

The undesired side reaction of allyl alcohol to propionaldehyde is caused by the catalytic action of both the support material and the rhodium complex. By the use of silica with a low aluminium content and of phosphine rich rhodium complexes this problem is circumvented.

The kinetics of the hydroformylation of allyl alcohol are studied; they differ from those found for propylene with SLP catalysts.

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5.2 INTRODUCTION

The industrial production of 1,4-butanediol and of tetrahydrofuran is currently based on the Reppe reaction of acetylene with formaldehyde giving 1,4-butynediol [1]. Because of a growing market for 1,4-butanediol and the rapidly increasing cost of acetylene, it became attractive to search for alternative processes for 1,4-butanediol production. An attractive process is the hydroformylation of allyl alcohol to 4-hydroxybutyraldehyde (Figure 1). Subsequent hydrogenation of 4-hydroxybutyraldehyde or of 2-hydroxytetrahydrofuran, gives either 1,4-butanediol or tetrahydrofuran, depending on the type of the catalyst and on the reaction conditions.

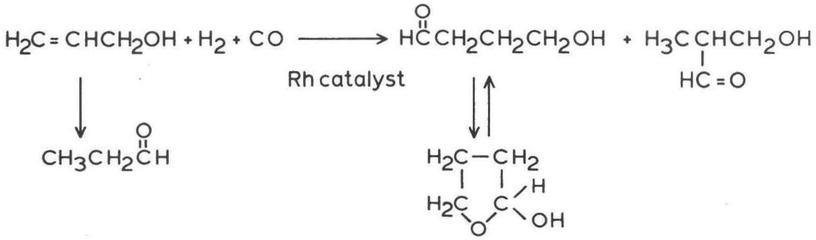

Figure 1 Hydroformylation of allyl alcohol.

Originally the hydroformylation of allyl alcohol was performed with cobalt catalysts; the yield of 4-hydroxybutyraldehyde does not exceed 30%, and the larger part of the allyl alcohol isomerizes to propionaldehyde [2-4]. However, the application of rhodium catalysts with an excess of phosphines leads to a suppression of the isomerization reaction [5]. Fell and Barl studied the hydroformylation of allyl alcohol with rhodium oxide triphenylphosphine catalysts at the very high pressure of 20 MPa, as a function of the ligand/rhodium ratio [6]. Above a ratio of five they did not find any isomerization nor an important variation in the *n*/iso ratio. Wilkinson studied the hydroformylation of allyl alcohol with hydridocarbonyltris(triphenylphosphine)rhodium(I) as a catalyst, at 65 kPa and 25°C, but did not specify the reaction products [7].

Recent work on the hydroformylation of allyl alcohol is mainly published in the patent literature. By far the best developed process originates from Kuraray [8-10], but other companies such as General Electric [11,12], Celanese [13,14] and Firestone [15] also disclosed patents in this field. All routes have in common homogeneous catalysis by rhodium complexes with PPh_3 added in excess, with either 4-hydroxybutyraldehyde or 2-hydroxytetrahydrofuran as the main product. An important drawback of these processes is the difficult separation of the rhodium catalyst from the reaction mixture. Heterogenizing of the rhodium complex may solve this problem.

Various methods of heterogenizing or immobilizing homogeneous catalysts have been developed [16-18]. Most attention has been paid to chemical anchoring of the rhodium complex to organic or inorganic supports. In case of liquid phase operation a serious drawback of such catalysts is the elution of the precious rhodium complex from the support [19]. However, in case of gas phase hydroformylation such an elution does not occur and both chemically anchored and supported liquid phase catalysts may be applied.

Gerritsen demonstrated supported liquid phase rhodium catalysts (SLP-catalysts) to be excellently suited for gas phase hydroformylation of ethylene and propylene under mild reaction conditions [20-22]. This type of catalyst combines an excellent stability with a good selectivity for *n*-aldehyde [23].

The present paper demonstrates the successful use of a SLP catalyst, $RhHCO(PPh_3)_3$ dissolved in PPh_3 or in tri-*p*-tolylphosphine, in the gas phase hydroformylation of allyl alcohol under continuous flow conditions [24]. The performance of this catalyst will be discussed with respect to parameters such as the type of support, the type of solvent ligand, and the reaction temperature. The kinetics of the reaction will also be presented.

5.3 EXPERIMENTAL

5.3.1 Materials

$RhHCO(PPh_3)_3$ was prepared by the method of Ahmad [25]. Triphenylphosphine (Fluka, Switserland, 99.5%) and tri-*p*-tolylphosphine (Strem, USA, 99.5%) were used as received. Toluene and benzene (Baker, The Netherlands, 99.8%) were dried over molecular sieve 3A (Union Carbide, USA). Nitrogen (99.98%), helium (99.98%) and carbon monoxide (99.5%) were both obtained from Air Products, USA, and were freed from traces of oxygen and water over BASF catalyst R3-11 and molecular sieve 3A, respectively. Carbon monoxide was freed from carbon dioxide over "Ascarite" (A.H. Thomas, USA). Hydrogen (Air Products, USA, 99.99%) was freed from oxygen and water over a Pd/Al_2O_3 catalyst (Engelhard, UK) and molecular sieve 3A. Allyl alcohol (Aldrich, Belgium) was distilled prior to use in order to remove propionaldehyde and polymeric products. Silica 000-3E, silica-alumina LA-30, γ-alumina 005-0.75E (all from Akzo Chemie, The

Netherlands), Kieselguhr MP-99 (Eagle Pitcher, USA), silica D11-11 (BASF, The Netherlands), silica S (not commercially available, DSM, The Netherlands) and "Amberlite XAD-2" (Serva, Germany) were crushed if necessary, and sieved to the desired size fraction.

5.3.2 Catalyst preparation and characterization

The catalysts were prepared after the method of Gerritsen [22].
The SLP catalyst is completely characterized by the following parameters:

-- : the type of support
-- : the type of ligand
δ : the degree of liquid loading, which is defined as the percentage of pore volume filled up with catalyst solution at 90°C
[Rh] : the rhodium complex concentration in the solvent ligand at 90°C (mol/m^3)
P/Rh : the molar phosphine/rhodium ratio.

In general a liquid loading, δ, of 50% was chosen.

