Development of Organic Polymer-bound Metal Complex Catalysts

Kiyotomi Kaneda1)* and David E. Bergbreiter2)

1) Dept. of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560
2) Dept. of Chemistry, Texas A&M University, College Station, Texas 77843-3255, U.S.A.

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Preparation of polystyrene and ethylene oligomer-bound transition metal complexes (metal: Pd, Rh, Ni, Ru and Nd) and their catalysis for various organic reactions have been studied. Heterogeneous phosphinated polystyrene-bound Pd(II) complexes prepared by the reaction of phosphinated polystyrene with PdCl2, which could be used for reusable catalysts for selective hydrogenation of olefins and acetylenes, and for codimerization of acetylenes and allylic halides. Cationic Pd(II) complexes obtained from the treatment of the polymeric Pd(II) complexes with AgBF4 had the catalytic activity for selective coooligomerizations of olefins. Reduction of the polymeric Pd(II) complexes with hydrazine gave polymer-bound Pd(0) complexes as stable species, which had catalytic activities for representative types of Pd(0)-induced organic reactions. Aminated polystyrene-bound Rh carbonyl cluster complexes (Rh6, Rh7, and Rh14 species) were selectively formed by the reaction of aminated polystyrenes with Rh6(CO)16 in the presence of H2O and CO. These polystyrene-bound Rh cluster anion complexes catalyzed deoxygenation of various N-O bonds (nitro compounds, oximes, hydroxyl amines, and N-oxides), hydroxyhydroxymethylation of olefins, and selective reduction of carbonyl compounds under the WGSR conditions. Amino moieties on polystyrene play an important role, both in the generation of active Rh species and the catalysis for the above reactions.

Functional linear ethylene oligomers (degrees of polymerization between 150—300) having phosphine, phosphinite, and carboxylate ligands were synthesized. The treatment of the functional oligomers with transition metal complexes of Pd, Rh, Ru, Ni, and Nd gave the corresponding oligomer-bound metal complexes, which were recoverable and reusable homogeneous catalysts for a wide variety of organic reactions (hydrogenation, oligomerization, allylic substitution, oxidation, etc.). Such oligomeric complexes dissolved completely in the above reaction conditions at 100—110°C and cooling the solutions led to quantitative recovery of heterogeneous catalysts. Their reactivity and selectivity in the above reactions accurately mirror those of low molecular weight analogs. A combination catalyst system of ethyleneoligomer-bound Rh(I) complex and polyvinylpyridine-bound Cr(VI) complex could be used for the two-step oxidation reduction sequence (Wolf and Lamb reaction); unsaturated alcohols gave directly saturated ketone in a H2 atmosphere.

1. Introduction

For the last several decades, a large number of homogeneous metal-catalyzed reactions have been developed to greatly contribute toward making an arsenal of synthetic methods available to organic chemists. For example, the development of chiral metal catalysts, that form optically active materials like amino acids and epoxy alcohols with stereoselectivities rivaling biocatalysts, are monumental achievements. The use of homogeneous metal catalysts on an industrial scale, however, still faces practical problems, e.g., difficulties associated with corrosion, plating out on the reactor wall, and catalyst or ligand recovery from the reaction mixture. The latter question of metal separation from products is of interest because of both the desire to reuse catalysts and the importance of excluding metal and ligand contaminants from products of high performance materials.

Chemically bonding metal complexes to an insoluble solid is a method designed to overcome these difficulties for homogeneous catalysts. This method which is the subject of this review achieves its goal by binding metal compounds to organic polymers or inorganic oxides containing ligand atoms. The catalysts prepared in such manner have attributes of both, those usually classified as...
"heterogeneous" and those as "homogeneous", and can be regarded as a new class of "hybrid catalysts". During the last quarter century, many approaches to the design of "hybrid catalysts" have been examined. These studies have led to the discovery of new catalytic functions including: (1) active site isolation, (2) cooperative catalysis by several sites, (3) steric control by supports on reaction intermediates, and (4) applications for simultaneous-sequential reactions. Furthermore, new and/or unstable metal species, e.g., coordinatively unsaturated metal and metal cluster complexes, have been isolated on the support matrices. The remarkable progress in this heterogenization of metal complexes using organic polymers or inorganic oxides has built up an attractive field in preparation of metal catalysts.

Here, we describe studies on the preparation of polystyrene and ethylene oligomer-bound metal complexes (metal: Pd, Rh, Ni, Ru, and Fe), and on their use in catalysis of various organic reactions. New catalyst functions originated from the heterogenized complexes are discussed also in relation to their counterparts, homogeneous catalysts.

2. Heterogeneous Polystyrene-bound Metal Catalysts

Generally, organic polymer-bound metal complexes have been prepared by introduction of coordinating ligands into organic polymers, followed by preparation of metal complexes with the functional polymers. Further polymerization of metal complexes having olefinic moieties yields the polymer-bound metal complexes. Among the various organic supports used in the above preparations, polystyrenes have been most widely used because of the ease with which various kinds of coordinating ligands can be introduced onto polystyrene. For example, we have heterogenized monomeric Pd complexes using phosphinated polystyrenes to give polymer-bound Pd(II) and Pd(0) complexes, and Rh carbonyl clusters using aminated polystyrenes to give polymer-bound Rh6 and Rh14 cluster anion complexes.

