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# Hydroformylation catalyzed by immobilized rhodium complex to polymer support

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## Abstract

The concept for conducting hydroformylation reactions by immobilized rhodium complex on solid supports has received considerable attention, as revealed by many recent publications and patents.

Among a variety of polymeric supports, including styrene-divinyl benzene copolymers or inorganic compounds functionalized with phosphines or amines, vinyl pyridine copolymer crosslinked with divinylbenzene was used as the primary support in this investigation.

Three types of heterogeneous rhodium complex catalysts were prepared and their properties, and activities, selectivities and n/i ratio were studied for hydroformylation of propylene and 1-octene at a temperature of 120–130°C, a pressure of 30–90 $Kg/cm^2$, and a H2/CO ratio of 1. The results of this study revealed that these novel heterogeneous catalysts were useful for hydroformylation of olefins and have commercial potential.

*Keywords:* Hydroformylation; Polymer support; Rhodium complex; Immobilization; Vinyl pyridine polymer

## 1. Introduction

Oxo alcohol production via olefin hydroformylation is one of the typical processes which employs homogeneous complex catalyst. Table 1 summarizes the current market [1] and the technology of oxo alcohol.

Oxo alcohols are mainly used as solvents (carbon number from 2 to 5), plasticizers (carbon number from 4 to 13), and in various detergent applications (carbon number from 11 and higher). The current worldwide capacity has reached approximately 6 million ton per year.

The process economics requires that expensive metal complex like rhodium should be recycled without any loss. Thus, it is one of the key technology to keep catalyst stability in the separation area of which temperature is raised and carbon monoxide partial pressure is decreased. For the hydroformylation of propylene, homogeneous rhodium complex modified with triphenyl phosphine or triphenyl phosphine sulfate is predominantly used, as it has excellent activity, selectivity and n/i ratio in mild reaction conditions, and it can be recycled by flashing separation or water–oil phase separation without precipitation [1]. On the contrary, higher oxo alcohol production technology requires higher temperature in order to separate higher boiling product, which results in catalyst pre-

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Table 1
Material and technology for oxo alcohol

| Carbon number | Use | Capacity ($10^3$ ta) | Catalyst | Separation |
|---|---|---|---|---|
| 2–5 | Solvent | 2,095 | Rh–$PPh_3$ | Flash |
|  | NBA, IBA |  | Rh–$P(PhSO_3Na)_3$ | Phase separation |
| 8 | 2-EH | 2,420 | (Aldol condensation of NBA) |  |
| 4–13 | Plasticizer | 1,180 | Co–$PBu_3$ | Flash |
|  | DOP, DINP, DIDP |  | Rh–$PPh_3$ = O | Disti./$PPh_3$ addition |
| 11 > | Detergent | 385 | Co | Conv. to metal/salt |
|  |  |  | Rh | Adsorption |

cipitation and loss. Therefore, the rhodium catalyst is limited to be used except if it is captured through adsorption bed at once through operation and recovered [2]. In addition, the cobalt complex catalyst, mainly used for higher olefin hydroformylation, has to be separated and recycled after conversion of the complex to a stable and separable compound such as metal or water soluble salt and then conversed to complex again.

The concept for heterogenization of homogeneous transition metal complexes to solid supports has received considerable attention for an essential and practical approach to improve the catalyst recovery system, as revealed by many recent publications and patents. In the field of hydroformylation, extensive research has been carried out to heterogenize homogeneous catalyst not only for lower oxo alcohol but especially for higher oxo alcohol production, to facilitate separation of the catalyst from the product and to improve the overall efficiency of the hydroformylation process.

As for the supports of transition metal complexes, the literature has illustrated the use of many functionalized polymers, including styrene-divinyl benzene copolymers [3–5] functionalized with tertiary phosphines, amines and thiols and vinyl pyridine-divinylbenzene copolymers [6,7]. Other types of supports, such as functionalized inorganic supports, including silica, alumina and zeolite [8] functionalized with organic silicone incorporating pendant groups [9], have been studied in the past.