5.3.3 Method of determining the catalytic performance

The catalytic performance in the gas phase hydroformylation of allyl alcohol was studied in a continuous flow apparatus suited for total pressures up to 0.6 MPa and temperatures up to 200°C (Figure 2).

Hydrogen, carbon monoxide, helium and nitrogen were purified by passing them over BASF catalyst R3-11, molecular sieve 3A and sodium hydroxide on asbestos ("Ascarite") as mentioned before in section 5.3.1. The gases were metered by using a PFD 112 mass flow controller, and mixed before passing evaporator ④ . Allyl alcohol stored under nitrogen in vessel ① and pumped to evaporator ④ by means of a Nikizo model 1N1c75-25-3CAK metering pump ③. The allyl alcohol flow was calibrated by means of burette ② . Next, the gas mixture was passed through heated stainless steel pipes to a 0.100 m long fixed bed reactor ⑥ (inner diameter 0.010 m) placed in an air fluidized bed oven ⑤ permitting isothermal operation to within 0.5°C by using an Eurotherm PID temperature controller. The operating conditions were chosen so as to assure ideal plug flow. The reaction mixture was periodically sampled via a Carle sampling valve ⑦ , analyzed gaschromatographically on a 5% silicon UCC-W-982 on Gaschrom Q 80/100 column [6] (4.0 m length, 0.003 m inner diameter) at 115°C. Helium was used as the carrier gas and the products were detected by flame ionisation using a Hewlett Packard 5704A electrometer. The peak areas were recorded and integrated on a digital integrator (LDC CRS 304). After release of the total pressure to 0.1 MPa ⑧ the liquid products are condensed in cooler ⑨. After measurement of the gas flow in soap film meter ⑩, the gases were vented. By turning the four-way valves between reactor and chromatograph it is also possible to sample the feed of the reactor.

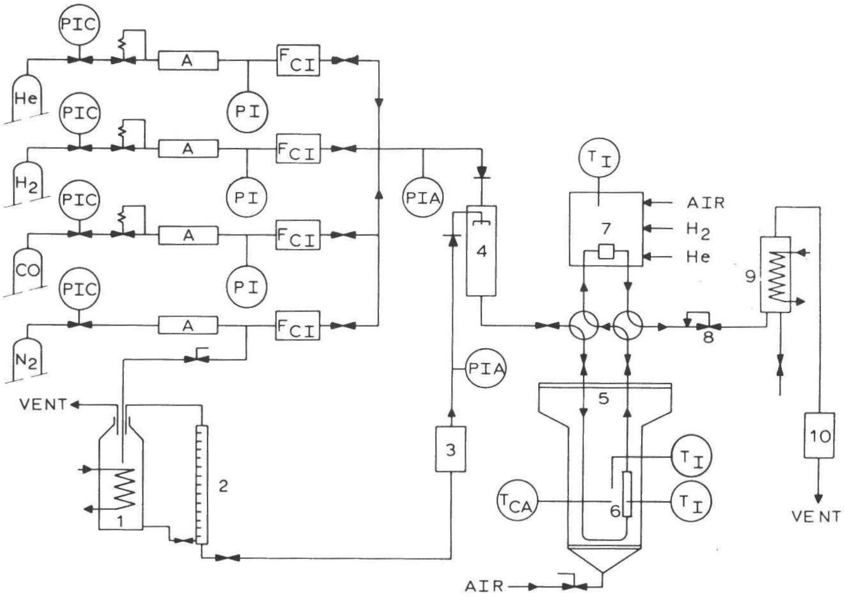

Figure 2 Continuous flow apparatus.
A = Purification, FCI = Flow controller and indicator, PI = Pressure indicator, PIA = Pressure indicator and alarm, TCA = Temperature controller and alarm, TI = Temperature indicator. Items 1-10 are mentioned in the text.

Propionaldehyde, 4-hydroxybutyraldehyde and 3-hydroxy-2-methylpropionaldehyde are the only products observed. The total conversion of allyl alcohol, ξ_T, is calculated as follows:

$$\xi_T = \frac{A_1R_1 + A_2R_2 + A_3R_3}{A_0 + A_1R_1 + A_2R_2 + A_3R_3}$$

where A_0, A_1, A_2 and A_3 are the integrated peak areas for allyl alcohol and the three products, respectively, and R_1, R_2 and R_3 are response factors correcting for the difference in sensitivity between allyl alcohol and the products. Similarly, the conversion of allyl alcohol to hydroformylation products, ξ_H, is calculated by omitting A_1R_1 in the numerator.

The selectivity, S, for the formation of *n*-aldehyde is calculated as the ratio of the amount of 4-hydroxybutyraldehyde to the allyl alcohol converted:

$$S = \frac{A_2R_2}{A_1R_1 + A_2R_2 + A_3R_3}$$

This definition of selectivity deviates from the one which is generally used in the hydroformylation literature, *viz.* the *n*/iso ratio.

The reactor was operated differentially; so the initial rate of hydroformylation, r, can be expressed as:

$$r = \frac{\xi_H}{(W/F)}$$

where W is the weight of rhodium metal in the reactor, and F is the flow rate of allyl alcohol; r is expressed in cm^3 gaseous allyl alcohol at 0.101 MPa and 25^oC (calculated from the liquid flow) per gram of rhodium metal and per second.

An experiment was started by raising the reactor temperature stepwise from room temperature to its final value in a period of two hours, whilst flowing a 1:1 mixture of hydrogen and carbon monoxide over the catalyst. After reaching the final temperature the metering pump was started in order to hydroformylate allyl alcohol.

5.3.4 Allyl alcohol isomerization

In order to determine which of the catalyst components is responsible for the undesired isomerization of allyl alcohol to propionaldehyde the support materials were tested separately in the continuous flow apparatus. A 2/2/1 mixture of hydrogen, carbon monoxide and allyl alcohol was passed over the bare support at 90^oC and 0.11 MPa total pressure.

All other catalyst components were tested homogeneously in a batch reactor of 0.250 l at various temperatures and at 0.1 MPa total pressure with different gases or gaseous mixtures. Toluene was used as a solvent. Samples were taken from the reactor with a syringe and analyzed gaschromatographically at 95^oC with the previously mentioned analysis system.