2.1. Preparation of Polystyrene-bound Metal Complexes

2.1.1. Preparation of Phosphinated Polystyrene-bound Pd(II) and Pd(0) Complexes

Phosphinated polystyrenes were synthesized by the reaction of p-chloromethylated polystyrene with diphenylphosphinolithium. Under a nitrogen atmosphere, phosphinated polymer (2.5g, 8.5mg-atom of P) was dissolved for 26h in a refluxing 1:2 benzene-ethanol (100ml) solution containing PdCl2 (1.5g, 8.5mmol). A precipitate was recovered by filtration and washed with ethanol until the filtrate was colorless. The solid was dried for 50h in vacuum to give a yellow polymeric Pd complex (3.8g). From the results of elemental analysis, IR, ESR, MAS NMR, and XPS, the polymeric palladium complexes seem to be mostly three-coordinated \( \text{Pd}^{II} \cdot \text{Cl}_2 \) (P is the phosphinated polymer ligand).

The polymer-bound palladium(II) complex (7.0g, 14.8mg-atom of Pd) was added to an ethanol (50ml) solution containing triphenylphosphine (9.1g, 34.7mmol). The mixture was stirred at room temperature for 3h. Then, hydrazine hydrate (6.0g, 0.12mol) was added to the mixture and stirring was continued for 2h. The resulting polymer was filtered, washed with ethanol and ether, and dried under vacuum to give a dark green polymeric complex (8.9g). All the above procedures were carried out under an argon atmosphere. The reduced complex seems to be an unsaturated, two-coordinated palladium(0) complex with two vacant sites as shown in Scheme 1.

Polymer chains sterically hinder the coordination of a sufficient number of phosphine ligands to form a coordinatively saturated Pd complex. Thus, they, in effect, stabilize the unsaturated Pd complex. The facile formation of unsaturated Pd complexes using polymeric ligands is one of the advantages of hybrid catalysts over homogeneous metal systems.

2.1.2. Preparation of Aminated Polystyrene-bound Rh6 and Rh14 Complexes

The reaction of Rh6(CO)16 (53mg, 0.05mmol) with aminated polystyrene (Ia, 0.16g, 0.8mg-atom of N) in H2O (2.88ml) and ethoxyethanol (2ml) was carried out under 6atm of CO at 40ºC. After 24h, a dark green polymer (0.14g) of \( [\text{Rh}_6(\text{CO})_{15}]^2- \) and \( [\text{Rh}_6(\text{CO})_{15}\text{H}]^- \) was obtained by filtration and further washed with ethoxyethanol and ethyl ether successively in a CO atmosphere. The polymer-bound Rh complexes were stable.

Scheme 1 Preparation of Phosphinated Polystyrene-bound Pd(II) and Pd(0) Catalyst

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The reaction of Rh6(CO)16 (53 mg, 0.05 mmol) with aminated polystyrene (Ia, 0.16 g, 0.8 mg-atom of N) in a mixed solvent of H2O (2.88 ml) and ethoxyethanol (2 ml) was carried out under 4 atm of CO at 80°C. After 24 h, a brown polymer (0.15 g) with \([\text{Rh}_{14}(\text{CO})_{24}]^-\) was obtained by filtration. It was further purified by washing with ethoxyethanol and ethyl ether successively in a CO atmosphere. This heterogenization method using the aminated polystyrenes in aqueous media can be applied to other metal carbonyl cluster anions, e.g., [Ru5(CO)11]2- and [Fe5(CO)11H]-14).

2.2. Catalysis of Polymer-bound Pd Complexes

2.2.1. Hydrogenation

The phosphinated polystyrene-bound palladium complexes are extremely efficient catalysts for hydrogenation of conjugated olefins and allylic compounds at ambient temperature and pressure. The activity of these catalysts is very sensitive to steric hindrance pertaining to the carbon-carbon double bond and to the molecular size of olefins15). Conjugated dienes are selectively reduced to monoenes; cyclopentadiene gave exclusively cyclopentene (Eq. (1))16).

\[
\text{[Pd-II]} + \text{H}_2 (1 \text{ atm}) \xrightleftharpoons[97\%]{\text{Pd-III}} \text{H}_2 \text{O}/\text{Ethanol} \quad \text{r.t.} \quad \text{(97\%)} \quad (1)
\]

Functional groups such as keto-, hydroxyl-, cyano, ether, ester, and carboxyl are not reduced under similar reaction conditions. The polymer-bound palladium complex is divalent, before and after being used for the hydrogenation. It can be reused without loss of the catalytic activity17). When the catalyst was pretreated with hydrogen in the presence of a solvent, the color of the catalyst changed from yellow to dark green and the induction period in the hydrogenation disappeared. Then, a hydride complex seems to be formed by the heterolytic fission of hydrogen by replacing one of the chlorines on the palladium.

On the basis of kinetic study, we can present a scheme containing Pd-H species for the hydrogenation (Scheme 2)17).

Using the principle of steady state, the rate is

\[
R = -\frac{d[S]}{dt} = \frac{k_1k_2[S][P][A]}{k_1 + k_1[S] + k_2}[P] \quad (2)
\]

where \(k_1\), \(k_1\), and \(k_2\) are the rate constants for the reaction equations, \([\text{H}_2]\) is the concentration of hydrogen, and \([S]\) and \([A]\) are the substrate and catalyst concentration, respectively.

The kinetic data at 25°C for hydrogenation of cyclohexene, styrene, and 1,3-cyclooctadiene obtained from these studies are given in Table 1. The activation entropies \(\Delta S^\ddagger\) are negative. The decrease in entropy corresponds to a considerable loss of freedom attributed to fixation of the catalyst molecule on the polymer matrix. The value of frequency factor \(A\) are about \(10^4\) to \(10^7\), and are very small compared with those of liquid phase homogeneous reactions, which are ordinarily about \(10^{12}\)17). The kinetic characteristics of catalysis with this polymer-bound palladium complex resemble those of heterogeneous catalysts rather than those of homogeneous catalysts. The polymeric complex is much more active for hydrogenation of olefins than an analogous homogeneous catalyst, PdCl2(PPh3)2-SnCl2; the homogeneous catalyst requires a higher pressure of hydrogen and stanous chloride as an activating agent18). The homogeneous catalyst hydrogenates nonconjugated dienes at a faster rate than conjugated dienes. On the other hand, the polymeric catalyst displays its reverse activity17).