SAPCs (Supported Aqueous Phase Catalyst) [10,11], which are composed of a water soluble organometalic complex dissolved in a film of water supported on hydrophilic solid, have also

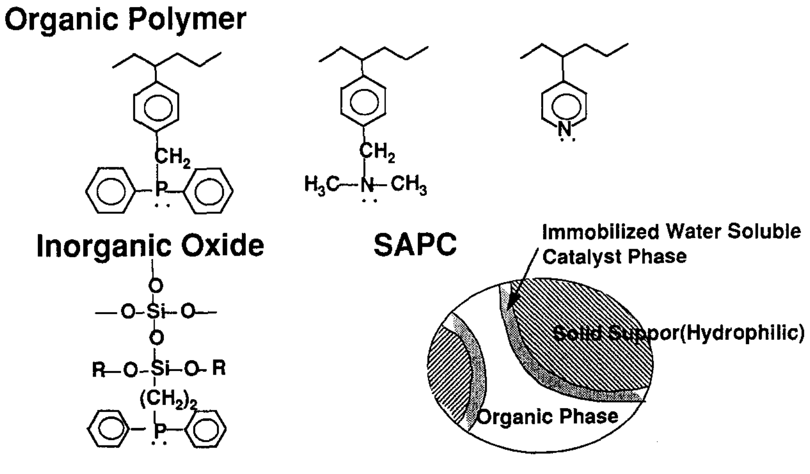

Fig. 1. Supports for Rh complex calatyst.

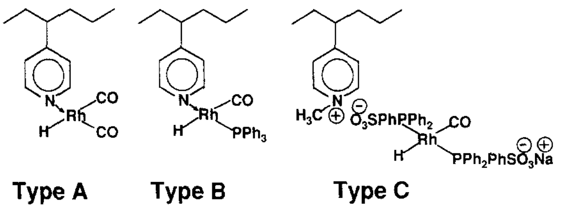

Fig. 2. Catalyst structure.

been investigated for hydroformylation. Fig. 1 illustrates the examples of the support for the rhodium complex referred here.

Styrene-divinylbenzene copolymers functionalized with anion exchange species like an amine group tend to decompose at around 100°C [12]. It is essential to select the stable support for prevention from rhodium leaching from the catalyst by decomposition of supporting materials. Although there are many types of functionalized styrene-divinylbenzene copolymers and inorganic compounds that may be used as supports, the crosslinked vinyl pyridine-divinylbenzene copolymer was used in this investigation, because of its superior thermal and chemical stabilities.

The present paper describes the preparation, structure and properties of rhodium carbonyl complexes bound to crosslinked vinyl pyridine-divinylbenzene copolymers and their use as catalysts [13,14] for the hydroformylation of propylene and 1-octene [15]. Studies of the activities, selectivities and normal/iso ratio of the products on these catalysts and the effects of ligands are presented.

Normal aldehydes are in general the desired product. While n-butyl aldehyde is essentially required to produce 2-ethyl hexanol via aldol condensation, both n-nonyl aldehyde and iso-nonyl aldehyde are the desired products as raw materials for plasticizer [16] as shown in Table 1. These catalysts were also characterized by solid $^{31}$P-NMR studies.

## 2. Experimental

### 2.1. Catalyst preparation

Three types of heterogeneous catalysts, type A, B and C, were prepared based on the vinyl pyridine-divinylbenzene copolymer. The pyridine polymer was prepared from 4-vinyl pyridine and divinylbenzene as crosslink agent in laboratory. It was porous and approximately 0.5 mm share.

As illustrated in Fig. 2, the catalysts were prepared in such way that rhodium in its complex should be coordination bonded by nitrogen in the pyridine polymer for type A, rhodium in its phosphine modified complex be also coordination bonded by nitrogen for type B and sulfonated phosphine rhodium anion complex be ionic bonded by methyl quaternized nitrogen in the pyridine polymer for type C.

The vinyl pyridine-divinylbenzene copolymers were treated with rhodium acetate, the required phosphine ligand, the olefin reactant and the solvent at the same time. Solvents of 20 weight parts of vinyl pyridine resin were used to

Table 2
Catalyst preparation conditions

| Reaction | $C_3'$ hydroformylation | | | $C_8'$ hydroformylation | |
|---|---|---|---|---|---|
| Structure | Type A | Type B | Type C | Type A | Type C |
| Catalyst | Cat. A | Cat. B | Cat. C | Cat. A1 | Cat. C1 |
| Temp. (°C) | | 120 | | 130 | |
| Press. (kg/cm$^2$) | | 30 | | 90 | |
| $H_2$/CO | | 1 | | 1 | |
| Solvent | Toluene | Butanol | Butanol | None | |
| Ligand | None | $PPh_3$ | $PPh_2PhSO_3Na$ | None | $PPh_2PhSO_3Na$ |

solve phosphine ligands completely. The mixture was subsequently heated for two hours under the reaction conditions shown in Table 2.

During the preparation of type C, the vinyl pyridine resin was treated with the mixture after it was quaternized with methyl bromide and the bromide anion was then converted to a hydroxyl anion and finally converted to a triphenyl phosphine mono sulfate.