5.4 RESULTS AND DISCUSSION

5.4.1 Allyl alcohol isomerization

Performing the initial experiments on the hydroformylation of allyl alcohol we observed an unwanted side reaction, *viz.* an appreciable isomerization of allyl alcohol to propionaldehyde. For instance a Kieselguhr MP-99 SLP rhodium catalyst showed a selectivity of only 40% for hydroformylation, whereas 60% of the converted allyl alcohol was isomerized to propionaldehyde. In order to determine which component(s) of the SLP catalyst is (are) responsible for this highly unwanted reaction we performed a number of experiments. The bare support materials were tested in the continuous flow system; the catalyst solution was studied in a batch reactor.

The results of the determination of the isomerization activity of the support materials, and the other data regarding the supports are listed in Table I. Only XAD-2 and silica S, a silica with an extremely low Na and Al content, are inactive for isomerization, which also holds for the empty reactor. Silica 000-3E has a low activity, whereas the other support materials give high conversions of allyl alcohol to propionaldehyde.

The data in Table I strongly suggest a positive relation between the Al content of the support and its isomerization activity. Gerritsen *et al.* [22] and Beranek and Kraus [26] found a relation between the Na content of a support and its aldol condensation activity. However, in our case we do not find a clear correlation between the Na content of the support and its allyl alcohol isomerization activity. The relation between the Al content of the support and its isomerization activity is much more obvious. Interesting in this respect is the work of Van Roosmalen, who observed that the rate of 1-butane isomerization over silica gel is proportional to the Al content [27]. He presents a mechanism of 1-butene isomerization, which is adapted by us for the isomerization of allyl alcohol (Figure 3). In Figure 3 the first step in the isomerization reaction is adsorption of allyl alcohol on a surface silanol pair (i), which is followed by acceptance of a proton from a neighbouring allyl alcohol molecule chemisorbed on an aluminium ion (ii). In the third step (iii) a proton is given back to the organic residue, which results in a chemisorbed vinyl alcohol species; finally, desorption gives propionaldehyde. This mechanism explains the low isomerization activity observed for silica 000-3E and silica S, which both have a low Al content.

Table I Texture data of the various supports, their aluminium and sodium content, and isomerization activity.

Support	V_{CUM} (cm^3/g)	S_{BET} (m^2/g)	$(\frac{dV}{dr_p})_{max}$ (nm)	Na content (w%)[a]	Al content (w%)[a]	Isomerization activity[b]
γ-alumina 005-0.75E[d]	0.74	170	8.5	0.080	52.9[c]	high
silica-alumina LA-30[e]	0.59	156	5.4/1800	0.070	6.9	high
Kieselgurh MP-99[e]	1.03	18	248.0	0.141	3.2	high
silica 000-3E[d]	0.85	203	5.7	0.49	0.5	low
silica D11-11[d]	0.87	120	15.1	0.100	0.3	medium
silica S[d]	1.05	101	17.0	0.0036	0.0076	none
silica S'[d]	0.68	70	20.0	0.0036	0.0076	none
XAD-2 (extracted)[d]	0.69	345	9.0	------[f]	------[f]	none

[a] Measured by neutron activation analysis.

[b] Measured by flowing allyl alcohol with 1:1 hydrogen/carbon monoxide over the supports at 90°C and 0.1 MPa.

[c] Not measured, calculated.

[d] Determined by nitrogen capillary condensation at −196°C in the region $2 < r_p < 50$ nm.

[e] Determined by mercury porosimetry in the region $5 < r_p < 7000$ nm.

[f] Not measured.

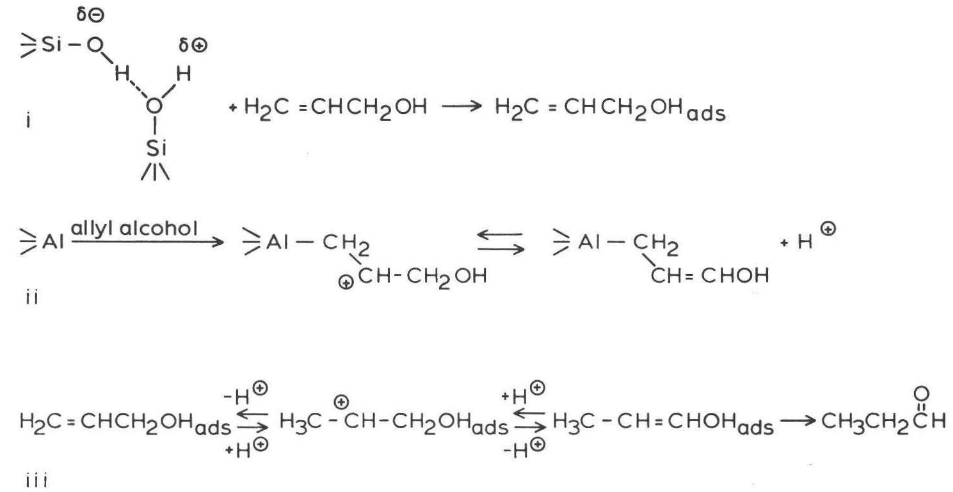

Figure 3 The isomerization of allyl alcohol to propionaldehyde on a silica surface, containing aluminium ions.

The isomerization activity of the catalyst solution was studied in a batch reactor with toluene as the solvent. We first tested each of the catalyst components separately and found that only rhodium complexes catalyse the isomerization of allyl alcohol. For two different rhodium concentrations we studied the influence of hydrogen and of a 1/1 mixture of hydrogen and carbon monoxide on the isomerization activity. We observed (Figure 4), that the isomerization activity is proportional to the rhodium concentration and that carbon monoxide suppresses isomerization. We also studied the influence the phosphorus to rhodium ratio has on the isomerization activity. In Figure 5 the conversion to propionaldehyde, after 20 minutes reaction time, is plotted as a function of the P/Rh ratio, with increasing phosphine concentration and at constant complex concentration. First an increase in activity occurs due to the fact that more active monomeric complexes are formed from rhodium dimers. At P/Rh ratios above 40 the activity is reduced by the addition of phosphine ligand. It is to be expected that in the absence of solvent and in the presence of a large excess of PPh_3 (as is in the case of our SLP catalysts) the isomerization activity is suppressed to a very low value.