The phosphinated polystyrene-bound palladium(II) complex is also an effective catalyst for the hydrogenation of acetylenes19). Partial hydrogenation of isolated triple bonds to cis-double bonds was accomplished with high selectivity (Eq. (3)).

\[
\text{CH}_3-\text{C}==\text{C}-\text{H}_2 + \text{H}_2 (1 \text{ atm}) \xrightarrow{\text{Polymeric Pd(II)}} \text{CH}_3-\text{C}==\text{C}-\text{H}_2 \quad \text{20°C, 24h, Benzene/Ethanol} \quad (91\%)
\]
is thought to be responsible for this success because the strength of coordination of triple bonds is much greater than that of double bonds. The selectivities observed here are comparable to those of the best catalyst systems for the selective hydrogenation of acetylenes to olefins reported earlier by homogeneous cationic rhodium and the heterogeneous Lindlar catalyst.

2.2.2. Codimerization and Cooligomerization

We have already found that the selective codimerization of various acetylenes and allylic halides proceeds smoothly with homogeneous palladium(II) catalysts. The reaction provides a useful 1,4-diene synthesis without isomerization to 1,3-dienes. The use of the phosphinated polystyrene-bound palladium(II) complex can heterogenize the codimerization reaction (Eq. (4)). In the case of the polymeric catalyst, the codimerization is more strongly affected by molecular size of acetylene compounds. In the homogeneous Pd(II) system, the acetylene compound must be added slowly to the allylic halide solution to prevent polymerization of acetylenes. Interestingly, the use of polymeric Pd(II) complex did not cause the polymerization even in high concentrations of the alkyne substrate. The polymeric palladium(II) complex catalyzes cotrimerization of styrene and ethylene or propylene in the presence of AgBF₄. The reaction of styrene and ethylene (1 atm) selectively gave cotrimers (Eq. (5)). On the other hand, under 5 atm of ethylene, 1:1 adducts of styrene and ethylene were obtained in almost quantitative yield (Eq. (6)). All of the above oligomers contain internal phenyl groups.

\[
\text{Ph} \rightarrow \text{CH} = \text{CH} \rightarrow \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{Pd(II)}} \text{1 atm} \text{Ph} \\
\text{H}_2 \text{C} = \text{C} \rightarrow \text{CH}_2 \text{CH}_3 + \text{H}_2 \text{C} = \text{C} \rightarrow \text{CH}_2 \text{CH}_3 \xrightarrow{50^\circ\text{C}} \text{Ph} \\
\text{C} = \text{C} + \text{H} + \text{Ph} = \xrightarrow{\text{C} = \text{C} - \text{Ph}} \\
\text{C} = \text{C} + \text{X} + \text{R} \xrightarrow{\text{a} - \text{aryl-PdX(PPh}_3)_2 \text{BF}_4} \text{C} = \text{C} - \text{Y} \\
\text{YH: alcohols, amines, carboxylic acids, phenol, water, and silanes} \\
\]

Various carbon–carbon formation reactions are listed in Table 2. In the reaction of styrene with iodobenzene (run 1), stilbene was formed at 86% yield and (E)-stilbene could be easily isolated at 75% yield by recrystallization. The reactions of the isomeric β-bromostyrenes with methylmagnesium iodide also induced the codimerization of styrene and butadiene and the homodimerization of styrene in the absence of ethylene or propylene. The polymeric complex separated after the reaction which it had catalyzed; the reaction of styrene with ethylene (5 atm) gave a 87% of the codimers. AgPF₆ and AgClO₄ were useful in generating the catalyst for the reaction. The active species for the above oligomerizations is probably a cationic palladium(II) complex formed by loss of a chloride ligand facilitated by the silver additive. The corresponding homogeneous cationic Pd catalyst, Pd(PPh₃)₄(BF₄)₂ efficiently catalyzed the homodimerization of styrene. Codimerization of olefins in the presence of homogeneous transition metal complexes has been extensively studied: codimers containing an internal phenyl group are also obtained by using α-aryl-PdX(PPh₃)₂BF₃ or (π-allyl-PdCl)₂-Lewis acid-tertiary phosphine, while PdCl₂ and (PdCl₂-PPh₂-PPh₂) give mainly external phenyl substituted codimers. It is significant to note that little is known concerning cotrimerization of monoolefins. A similarly selective cotrimerization could be observed in the reaction of styrene with propylene (1 atm).

2.2.3. Carbon–Carbon Bond Formation

The polymer-bound palladium(0) complex has high catalytic activities for two representative types of Pd(0)-induced organic reactions (Eqs. (7)—(10)). One consists of carbon–carbon bond formation reactions involving the oxidative addition of organic halides to the metal (a) vinylic hydrogen substitution with aryl halides, (b) acetylenic hydrogen substitution with aryl halides, and (c) vinylic halogen substitution with Grignard reagents), and another is telomerization of conjugated diene with nucleophiles.
proceed quantitatively and show a high stereospecificity (runs 7 and 8). The polymeric Pd complex, which was separated from the reaction mixture by centrifuge in air, could be reused with some loss of activity (runs 1-3). Even after the catalyst had been exposed to air for 6 days at room temperature, its catalytic activity did not remarkably decrease (run 4).

The reaction of butadiene with secondary amines gave two regioisomers of 1-amino-2,7-octadiene and 3-amino-1,7-octadiene, and 1,3,7-octatriene was a minor product. In the case of formic acid, (formyloxy) octadiene of 2:1 adduct could not be detected, and 1,7-octadiene was exclusively formed.