After the catalyst preparation, the catalysts were washed by the solvent or 1-octene used in the preparation step to remove rhodium and ligands not bound to vinyl pyridine resin.

## 3. Catalyst structure

The prepared catalyst C was characterized by solid $^{31}$P-NMR analysis. The $^{31}$P-NMR spectra were measured to discuss chemical circumstance around P atom as shown in Fig. 3. The $^{31}$P-NMR spectra ($\delta = -4.1$) of quaternized vinyl pyridine copolymer after treatment of triphenyl phosphine mono sulfate was assigned to P of $PPh_2PhSO_3$ bound to resin, as P of $PPh_3$ shows $\delta = -9.3$. But this peak ($\delta = -4.1$) disappeared and a new peak ($\delta = 31.4$) corresponding to Rh–P–Ph of $Rh(PPh_3)_2ClCO$ ($\delta = 31.3$) appeared after catalyst preparation for catalyst type C by the above method as shown in Fig. 3.

This results indicate that triphenyl phosphine mono sulfate is converted to rhodium phosphine hydride carbonyl complex on the resin and the electron of P is donated to the Rh side. Therefore, a rhodium phosphine complex ($Rh(PPh_3SO_3)_2HCO$) bound to the vinyl pyridine copolymer was obtained and its structure is considered to be that shown in Fig. 2.

Thus, we conclude that the rhodium complex in catalyst C is fixed to the pyridine group of the vinyl pyridine copolymer by ionic bond.

Regarding the other catalysts type A and B, we estimated the structures for them as shown in Fig. 2 based on the result that nitrogen of pyridine is easy to form a coordination bond with rhodium.

## 4. Reaction

As shown in Fig. 4, the batch reaction experiments for hydroformylation of propylene and 1-octene were conducted in a 200 ml stirred autoclave, equipped with automatic pressure and temperature controllers under the reaction conditions.

The pressure was kept constant by make up of synthesis gas ($H_2/CO$ ratio of 1) from pressure reserved vessel. The reaction rate was determined by the decreasing rate of pressure reserved vessel. The leached rhodium from the

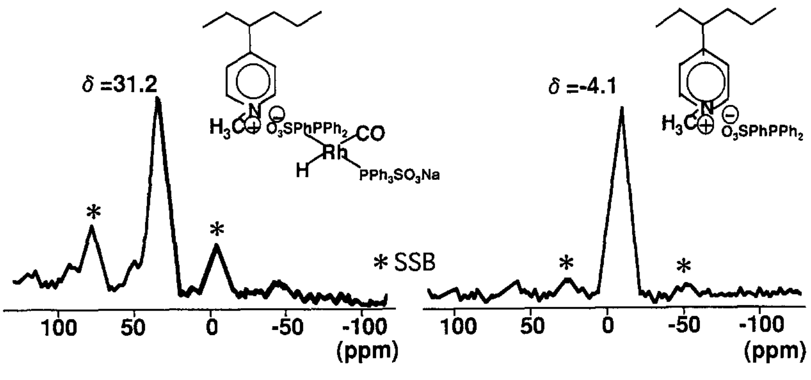

Fig. 3. $^{31}$P-NMR spectra data for catalyst C.

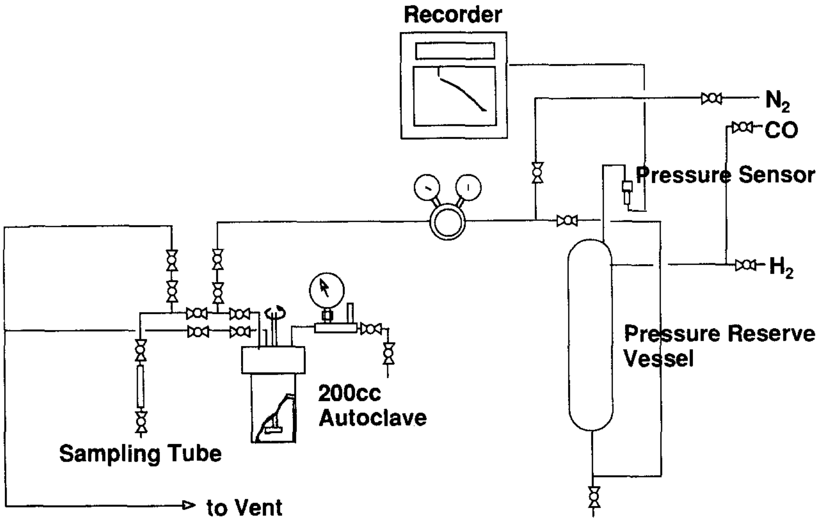

Fig. 4. Batch test unit.

catalyst to the liquid fase was investigated to analyze the sample in situ through the sampling line to the sampling tube during the reaction.