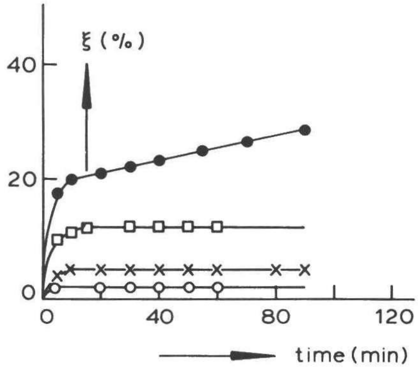

Figure 4 The isomerization conversion of allyl alcohol as a function of reaction time in the presence of hydrogen and 1/1 hydrogen/carbon monoxide (conversion to propionaldehyde in %). Toluene as a solvent, $RhHCO(PPh_3)_3$ as the complex, [allyl alcohol] 1.5 mol/l, t = 40^oC and P_t = 0.1 MPa.

x: [Rh] = 1.5 mmol/l; H_2

●: [Rh] = 4.5 mmol/l; H_2

o: [Rh] = 1.5 mmol/l; 1/1 H_2/CO

□: [Rh] = 4.5 mmol/l; 1/1 H_2/CO.

In Figure 6 a possible reaction mechanism for the isomerization and hydroformylation of allyl alcohol over $RhHCO(PPh_3)_3$ is shown, based on the associative mechanism by Wilkinson *et al.* [28]. After formation of complex I, the subsequent addition reaction can give either complex II, which finally leads to the formation of 4-hydroxybutyraldehyde, or complex III, which can react in two different ways. Complex III can give either a coordinated vinyl alcohol complex IV, which desorbs as propionaldehyde, or an acyl complex, which will be reduced to the iso-product. In Figure 6 the reaction I → II and I → III are drawn for carbon monoxide, but for PPh_3 the same reactions apply. The presence of excess PPh_3 favours reaction I → II (*n*-addition), because of the steric and electronic influences of PPh_3. Reaction III → IV may proceed, provided as a carbon monoxide ligand splits of the complex in order to give complex IV, and this explains the observed suppression of the isomerization by carbon monoxide. The rhodium catalyzed isomerization of allyl alcohol is also suppressed by an excess of phosphine ligand, which favours *n*-addition.

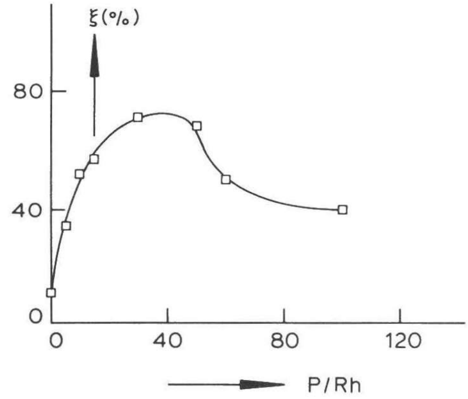

Figure 5 Conversion of allyl alcohol to propionaldehyde, after 20 minutes reaction time, as a function of the phosphorus to rhodium ratio.
Toluene as solvent (100 ml), $RhHCO(PPh_3)_3$ as complex, PPh_3 as ligand, t = 70°C and P_t = 0.1 MPa; [Rh] = 4.5 mmol/l; [allyl alcohol] 1.5 mmol/l; 1/1 H_2/CO.

5.4.2 The performance of SLP catalysts in allyl alcohol hydroformylation

The performance of silica SLP catalysts for allyl alcohol hydroformylation was tested in the continuous flow apparatus. The characteristics of the catalysts are listed in Table II. Triphenylphosphine (melting point 79.3°C) and tri-*p*-tolylphosphine (melting point 147.4°C) are used as the solvent ligand in the catalysts. In the temperature range of 88-108°C and 0.1-0.4 MPa total pressure propionaldehyde and 4-hydroxybutyraldehyde are the only products observed. 4-Hydroxybutyraldehyde is detected in the GC, but in the condensor it cyclisizes to 2-hydroxytetrahydrofuran [29]. In all our experiments an excess of hydrogen and carbon monoxide was used in order to avoid condensation of allyl alcohol and its hydroformylation products.

Results are listed in Table III. The selectivity for 4-hydroxybutyraldehyde is very high (max. 99%); catalysts with silica 000-3E and silica S as the support give higher selectivities than silica D11-11. The observed high selectivity for *n*-product formation is analogous to the results for propylene hydroformylation, but the activities of SLP catalysts for hydroformylation of propylene are 10-30 times lower than for allyl alcohol hydroformylation [30].

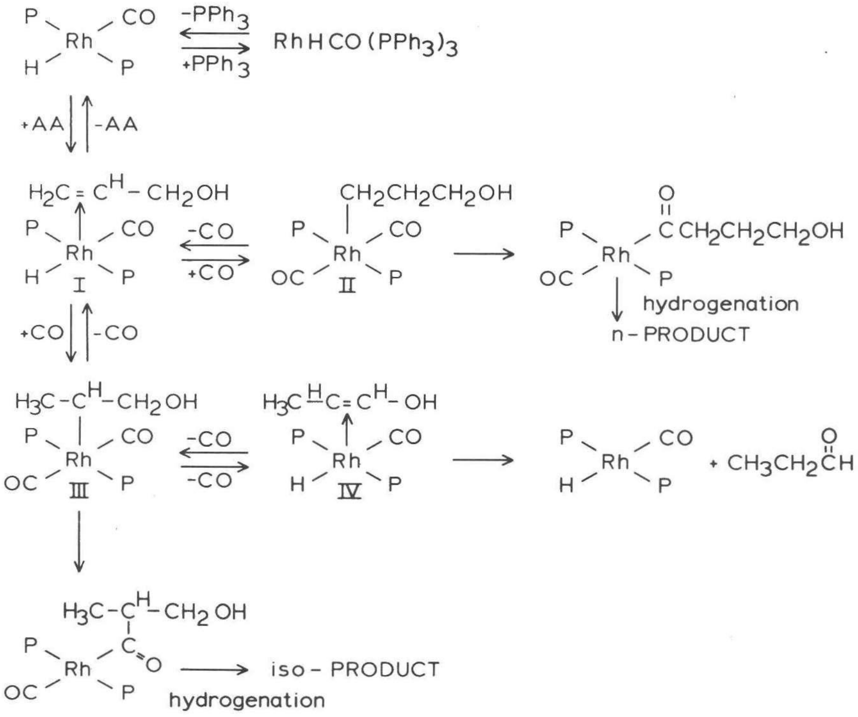

Figure 6 Mechanistic scheme for the hydroformylation and isomerization of allyl alcohol with $RhHCO(PPh_3)_3$ as a catalyst; AA = allyl alcohol.