In contrast, 1,6-octadiene was exclusively obtained in the presence of the homogeneous Pd(OAc)$_2$ catalyst.

### 2.3. Catalysis of Rh Carbonyl Cluster Complexes

#### 2.3.1. Homogeneous Rh Carbonyl Clusters

During development of efficient metal catalysts for organic synthesis in aqueous system, it was found that homogeneous Rh carbonyl clusters in the presence of CO and H$_2$O effectively catalyzed deoxygenation of various N-O bonds, chemoselective reduction between carbonyl and olefinic functions, and hydrohydroxymethylation of olefins via hydroformylation in Scheme 3 (Eqs. (11)-(18)). Typical results of the deoxygenation are shown in Table 3. Amines and pyridines are effective additive bases that accelerate the catalytic activities of the above reactions.

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![Scheme 3 Various Organic Reactions Catalyzed by Rh Clusters in the Presence of CO and H$_2$O](image-url)
H₂, while an α-substituent effect was not observed in the nitrobenzene deoxygenation. Strong basicity of the pyridines with high pKa values is an essential factor for attaining high yields of aniline in the deoxygenation of nitrobenzene.

2.3.2. Aminated Polystyrene-bound Rh Carbonyl Clusters

1) Deoxygenation

The effect of amino functions on the above deoxygenations was examined by using various aminated polymers (Scheme 4, Ia—Id). A polymer having 1,3-propanediamine (8 mmol) instead of N,N,N',N'-tetramethyl-1,3-propanediamine (5 mmol) in the homogeneous system is the most effective additive. Selective deoxygenations were achieved in relatively small amounts of amino moieties, compared with the case of the homogeneous systems.

Table 3 Deoxygenation of Various N-O Bonds with Use of CO and H₂O in the Presence of Rh₆(CO)₁₆-Aminated Polystyrene Catalyst

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction time [h]</th>
<th>Products [yield, %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₆H₅)₃NOH</td>
<td>5 (5)</td>
<td>(C₆H₅)₃NH [89(93)]</td>
</tr>
<tr>
<td>(C₆H₅)₂CHNOH</td>
<td>5 (5)</td>
<td>(C₆H₅)₂CNH [96(70)]</td>
</tr>
<tr>
<td>Ph·N'-Ni-O</td>
<td>24 (5)</td>
<td>Ph·Ni·(C₆H₅) [99(75)]</td>
</tr>
<tr>
<td>C₆H₅CH·N-O</td>
<td>48 (5)</td>
<td>C₆H₅CN [61(61)], C₆H₅OH [20(20)]</td>
</tr>
<tr>
<td>cyclohexyl·CH·N-O</td>
<td>48 (5)</td>
<td>c·C₆H₅CN [65(71)], c·C₆H₅CH·OH [35(12)]</td>
</tr>
<tr>
<td>PhCH₃·CH·N-O</td>
<td>48 (5)</td>
<td>Ph·CH₃·CH·CN [83(84)]</td>
</tr>
<tr>
<td>C₆H₅NO₂</td>
<td>48 (24)</td>
<td>C₆H₅CN [75(71), 44%], C₆H₅OH [19(15), 20%]</td>
</tr>
<tr>
<td>PhCH₃·CH·CH₂·NO₂</td>
<td>48 (24)</td>
<td>Ph·CH₃·CH·CH₂·CN [85(84)]</td>
</tr>
</tbody>
</table>

a) Conditions: Rh₆(CO)₁₆, 0.05 mmol; aminated polymer Ia, 0.16 g (0.8 mmol of N); substrate, 5 mmol; 2-ethoxyethanol, 2 ml; H₂O, 2.08 ml; P(CO) = 8 atm; 40℃. b) Values in parentheses are for the corresponding homogeneous Rh₆(CO)₁₆ system, and the same reaction conditions as for the heterogeneous system were used except for the addition of N,N,N,N',N'-tetramethyl-1,3-propanediamine (5 mmol). c) P(CO) = 16 atm. d) The propanediamine (0.4 mmol).

Table 4 Additive Effect of Various Amines and Pyridines on Deoxygenation of Nitrobenzene and the Water Gas Shift Reaction Using Rh₆(CO)₁₆

<table>
<thead>
<tr>
<th>Base (pKa)</th>
<th>Deoxygenation Reaction time [h]</th>
<th>Yield of aniline [%]</th>
<th>WGSR Yield of H₂ [mol H₂/mol Rh₆(CO)₁₆]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃·CH₂·CH₃·NH₃ (9.97)</td>
<td>10</td>
<td>79</td>
<td>22°</td>
</tr>
<tr>
<td>NH₂·(CH₂)₄·NH₂ (10.65)</td>
<td>10</td>
<td>72</td>
<td>1</td>
</tr>
<tr>
<td>NH₃·(CH₂)₄·NH₃ (10.64)</td>
<td>10</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>C₆H₅·CH·NH·CH·NH·CH₃ (9.5)</td>
<td>10</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>(C₆H₅)₃·N·CH·NH·CH₂·CH₃ (8.97)</td>
<td>4</td>
<td>&gt;99</td>
<td>2.5</td>
</tr>
<tr>
<td>(C₆H₅)₃·N·(CH₂)₄·NH·CH₃ (10.2)</td>
<td>2.5</td>
<td>&gt;99</td>
<td>0</td>
</tr>
<tr>
<td>N·(C₆H₅)₂ (10.65)</td>
<td>10</td>
<td>83</td>
<td>0</td>
</tr>
</tbody>
</table>