Liquid samples were analyzed by gas chromatography to know the aldehyde selectivity and the n/iso ratio. The rhodium concentration was determined using the flame atomic adsorption method.

## 5. Results and discussion

### 5.1. Propylene hydroformylation

Table 3 summarizes the test conditions and the experimental results for hydroformylation of propylene using the heterogeneous catalyst, prepared according to the procedure described above under 120°C of temperature, 30 Kg/cm2 of pressure, and a $H_2/CO$ ratio of 1. Toluene of 20 weight parts of catalyst was used as solvent as the same catalyst preparation.

Table 3
Propylene hydroformylation @120°C, 30 kg/cm$^2$G, $H_2/CO = 1$

| | $PPh_3/Rh$ (mol/mol) | Rate (mol/ molRh/hr) | n/i (mol/mol) |
|---|---|---|---|
| Homogeneous rhodium | 14 | 190 | 1.2 |
| | 78 | 2300 | 2.2 |
| Catalyst A | – | 0 | – |
| Catalyst B | – | 12 | 8.1 |
| Catalyst C | – | 130 | 4.4 |
| Cat. B + $PPh_3$(l) | 69 | 2700 | 1.5 |

The reaction liquid products only consisted of n-butyl aldehyde and its isomer, 2-methyl propanal. No hydrogenated products such as n-butanol or 2-methyl propanol were detected. The rhodium concentrations of the reaction liquid for catalyst A, B and C were negligible small so that the rhodium leaching was negligible and the reaction was caused by the rhodium complex bound to the resin support.

Catalyst A, B and C, and the homogeneous catalyst used as controls, showed low activities for the propylene hydroformylation, unless modified as described below.

The effect of ligand concentration on the catalyst activity were studied using a homogeneous rhodium catalyst. The homogeneous catalyst studies showed a low propylene hydroformylation activity at a ratio less than 20 of $PPh_3/Rh$, but showed significant activity (over 1000 mol/mol-Rh · hr) at a ratio of $PPh_3/Rh$ of 78.

The results suggest that the catalyst comprised of the rhodium phosphine hydride carbonyl complex requires existence of $PPh_3$ as high concentration to rhodium in order to obtain high catalyst activity [17].

To demonstrate this fact in our heterogeneous system, an excess of triphenyl phosphine was added in the liquid phase to increase the $PPh_3$/Rh ratio of catalyst B. Catalyst B then showed a significant activity as shown in Table 3. $PPh_3$/Rh, defined as the molar ratio of $PPh_3$ in the liquid phase to Rh on the catalyst for heterogeneous catalyst system, was 69, which gave high activity. In addition, rhodium leached from the catalyst is a little higher compared to that without addition of ligand in the liquid phase, but almost all rhodium was bound to the catalyst.

As a result, we concluded that a high ratio of $PPh_3$/Rh is essential for propylene hydroformylation.

As illustrated in Fig. 5, a number of different structures of rhodium complexes exist in the reaction system and the structures are believed to be changed according to the equilibrium concerning phosphine concentration, hydrogen and carbon monoxide pressures [18]. Among them, $HRh(CO)_2(PR_3)_2$ and $HRh(CO)(PR_3)_2$, which are present under a higher $PPh_3$/Rh ratio than 60, are considered to have higher hydroformylation activity. When the $PPh_3$/Rh ratio is increased more than 60 by addition of a ligand (catalyst B + PPh3), the structure will be that shown in Fig. 6 similar to the $HRh(CO)(PR_3)_2$ type structure active for propylene hydroformylation.

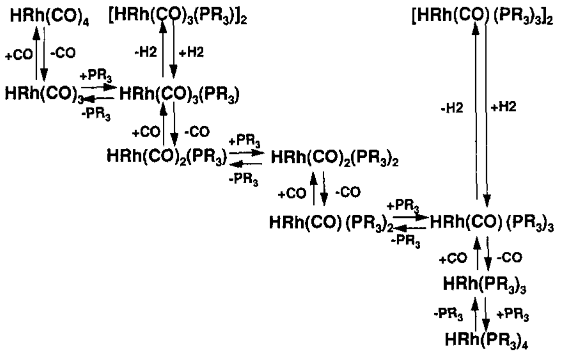

Fig. 5. Possible Rh complex species.