Figure 7 shows the catalytic performance of a typical SLP catalyst in the hydroformylation of allyl alcohol.

From Table III we see that, for catalyst B, total pressure variation hardly effects activity and selectivity. Variation of the total flow (space time) however strongly influences both activity and selectivity (see results for catalyst C and D; both are supported by silica S with a large particle size). Through the absence of film diffusional retardation (much smaller particle size) a marked improvement in activity and selectivity is noted with catalysts E, F and G.

Tri-*p*-tolylphosphine is used as the solvent ligand instead of PPh_3, because it can be used at higher temperatures due to its higher melting point and its lower volatility. The use of tri-*p*-tolylphosphine results in lower selectivities and activities than with PPh_3 under similar conditions (catalyst C and D), but

Table II Characteristics of SLP catalysts studied in allyl alcohol hydroformylation

Catalyst ---	Support[a] ---	Ligand ---	δ ---	[Rh] $(\frac{mol}{m^3})$	P/Rh $(\frac{mol}{mol})$	Particle size (mm)
A	Silica D11-11	PPh_3	0.50	28.7	140	0.35 - 0.42
B	Silica 000-3E	PPh_3	0.50	42.7	100	0.42 - 0.50
C	Silica S	PPh_3	0.50	40.9	100	1.2 - 1.7
D	Silica S	*b*	0.50	30.3	116	1.2 - 1.7
E	Silica S'	*b*	0.75	35.2	100	0.35 - 0.60
F	Silica S'	*b*	0.75	6.8	517	0.35 - 0.60
G	Silica S'	*b*	0.75	4.4	800	0.35 - 0.60

[a] Texture data of the supports are listed in Table I.
[b] Tri-*p*-tolylphosphine.

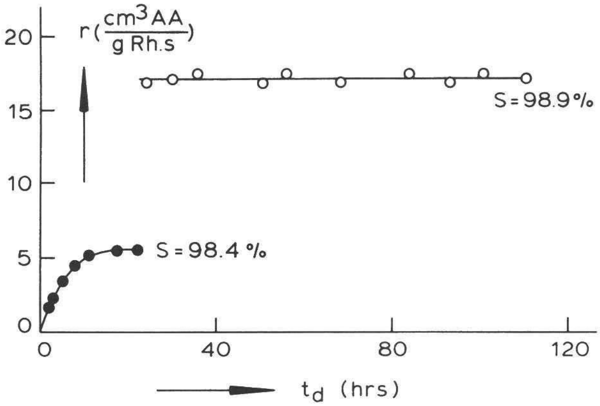

Figure 7 Catalytic performance of a typical SLP catalyst in allyl alcohol hydroformylation
Catalyst F; ●: $H_2/CO/AA = 40/40/5.5$; o: $H_2/CO/AA = 60/60/5.5$; conditions see Table III.

but by adjusting the reaction conditions, for instance by increasing the temperature, the same activities and selectivities are obtained. Another advantage of working at higher temperatures is, that soaking of the catalyst by product condensation in the pores of the catalyst is avoided.

The stability of all SLP catalysts is high. After 250 hrs of testing catalyst D showed no sign of deactivation. The results listed in Table III are obtained over a period of at least 24 hrs, and always reflect steady state operation. The results obtained demonstrate that silica supported SLP catalysts are very attractive in the production of 4-hydroxybutyraldehyde.

Table III Performance of SLP catalysts in allyl alcohol hydroformylation

Catalyst[a]	ξ_T %	ξ_H %	S %	r $(\frac{cm^3\ AA}{g\ Rh.s})$	t ^oC	P_t MPa	W/F $(\frac{mg\ Rh.s}{cm^3\ AA})$	Feed composition [b]
A	34.4	27.8	80.8	5.78	90	0.12	48.1	20/20/6
B	17.6	16.8	90.3	3.25	90	0.15	52.0	30/30/6.7
	21.4	20.2	94.4	3.90	90	0.20	52.0	30/30/6.7
	21.1	19.8	93.8	3.77	90	0.25	52.5	30/30/6.6
	19.8	18.7	94.4	3.40	90	0.30	55.0	30/30/6.3
	22.4	20.4	91.1	3.71	90	0.30	55.0	40/40/6.3
C	11.3	9.8	86.7	4.03	90	0.40	24.3	17/17/4.3
	14.1	13.6	96.4	10.00	90	0.40	13.6	31/31/7.7
	12.3	11.8	95.9	12.69	90	0.40	9.3	45/45/11.2
	12.9	12.8	99.0	20.48	90	0.40	6.3	67/67/16.7
	9.9	9.8	99.0	21.44	90	0.40	4.6	90/90/22.8
D	6.3	5.1	81.0	1.91	88	0.40	26.7	42/42/5.5
	13.2	10.5	79.5	3.93	108	0.40	26.7	42/42/5.5
	16.7	15.0	89.8	11.03	108	0.40	13.6	81/81/10.8
E	20.4	19.8	97.1	2.30	100	0.40	86.2	40/40/5.5
F	6.1	6.0	98.4	5.36	100	0.40	11.2	40/40/5.5
	18.8	18.6	98.9	16.61	100	0.40	11.2	60/60/5.5
G	3.3	3.2	97.0	6.0	100	0.40	5.3	60/60/5.5

[a] See Table II for the characteristics.

[b] cm^3 hydrogen/cm^3 carbon monoxide/cm^3 allyl alcohol(gas).

5.4.3 Kinetics of allyl alcohol hydroformylation

In order to check whether the reactor operates differentially the degree of allyl alcohol conversion was studied as a function of space time. Figure 8 shows that, up to 7% conversion, the reactor operates differentially indeed. From 0 to 7% conversion the selectivity remains constant.