a) For deoxygenation: nitrobenzene 1.5 mmol, Rh₆(CO)₁₆ 0.05 mmol, base 15 mmol, H₂O 0.72 ml, 2-ethoxyethanol 3 ml, P(CO) = 700 mmHg, 80℃. For WGSR: Rh₆(CO)₁₆ 0.05 mmol, base 85 mmol, H₂O 0.72 ml, 2-ethoxyethanol [10-base] ml, P(CO) = 700 mmHg. b) Yield of H₂ mol of H₂ per 6 h. c) Base 17 mmol, ethoxyethanol 10 ml, 120℃.
the amines in polymers increase the basicity of reaction media near the polymer surface. This facilitates formation of Rh carbonyl cluster anions as active species and also promotes stability of the Rh cluster anions through ammonium ions. Structure of amino moieties in polymers is a crucial factor to design a suitable polystyrene support for selective deoxygenations. Functions of amino moieties in the polymers are summarized as follows: (1) generation of OH• in aqueous media to yield Rh-carbonyl cluster anions as active species, (2) stabilization and heterogenization of the Rh-cluster anions by forming ion-pair, and (3) control for reaction course through coordination of amines to Rh clusters.

In the deoxygenations of aliphatic nitro compounds, oximes, hydroxyl amines, and N-oxides at 40 ºC, dark green polymers with [Rh6(CO)15]2− and [Rh6(CO)15H]− species were isolated, while deoxygenation of nitrobenzene at 80 ºC gave a dark brown polymer with [Rh14(CO)25]4− species. The isolated polymeric Rh complexes can be reused as catalysts for the above deoxygenations. By the use of such aminated polymer ligand, various Rh carbonyl clusters can be generated as stable species in the polymer resins.

2) Hydrohydroxymethylation

Since H2O acts as (1) hydrogen source for products, (2) generation of OH• to lead formation of Rh cluster anions, and (3) formation of ammonium ions by reaction with amino moieties, large amounts of water are required in the selective deoxygenation of N-O bonds. Therefore, solvents must be well miscible, both with substrates of organic compounds and water. In the homogeneous Rh cluster catalysis, it was found that the hydroxyl and ether groups in solvent molecules were essential for attaining high yields of the deoxygenation products. In order to design more efficient polymer-bound Rh catalysts in aqueous media, the aminated polymers having hydroxyl and ether groups (II−IV) were prepared according to Scheme 5. Results of carbonylation of 1-octene using the above aminated polymers (I−IV) are shown in Table 5. Increasing hydroxyl group concentration in aminated polymers increases the yield of the alcohols; in benzene, a hydrophobic solvent, aminated polymers of I and IV without hydroxyl groups showed extremely low catalytic activities for the hydrohydroxymethylation. Introduction of hydroxyl groups into the polymers leads to appearance of a new catalyst function, the formation of a “triphase system” for the olefin hydrohydroxymethylation. This heterogenization of solvents using polymers called, “solid

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Scheme 4 Preparation of Aminated Polystyrenes

Scheme 5 Preparation of Bifunctional Polystyrenes

Table 5 Reaction of 1-Butene Using CO and H2O in the Presence of Various Aminated Polymers and TMPDA

| Solvent | Polymer (Ia) | (II) | (III) | (IV) | TMPDA
|---------|-------------|------|-------|------|-------
| THF     | 41 (1.74)   | 60 (1.62) | 83 (1.68) | 46 (2.17) | 27 (2.72) |
| benzene | 8 (1.89)    | 55 (1.29) | 79 (1.28) | 5 (3.18)  | 8 (3.04)  |

a) Rh6(CO)15 0.05 mmol, 1-buten 5 mmol, polymer 0.8 mg-atom of N, solvent 4 ml, H2O 0.72 ml, P(CO) = 20 atm, 80 ºC, 24 h.

b) Yields are based on 1-butene used and l/b indicates product ratio between pentanol and 2-methyl-1-butanol.
c) TMPDA 5 mmol, 5 h.

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Fig. 1 Bifunctional Polystyrene-bound Rh6(CO)152− Catalyst
solvent”, allows the use of wide variety of solvents in aqueous media, which results in simplification of work-up procedure. After the reaction, Rh6-cluster anions [Rh6(CO)15]2− and [Rh6(CO)15H]− were observed in the polymers. A possible model of polymer-bound [Rh6(CO)15]2− cluster complex is shown in Fig. 1.

The combined system of Rh6(CO)16 and the aminated polymer (IV) also is a unique catalyst for chemoselective reduction of nitro function among nitro, olefinic, halogeno, ester groups. For an example, 2-chloro-5-nitro-ethylcinnamate gave exclusively 5-amino-2chboro-ethylcinnamate (Eq. (19))

3. Soluble Polymer-bound Catalysts

An alternative to insoluble cross-linked polystyrene-bound catalysts are soluble polymer-bound catalysts. In contrast to the catalysts discussed above, these polymeric systems are designed to be homogeneous during a reaction. Separation of the catalyst from the reaction product and recovery of the catalyst are effected as a separate step at the end of the reaction and is facilitated by the properties of a macromolecular ligand.

Two general approaches have been used in preparing soluble polymeric catalysts. The first of these arose from the pioneering work in this area began in the 1970’s by Bayer’s group and was based on a peptide synthesis strategy —liquid phase peptide synthesis42,43). Both linear polystyrene and poly(ethylene glycol) derivatives were used as soluble polymeric ligands44). End group modifications of poly(ethylene glycol) and other water soluble polymers have also been described as a way to produce water soluble phosphate ligands45,46). A chloromethylated polystyrene was first prepared. Substitution with potassium diphenylphosphide then was used to make alkylidriarylphosphine ligands. These soluble macromolecular phosphines were in turn used to complex a transition metal. The second general approach to preparing soluble polymeric catalysts was developed by our group and has involved use of polyethylene oligomers47). Our group has shown that linear polyethylene oligomers with degrees of polymerization between 150—300 have the same solubility properties as high density polyethylene. Such oligomers are completely insoluble in solvents such as toluene or dibutyl ether at 25°C but dissolve readily in such solvents at 100—110°C. This temperature dependent solubility can be used in catalysis as illustrated in Scheme 6.