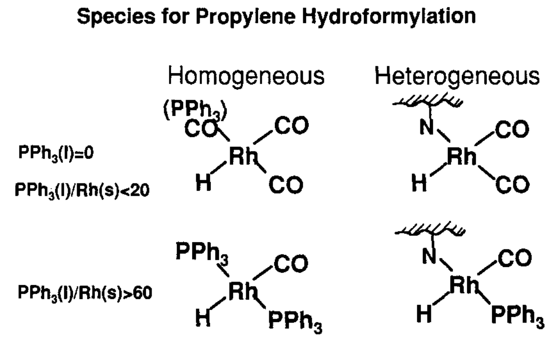

Fig. 6. Required condition and active catalyst species for propylene hydroformylation.

We note that, when $PPh_3$/Rh ratio is less than 20, most part of catalyst B is still considered to have the structure of type A and a small part of type B. When the $PPh_3$/Rh ratio is more than 60, the structure of catalyst B is believed to be that of type B shown in Fig. 2.

The n/i ratio defined as the molar ratio of n-butyl aldehyde to iso-butyl aldehyde for catalyst B and C was higher than that for homogeneous catalyst. The reason is that these heterogeneous catalysts are steric hindered by pyridine polymer as higher molecular compounds. However, catalyst B + $PPh_3$ showed the same or lower n/i ratios, which must be further investigated.

## 6. Octene hydroformylation

In contrast to propylene hydroformylation, as octene hydroformylation requires lower ligand/rhodium ratio to obtain high catalyst

Table 4
1-Octene hydroformylation @130°C, 90 kg/cm$^2$G, $H_2$/CO = 1
No $PPh_3$ ligand addition

| | Rate (mol/molRh/hr) | n/i (mol/mol) |
|---|---|---|
| Homogeneous | 7800 | 0.22 |
| Catalyst A1 | 4800 | 0.38 |
| Catalyst C1 | 1700 | 0.86 |

activity [2], our proposed heterogeneous catalyst is expected to show a significant activity without any addition of phosphine ligand.

Hydroformylation of 1-octene was conducted using the same batch autoclave under 130°C, 90 $Kg/cm^2$ of pressure, and $H_2/CO$ ratio of 1. No alcohols were produced by the hydrogenation of the C9 aldehyde. As shown in Table 4, the heterogeneous catalyst A1 and C1 displayed a high activity without any addition of ligand in the liquid phase and it produced only n-nonanal and 2-methyl octanal as products.

The normal to iso aldehyde ratio was improved with our heterogeneous catalyst A1 and C1. Moreover, catalyst C1 is affected by steric hindrance in comparison to catalyst A1. Thus, catalyst C1 showed a higher n/i ratio and a lower activity.

Although $PPh_3$ suppresses the catalyst activity for octene hydroformylation [19] due to strong coordination affinity, the homogeneous processes requires addition of a ligand such as $PPh_3$ to maintain catalyst stability in a separation system, where the catalyst is heated. In this regard, the latest mixed octene hydroformylation process employs a rhodium complex modified with $PPh_3 = O$ ligand in the reaction system and combined ligands of $PPh_3 = O$ with $PPh_3$ in the separation system. Separation of the product and the rhodium complex catalyst is conducted under addition of $PPh_3$ and then after separation, $PPh_3$ is oxidized to $PPh_3 = O$ and recycled to the reactor [19]. As a result, this process might require addition of $PPh_3$.

Consequently, our heterogeneous process could offer advantage for homogeneous process, as it does not require costly rhodium recovery systems like an adsorption system or addition of $PPh_3$.

## 7. Conclusion

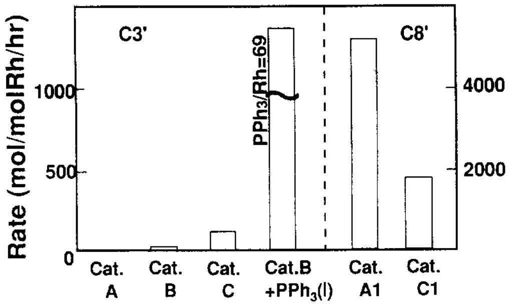

Fig. 7. Catalyst activity.

Novel heterogeneous rhodium complex catalysts bound to vinyl pyridine copolymer were found through the present study. These novel catalysts are proposed as solid catalysts for propylene and 1-octene hydroformylations as summarized in Fig. 7. The solid catalysts are to be used with excess $PPh_3$ ligand in the liquid phase for propylene hydroformylation and with no $PPh_3$ ligand in the liquid phase for 1-octene hydroformylation at temperature of 120–130°, 30–90 $Kg/cm^2$ pressure, and $H_2/CO$ ratio of 1.

These novel catalysts appear to have commercial applications for the production of a wide range of oxo alcohol products and offer advantage for homogeneous process especially for higher oxo alcohol, as it does not require a costly catalyst separation and recovery system.

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