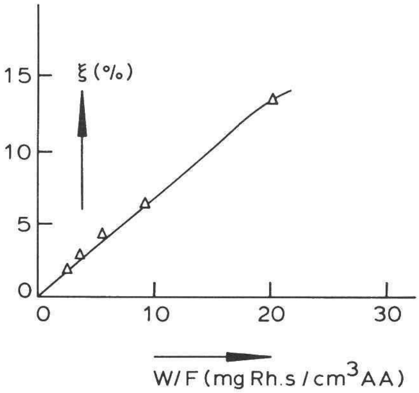

Figure 8 Conversion of allyl alcohol as a function of reactor space time.
P_t = 0.4 MPa; t = 100°C; H_2/CO/AA = 7/7/1; W/F = variable; catalyst G.

The reaction is determined as a function of the partial pressure of each of the reactants, although in a relatively small range. One of the partial pressures is varied, while the other two are kept constant. By addition of helium the total flow is kept constant at 2.26 cm^3/s and the total pressure at 0.4 MPa. No changes in selectivity are observed under the influence of varying partial pressure (S = 98%). The results are shown in Figure 9.

The results are fitted into a power rate equation of the form:

$$r = k \cdot p_{AA}^{a} \cdot p_{H_2}^{b} \cdot p_{CO}^{c}$$

The reaction orders, which are determined from the results shown in Figure 8 by means of the least squares method are: $a = 0.14$, $b = 0.63$ and $c = 0.07$. With catalyst D an apparent activation energy of 40.0 kJ/mol in the temperature range of 88-108°C is determined.

The kinetics differ from those found by Gerritsen for propylene hydroformylation [23]. He found about zero order in hydrogen and first order in propylene, although at a higher total pressure of 1.6 MPa. However, in *homogeneous* hydroformylations, where the oxidative addition of hydrogen is generally considered to be rate determining, the reaction is first order in hydrogen [31]. For all our catalysts we see an activation during the first 10 - 20 hrs of an experiment, which is perhaps due to some product condensation in the pores of the catalyst. Thus, the behaviour of our catalytic system would be more similar to that of a homogeneous catalyst. It is interesting to note that Cavalieri d'Oro *et al.* [32], in studying homogeneous hydroformylation with a relatively large excess of PPh_3 in toluene, arrived at zero order in hydrogen and an order of 0.55 for propylene, although at much higher pressures than applied here. The differences in kinetic behaviour and the influence the total pressure has, asks for further study in order to arrive at a full explanation of our results.

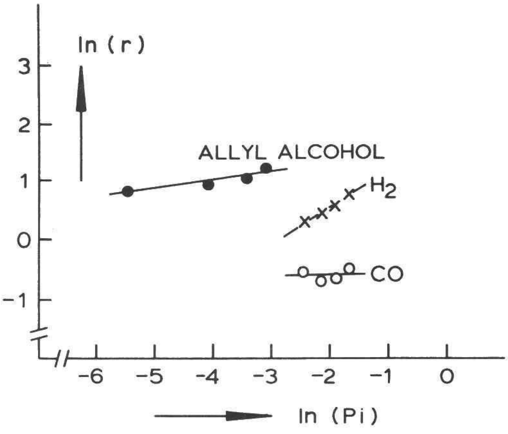

Figure 9 Reaction rate for allyl alcohol hydroformylation as a function of the partial pressures of the reactants.
P_t = 0.4 MPa; t = 100°C; total flow 2.26 cm^3/s; 3.5 g catalyst; catalyst F.

5.5 CONCLUSIONS

SLP rhodium catalysts are very attractive for the hydroformylation of allyl alcohol. They possess a high activity together with an excellent selectivity for 4-hydroxybutyraldehyde. In view of their catalytic performance these catalysts can well be used for the synthesis of 1,4-butanediol or of tetrahydrofuran.

The undesired isomerization of allyl alcohol to propionaldehyde is prevented by selection of a support with a low aluminium content and by using rhodium complexes in the presence of excess phosphine.

The observed kinetic behaviour is similar to that found for homogeneous hydroformylation of propylene at low total pressure, but differs from that found for both SLP catalysts and homogeneous catalysts at higher total pressures. Spectroscopic and kinetic studies are necessary in order to determine if there are differences between allyl alcohol and propylene in coordination to rhodium phosphine complexes, and to determine the influence of the total pressure on the kinetic behaviour.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

A_i	peak area of component i	a.u.
AA	allyl alcohol	----
F	flow of gaseous allyl alcohol calculated at 0.1 MPa and $25^{o}C$	cm^3/s
P/Rh	molar phosphorus to rhodium ratio	mol/mol
P_t	total pressure	MPa
R	response factor	----
r	reaction rate for hydroformylation	cm^3/g Rh.s
S	selectivity for 4-hydroxytetrahydrofuran	%
t	reaction temperature	^{o}C

t_d	streamtime	hrs
W	weight of rhodium metal in the reactor	g

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SUMMARY

In several important industrial processes synthesis gas, a mixture of hydrogen and carbon monoxide, is used as a feedstock, for instance in the Fischer-Tropsch synthesis of hydrocarbons, in the synthesis of methanol, in the synthesis of acetic acid, and in the production of aldehydes and alcohols by hydroformylation of alkenes. The discovery of a large number of highly active and selective transition-metal complex catalysts led to an improvement or to the new development of such processes. The main theme of this thesis is the application of immobilized transition-metal complex catalysts in the *gas phase hydroformylation of alkenes*.

Hydridocarbonyltris(triphenylphosphine)rhodium(I) ($RhHCO(PPh_3)_3$) is an excellent homogeneous catalyst for the hydroformylation of alkenes to aldehydes, active at relatively low pressures and temperatures (0.1-2.0 MPa; 90-130°C). In the hydroformylation of propylene it possesses an extremely high activity, combined with a high selectivity for *n*-butyraldehyde, whereas side-product formation is very low. The high price of rhodium (about $ 35,000/kg) requires a total recovery of this precious catalyst. *Immobilizing or heterogenizing the rhodium complex on a support* will result in a technologically attractive and economical process with the additional advantage of a continuous separation of feed and products from the catalyst.