Several features of this scheme are noteworthy. First, the catalyst is truly a homogeneous catalyst. Studies comparing a variety of phosphate and phosphite ligated transition metal catalysts, where electronically analogous high and low molecular weight phosphine and phosphite ligands were used, have demonstrated that catalyst activity and selectivity are not affected by the presence of the polyethylene ligand48,55). Contrary to what some might have expected, the polyethylene ligand has no significant steric effect on a reaction. Thus, ligand/metal ratios or ligand design and steric can be modified and optimized with a low molecular weight ligand. Subsequent attachment of an optimal ligand to a polyethylene oligomer can then be accomplished, using straightforward organic chemistry, and the resulting catalyst is expected to retain the same activity as its low molecular weight counterpart. We have shown that a wide range of end-functional ethylene oligomers are available for attachment of catalyst ligands48). The synthetic route leading to these ligands is in some ways more simple than that leading to an insoluble polystyrene bound ligand. This is because the oligomerization, functional and metal exchange described below all produce soluble oligomeric products which can be analyzed by solution-state 1H-NMR spectroscopy.

\[
\text{H} \text{ Cl} \text{ COOEt} + \text{CO}_2/\text{H}_2\text{O} \rightarrow \text{Rh}_6(\text{CO})_{15} - \text{Aminated polymer(IV)} \\
80^\circ\text{C}, \text{Benzene, 24 h} \\
\text{H} \text{ Cl} \text{ COOEt} + \text{CO}_2 (98\%) \\
\text{NH}_2 \text{ Cl} \text{ H} \\
\text{Material surrounded by a solid lined box are insoluble. Components surrounded by a dashed lined box are soluble.}
\]

Scheme 6 Use and Recycling Polyethylene-bound Catalysts

石油学会誌 Sekiyu Gakkaishi, Vol. 36, No. 4, 1993
at elevated temperature. Analysis and characterization of the always insoluble polystyrene catalysts can be more difficult and has typically been limited to IR and elemental analysis.

3.1. Preparation of Soluble Polymer-bound Metal Complexes

3.1.1. Preparation of Linear Polystyrene-bound Rh(I) Complex

Linear soluble polystyrene diphenylphosphine was prepared starting with unsubstituted polystyrene (MW ca. 100,000). Chloromethylation (ClCH₂OCH₃, SnCl₄) was first used to generate an electrophilic site on the polymer. The resulting polymers contained multiple chloromethylated sites per polymer chain. The product chloromethylated polymer was then allowed to react with potassium diphenylphosphide to produce a phosphinilated ligand containing 2.42% P. This ligand (256 mg) was in turn equilibrated with 30 mg of RhH(CO)(PPh₃)₃ (Rh: polymeric phosphine = 1:6) in 35 mL of benzene for 24 h at 22°C. Membrane filtration through a polyamide membrane (MW cutoff 10,000) yielded a yellow solution of the product catalyst.

3.1.2. Preparation of a Water Soluble Polymer-bound Hydrogenation Catalyst

A monomethyl ether poly(ethylene glycol) (2.5 g, ca. 0.5 mmol) and Et₃N (2 mmol) were dissolved in CH₂Cl₂ and treated first with 0.54 mmol of phosgene and then with 0.5 mmol of (Ph₂PCH₂CH₂)₂NH+2Cl-. The product chelating phosphine was isolated after filtration by removal of solvent and was characterized by elemental analysis and IR spectroscopy. In a typical procedure, 17.5 mmol of a water soluble chelating phosphine ligand was allowed to react with the soluble product formed from reaction of 3.6 mg (8 mmol) of [Rh(NBD)Cl]₂ with 4 mg (16 mmol) of AgOSO₂GF₃ in dioxane. The catalyst so formed was used directly. The above procedure is shown in Scheme 7(a).

3.1.3. Preparation of Polyethylene-bound Pd(0) Catalyst

Preparation of a polyethylene bound catalyst requires synthesis of an appropriate ligand followed by preparation of the desired metal complex. The preparation of tetrakis (polyethylene-diphenylphosphine) palladium (0) shown in Scheme 7(b) is representative of the procedures used to prepare phosphine and phosphite-ligated catalysts. In this synthesis, ethylene was first anionically oligomerized using 6 mL of BuLi and TMEDA in heptane at 25°C. The product living oligomer was formed as a heterogeneous suspension. Addition of 7 g (32 mmol) of chlorodiphenylphosphine produced the phosphine ligand. Synthesis of the palladium(0) complex was accomplished by adding 1.25 g (0.75 mmol) of the phosphinilated ligand to 0.02 mmol of (Ph₃P)₄Pd in toluene. After heating to 100°C and then cooling to room temperature, the ethylene oligomer-ligated catalyst is isolated as an insoluble precipitate (1.25 g) by filtration. ¹H- and ³¹P-NMR analysis of the filtrate showed that triphenylphosphine had formed as shown in Scheme 7(b).

3.1.4. Formation of a Polyethylene Carboxylate Ligated Catalyst

Transition metal catalysts attached to an ethylene oligomer via an anionic carboxylate are prepared by a very analogous route to that described above for a diphenylphosphine-terminated ethylene oligomer. In this case, a carboxyl-terminated ethylene oligomer is first prepared from the lithiated oligomer by reaction with CO₂ at -78°C. Acidification yields the carboxylic acid. Addition of 1.8 g of this carboxylic acid (1 mmol) to a solution containing 0.14 mmol of the hepta-carboxylate mixed valence ruthenium complex followed by heating to 110°C and cooling yielded a clear filtrate and a greenish solid containing 1.9 g
of the polyethylene carboxylate ligated ruthenium cluster catalyst (1.09% Ru) as shown in Scheme 7(c).