The immobilization of homogeneous catalysts has been a subject of intensive research during the past ten years. Problems, such as a low stability due to gradual thermal degradation, too low a selectivity for the desired product and a slow elution of the organometallic complex in case of liquid phase operation, proved to be serious disadvantages for the technical application of these catalysts.

Some methods of immobilization of organometallic complexes are: strong physical adsorption on a support, capillary condensation of a solution of the complex in a porous support (supported liquid phase catalysts), and chemical anchoring of the organometallic complex to the surface of an organic or inorganic support.

This thesis deals with the application of immobilized rhodium complex catalysts in the heterogeneous gas phase hydroformylation of propylene and allyl alcohol. The catalysts are tested in a continuous flow system with a fixed bed reactor. The hydroformylation of propylene is studied both with chemically anchored phosphine rhodium complexes and with physically adsorbed rhodium complexes, and in both cases macroporous polystyrene-divinylbenzene resins are used as the support. For the hydroformylation of allyl alcohol,

supported liquid phase catalysts are used; the rhodium phosphine complex is dissolved in its phosphine ligand, and this solution is capillary condensed in the pores of the support.

Various preparation techniques for chemically anchoring rhodium phosphine complexes to supports are discussed in Chapter 2. The methods of functionalization of the porous resin with phosphine and phosphite ligands by means of chloromethylation and chlorophosphonation are studied and correlated with the performance of the catalyst. The method of coupling the rhodium complex to the functionalized support influences the activity and selectivity of the catalyst. By laser-Raman spectroscopy the presence of a high content of unpolymerized vinyl groups in the resin is shown, and functionalization substantially lowers the amount of these vinyl groups. The textures of supports and catalysts are studied by physical adsorption and by capillary condensation of nitrogen. The original support texture is hardly affected by the catalyst preparation.

The performance of chemically anchored rhodium complex catalysts was studied in the heterogeneous gas phase hydroformylation of propylene at 90°C and 0.1 MPa total pressure. Catalysts prepared via chlorophosphonation are perfectly stable and show a selectivity (*n*/iso ratio) for *n*-butyraldehyde formation of 1. Catalysts prepared via chloromethylation deactivate slightly, but their selectivity is higher (*n*/iso = 3). The addition of a small amount of triphenylphosphine (2-3 mol/mol Rh) to catalysts with chemically anchored ligands, prepared via chlorophosphonation raises both activity and selectivity. The hydroformylation activity per unit weight of rhodium for catalysts with anchored diphenylphosphines prepared via chlorophosphonation, decreases with increasing phosphorus ligand coverage (Chapter 3).

Mixtures of triphenylphosphine and rhodium complex monomolecularly dispersed over the surface of polystyrene-divinylbenzene, have been used in the hydroformylation of propylene between 58 and 92°C and at 0.1 MPa total pressure (Chapter 4). For stable catalysts the activity for propylene hydroformylation decreases and the selectivity for *n*-butyraldehyde increases with increasing triphenylphosphine coverage. The influence of the temperature on the catalytic performance was studied. In the temperature interval from 58 to 75°C an apparent activation energy of 61.6 kJ/mol is found, whereas between 75 and 92°C a value of 32.8 kJ/mol is obtained. The selectivity is constant up to 83°C, but decreases sharply at higher temperatures.

The hydroformylation of allyl alcohol, resulting in 4-hydroxybutyraldehyde as the main product, is of particular importance for the industrial preparation of 1,4-butanediol and tetrahydrofuran. In Chapter 5 we discuss the application of SLP catalysts in the heterogeneous gas phase hydroformylation of allyl alcohol. Rhodium complexes dissolved in triphenylphosphine or in tri-*p*-tolylphosphine and capillary condensed in the pores of a support material are highly stable catalysts with very high selectivity (98%) for 4-hydroxybutyraldehyde. The undesired side reaction of allyl alcohol to propionaldehyde is caused by the catalytic action of both the support material and phosphine-poor rhodium complexes. By the use of silica with a low aluminium content and of phosphine-rich rhodium complexes this problem is circumvented. The kinetics of the allyl alcohol hydroformylation are studied, and compared with those found for propylene hydroformylation.

SAMENVATTING

In een aantal belangrijke industriële processen wordt synthese gas, een mengsel van waterstof en koolmonoxide, gebruikt als grondstof, en wel in de Fischer-Tropsch synthese van koolwaterstoffen, de bereiding van methanol, de bereiding van azijnzuur, en in de vervaardiging van aldehyden en alcoholen door middel van hydroformylering van alkenen. De ontdekking van een groot aantal zeer actieve en selectieve overgangsmetaalcomplexen leidde tot de verbetering of ontwikkeling van dergelijke processen. De toepassing van geïmmobiliseerde overgangsmetaalcomplex katalysatoren is het hoofdonderwerp van dit proefschrift.

Hydridocarbonyltris(trifenylfosfine)rhodium(I) ($RhHCO(PPh_3)_3$) is een uitstekende homogene katalysator voor de hydroformylering van alkenen tot aldehyden, en is reeds actief bij relatief lage drukken en temperaturen (0,1-2,0 MPa; 90-130^oC). Het bezit in de hydroformylering van propeen een zeer hoge activiteit, tezamen met een hoge selectiviteit voor *n*-butyraldehyde, terwijl de vorming van bijprodukten gering is. De hoge prijs van het rhodium (ca. ƒ 70.000/kg) maakt een volledige terugwinning van deze kostbare katalysator noodzakelijk. Immobilisatie of heterogenisatie van het rhodiumcomplex op een drager zal leiden tot een technologisch aantrekkelijk en economisch proces, met als bijkomend voordeel dat de voeding en de produkten voortdurend van de katalysator gescheiden worden.

De laatste tien jaren is in het wetenschappelijk onderzoek aan de immobilisatie van homogene katalysatoren veel aandacht besteed. Problemen, zoals een geringe stabiliteit als gevolg van een langzame thermische ontleding van het complex, een te geringe selectiviteit voor het gewenste produkt, en een langzame afspoeling van het organometaalcomplex indien in de vloeistoffase gewerkt wordt, bleken belangrijke nadelen voor de technische toepassing van deze katalysatoren te zijn.