3.2. Catalysis

The principal advantage of using a soluble polymer-bound catalyst is its homogeneity under reaction conditions. In cases where a linear polystyrene or a poly(ethylene glycol) have been used as ligands, catalyst separation and recovery has been possible using semipermeable membranes or solvent precipitation. Catalysts on a linear polymer often resemble their lower molecular weight counterparts, though extensive studies to demonstrate this point are at present largely confined to examples with polyethylene-bound catalysts.

Polyethylene-bound catalysts have been used in a wide variety of reactions. Examples of reactions where they have been successfully used are listed in Table 6. Also listed in Table 6 are the percentages of the charged metals lost as leachate after 1 or 2 cycles of catalyst dissolution-precipitation in cases where this analysis was performed.

3.2.1. Hydrogenation

One example of a soluble polymer catalyst would be the hydrogenation catalyst (Fig. 2(a)). Studies by Bayer’s group showed both catalysts to be effective and comparable to low molecular weight analogs in benzene solution43,44. These catalysts and related poly(ethylene glycol) catalysts were separated from the reaction products either by precipitation of the polymer with a non-solvent for the polymer (e.g. hexane for polystyrene) or through membrane filtration.

Water soluble polymeric ligands for hydrogenation catalysts have also been studied by Whitesides45,46. Water soluble polymers studied included both main chain derivatives of a poly(vinyl ether) (maleic anhydride) copolymer and terminally substituted poly(ethylene glycols). Both polymers were substituted with a chelating phosphine ligand. The main interest was the preparation of water soluble cationic rhodium(I) hydrogenation catalysts. Procedures for catalyst recovery were not described.

The catalyst [(PEOlig-PPh2)3RhCl] was studied extensively as a hydrogenation catalyst48. In direct comparisons to an insoluble polystyrene-bound analog, it was superior. The polyethylene-bound catalyst was typically 50 times more reactive than the polystyrene-bound Rh catalyst and had about 80% of the activity of the well known catalyst [(PPh3)3RhCl] under the same conditions. The polyethylene-bound catalyst more accurately mirrored its selectivity and reactivity toward substrates of the known homogeneous catalyst, which is also other advantages over heterogeneous polymer-bound catalysts. The lack of similarity between a homogeneous and a heterogeneous polymer-bound catalyst, while occasionally advantageous, is rather an unfavorable factor in that optimization of catalytic activity is often easier with the more readily available low molecular weight ligands. Thus, changes in catalytic activity on transferring a transition metal from a low molecular weight ligand to a polymer ligand pose problems in that they made such optimization studies less useful.

3.2.2. Oligomerization and Polymerization

Polyethylene bound neodymium carboxylate catalysts have been successively used for highly stereospecific butadiene polymerization. Using the catalyst Nd(O2C-PEOlig)2.3Cl0.7 and a cocatalyst composed of a 20:1 mixture of i-Bu3Al: AlEt2Cl produced polybutadiene that was >90% cis-1,4, a selectivity that was nearly the same as that obtained...
using a similar insoluble cross-linked polystyrene-bound neodymium carboxylate catalyst\(^5\).

Oligomerization of dienes to form cyclodimers and trimers using Ni(0) catalysts is an important industrial reaction and was one of the first examples studied where a soluble polyethylene-bound catalyst was used\(^49\),\(^57\). This reaction which had been studied extensively by Wilke and Heimbach is quite sensitive to ligand structure and ligand/catalyst ratios. It thus served an excellent test of the similarity of these polyethylene-bound catalysts and their low molecular weight analogs. In a comparison of an oligomeric and octadecyl-diarylphosphite ligand, excellent correspondence in product ratios and reactivity as the ligand : Ni ratio was changed over several orders of magnitude was found. This indicated that these polyethylene-ligated catalysts are true homogeneous catalysts and that they accurately mirror the reactivity and selectivity of their low molecular weight analogs.

### 3.2.3. Hydroformylation

Hydroformylation has been studied with both linear polystyrene and polyethylene-bound catalysts. In the case of the polystyrene-bound catalysts (Eq. 2(b)), hydroformylation of 1-pentene yielded 77% 1-hexanal, with the balance of the product being 2-methylpentanal\(^43\). The catalyst was successfully recycled twice without causing any changes in these n/b ratios. A polyethylene-bound hydroformylation catalyst \([\text{PE}_{\text{lig}}-\text{PPh}_2]_3\text{Rh(CO)}\] was also prepared. It was recycled over 6 times. Selectivity (n/b) varied from ca. 1:1 to 10:1. As is true for the low molecular weight catalyst, these selectivities could be changed by use of excess phosphine ligand\(^52\).