Een aantal methoden om organometaalcomplexen te immobiliseren zijn: sterke fysische adsorptie op een drager, capillair condensatie van een oplossing van het complex in een poreus dragermateriaal (supported liquid phase katalysatoren), en chemisch binden van het organometaalcomplex aan het oppervlak van een organisch of anorganisch dragermateriaal.

Dit proefschrift handelt over de toepassing van geïmmobiliseerde rhodiumcomplexkatalysatoren in de heterogene gasfase hydroformylering van propeen en allylalcohol. De katalysatoren werden dynamisch in een vastbed reactor beproefd. De hydroformylering van propeen is zowel met chemisch gebonden rhodiumfosfinecomplexen als met fysisch gebonden rhodiumfosfinecomplexen bestudeerd, en in beide gevallen zijn macroporeuze polystyreen-divinylbenzeen polymeren als dragermateriaal gebruikt. Voor de hydroformylering van allylalcohol zijn supported liquid phase katalysatoren toegepast; het rhodiumfosfinecomplex is opgelost in zijn eigen fosfineligand, en deze oplossing is capillair gecondenseerd in de poriën van een dragermateriaal.

Diverse bereidingsmethoden om rhodiumfosfinecomplexen aan dragermaterialen chemisch te verankeren worden in Hoofdstuk 2 besproken. Verschillende methoden om het poreuze polymeer te functionaliseren met fosfine en fosfietliganden, door middel van chloormethyleren en fosforchloreren, zijn onderzocht, en in verband gebracht met het gedrag van de katalysator. De methode waarop men het rhodiumcomplex aan de drager bindt, beïnvloedt zowel de activiteit als de selectiviteit van de katalysator. Met behulp van laser-Ramanspectroscopie is de aanwezigheid van een hoog gehalte aan niet-gepolymeriseerde vinylgroepen aangetoond, doch functionaliseren vermindert het vinylgroepengehalte aanzienlijk. De textuur van de dragers en de katalysatoren is met behulp van fysische adsorptie en stikstof capillaircondensatie onderzocht. De oorspronkelijke textuur van de drager wordt door de katalysatorbereiding nauwelijks gewijzigd.

Bij 90°C en 0,1 MPa totaaldruk werden de chemisch gebonden rhodiumcomplexkatalysatoren in de heterogene gasfase hydroformylering van propeen onderzocht. Katalysatoren die door fosforchlorering bereid zijn, zijn volledig stabiel en hebben een selectiviteit (*n*/iso verhouding) voor *n*-butyraldehyde van 1. Katalysatoren die door chloormethylering bereid zijn deactiveren langzaam, maar hun selectiviteit is hoger (*n*/iso = 3). Door de toevoeging van een geringe hoeveelheid trifenylfosfine (2-3 mol/mol Rh) aan katalysatoren met chemisch gebonden liganden die bereid zijn door fosforchlorering, wordt zowel de activiteit als de selectiviteit verhoogd. Voor katalysatoren met gebonden fosfines, die door fosforchlorering bereid zijn, neemt de hydroformyleringsactiviteit per gewichtseenheid rhodium af met een toenemende bedekking aan fosfineliganden (Hoofdstuk 3).

Mengsels van trifenylfosfine en rhodiumcomplex die monomoleculair verdeeld zijn over het oppervlak van polystyreen-divinylbenzeen, zijn toegepast voor de hydroformylering van propeen van 58 to 92°C en bij 0,1 MPa totaaldruk (Hoofdstuk 4). Voor stabiele katalysatoren neemt de activiteit voor propeenhydroformylering af en de selectiviteit voor *n*-butyraldehyde toe met een stijgende bedekking aan trifenylfosfine. De invloed van de temperatuur op het katalytisch gedrag werd onderzocht. In het temperatuurgebied van 58-75°C is een schijnbare activeringsenergie van 61,6 kJ/mol gevonden, terwijl tussen 75 en 92°C een waarde van 32,8 kJ/mol is verkregen. De selectiviteit is constant tot een temperatuur van 83°C, maar neemt daarboven sterk af.

De hydroformylering van allylalcohol, met als belangrijkste produkt 4-

hydroxybutyraldehyde, is van uitzonderlijk belang voor de industriële vervaardiging van 1,4-butaandiol en tetrahydrofuran. In Hoofdstuk 5 bespreken we de toepassing van SLP katalysatoren in de heterogene gasfase hydroformylering van allylalcohol. Rhodiumcomplexen opgelost in trifenylfosfine en tri-*p*-tolylfosfine en capillair gecondenseerd in de poriën van een dragermateriaal zijn zeer stabiele katalysatoren met een bijzonder hoge selectiviteit voor 4-hydroxybutyraldehyde. De ongewenste nevenreactie van allylalcohol tot propionaldehyde wordt veroorzaakt door de katalytische werking van zowel het dragermateriaal als van fosfine-arme rhodiumcomplexen. Door de toepassing van silica's met een laag aluminiumgehalte en van fosfine-rijke rhodiumcomplexen wordt dit probleem ondervangen. De kinetiek van de hydroformylering van allylalcohol is onderzocht en vergeleken met de kinetiek die voor propeenhydroformylering gevonden is.

CURRICULUM VITAE

Nico A. de Munck werd op 10 april 1952 geboren te Maastricht. Na de lagere school te Ede en Dordrecht doorlopen te hebben, ving hij in 1964 zijn middelbare schoolopleiding aan aan het "Het Christelijk Lyceum" te Dordrecht. In 1970 werd het diploma HBS-B behaald.

In datzelfde jaar werd de studie voor scheikundig ingenieur aan de Technische Hogeschool Delft aangevangen. Na een afstudeerperiode onder leiding van Prof.Dr.Ir. H. van Bekkum werd deze studie in april 1976 met het ingenieursexamen bekroond.

Per 1 mei 1976 trad hij in dienst van de Technische Hogeschool Delft als wetenschappelijk assistent, werkzaam in het Laboratorium voor Chemische Technologie in de werkgroep Katalyse, alwaar onder leiding van Prof.Dr. J.J.F. Scholten het promotieonderzoek uitgevoerd werd.

Per 1 mei 1980 trad hij in dienst van Essochem Holland te Rozenburg.