### 3.2.4. Allylic Alkylation

Palladium(0) catalysts containing a \text{PE}_{\text{lig}}-\text{PPh}_2 ligand in place of \text{PPh}_3 have been successfully used repeatedly in allylic substitution chemistry (Eqs. (20) and (21)). Representative examples are shown in Table 7. In both of these cases, the catalyst could be recycled 10 or more times, provided that oxidation by adventitious oxygen is rigorously avoided.

\[
\text{O} + \text{R} - \text{R}' \xrightarrow{\text{(PE-CO}_{\text{Ph}}\text{R}_{\text{Ph}}\text{O}_{\text{H}}\text{O}, 100°C)} \text{PE-CO}_{\text{Ph}}\text{R}_{\text{Ph}}\text{O}_{\text{H}}\text{O} \\
\text{R} = \text{alkyl or aryl} ; \text{R}' = \text{alkyl, aryl or H}
\]

### 3.2.5. Oxidation

Polyethylene-bound catalysts would likely be useful in oxidation chemistry. Our studies, to date, of this chemistry have, however, been limited to one example using a triruthenium cluster catalyst to oxidize alcohols with air. The preparation of cluster catalyst was described above, in Scheme 7(c). This catalyst has been used in oxidation of alcohols to aldehydes and ketones, as shown in Eq. (22) and Table 8. In a typical reaction, 0.282 g of the polyethylene-bound oxidant was suspended in 50 ml of chlorobenzene. An alcohol, e.g. cyclohexanol (0.305 g, 3 mmol), was added and the mixture was heated to 100°C. At the elevated temperature, the solution was homogeneous. Oxidations were carried out for varying lengths of time with turnover numbers of 20—30 moles of alcohol oxidized per mole of catalyst per day. The longest run of study was 5 days.

### 3.2.6. Multistep Reactions

Multistep reactions are a good example of the sort of reactions that can be accomplished with soluble polymeric catalysts. In such chemistry, the soluble polymeric ligand is used both as a means of recovering a catalyst and as a means of kinetically isolating a catalyst from other species. Similar chemistry can be accomplished with

<table>
<thead>
<tr>
<th>Table 7 Decarboxylation-allylic Substitution of Allylic Esters of β-Keto and β-Cyano Carboxylic Acids Using Tetakis (polyethylenediphenyl phosphine) Palladium (0)(^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate</strong></td>
</tr>
<tr>
<td>H(_2)C(=)CH(_2)O(=)C(=)CH(_2)C(=)CO(=)CH(_3)</td>
</tr>
<tr>
<td>H(_2)C(=)CH(_2)C(=)CH(_2)OC(=)CO(=)CH(_3)</td>
</tr>
<tr>
<td>(E)-CH(_2)CH=CH(_2)OC(=)CO(=)CH(_3)</td>
</tr>
<tr>
<td>(E)-2-butenyl-2-oxocyclohexanecarboxylate</td>
</tr>
<tr>
<td>1-methyl-2-propenyl-2-oxocyclohexanecarboxylate</td>
</tr>
<tr>
<td>H(_2)C(=)CH(_2)C(=)CO(=)CH(_3)</td>
</tr>
</tbody>
</table>

a) Reactions were carried out at 100°C in toluene solution using a 50:1 (mol/mol) substrate/catalyst ratio.

b) Yields were determined by gas chromatography using internal standards.

c) Acetonitrile was formed as the other C=O containing product.
insoluble polystyrene-bound catalysts. However, soluble polymeric catalysts can typically be used without any significant alteration in the catalysis. Examples of this idea illustrating the effectiveness of both poly(ethylene glycol)-bound catalysts and of polyethylene-bound catalysts are briefly described below.

The phase separation of one macromolecule from another and the separation of catalyst from products inherently possible with a soluble macromolecular catalyst have been combined in a very interesting manner in the case of the hydrogenation catalyst (PEG-Rh, Fig. 3). In this case, the hydrogenated form of the catalyst (PEG-Rh-H) was used to hydrogenate NAD+ to NADH+ in an aqueous solution in an ultrafiltration membrane flow reactor. The result was a coupled enzymatic reactor where the PEG-Rh catalyst used formate as the penultimate reluctant to reduce a polyethylene glycol-bound NAD+ which in turn served as a cofactor for alcohol dehydrogenase. The water soluble polymeric rhodium catalyst in effect replaced the enzyme formate dehydrogenase in an intriguing example of chemical catalysis in biotechnology.

The other example from our laboratories where a polyethylene-bound catalyst was used is the two step oxidation reduction sequence shown in Eq. (23). This sequence, a strong Cr(VI)-containing oxidizing agent was combined with a soluble polyethylene-diphenylphosphine-bound rhodium(I) hydrogenation catalyst to form a saturated ketone from an unsaturated alcohol. Here, the soluble hydrogenation catalyst was kinetically isolated from a heterogeneous Cr(VI) oxidant. The phase separation and kinetic isolation were achieved because the hydrocarbon oligomer was incompatible with, and did not diffuse into, the polar polyvinylpyridine ion exchange resin. Hence, the phosphine group cannot be oxidized by the Cr(VI). Likewise, the rhodium(I) complex, which always had at least two oligomeric phosphine ligands attached, was prevented from reacting with the Cr(VI) reagent. This concept in which pairs of otherwise incompatible reagents or catalysts are usefully mixed with one another will likely receive additional attention, as catalyst chemists seek ways to circumvent unfavorable equilibria or to combine biological and chemical catalysis.

4. Conclusion

Polymer-bound catalysts have received considerable industrial and academic interest in the past twenty-five years. Their potential utility, however, is only beginning to be tapped. Many examples now exist which detail the simple advantages of recovery and recycling given a stable
catalyst. Many other examples in the literature describe unique or enhanced reactivity for a catalyst bound to a polymer. Even schemes like those employing soluble polymers which generate catalysts with equivalent reactivity have substantial merit (and may in cases be even more desirable than a less predictable change in activity). The research to date on polymer-bound catalysts has mainly focused on using the physical properties to separate catalysts from each other or from products. It seems likely, however, that the importance of process chemistry will lead to further developments in this sort of ligand chemistry. The importance of new strategies to, and the need improve on, existing processes efficiency will inevitably lead to the development of new catalyst methodologies and reactions. It is likely that polymer-bound catalyst chemistry will figure predominantly in these future developments.

References

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15) Kaneda, K., unpublished results.
Keywords
Heterogeneous catalysis, Homogeneous catalysis, Supported catalyst, Polystyrene, Ethylene oligomer