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Supported Homogeneous Film Catalysts

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Supported homogeneous film catalysts are described which, in effect, heterogenize biphasic systems. Water-soluble catalysts are added to hydrophilic films, e.g., polyethylene glycol 600, to catalyze the reactions of hydrophobic substrates. Activities are obtained for the hydroformylation of 1-hexene equal to those obtained in homogeneous systems. Experiments are described that indicate that the reactions are occurring in the homogeneous film dispersed over the solid support. © 1995 Academic Press, Inc.

INTRODUCTION

The homogeneous hydroformylation of olefins has evolved into the largest commercial process for the conversion of olefins to functionalized products. The products are separated from the reaction mixture by distillation. Unfortunately, for higher olefins (a carbon length greater than 6) the boiling points of the product aldehydes exceed the temperatures at which active rhodium-based catalysts are stable. Costly extraction and purification steps are required for product separation.

A variety of approaches have been attempted to facilitate separation of the products from the catalyst in hydroformylation reactions (1) Water-soluble ligands and complexes are used in biphasic catalysis (2–9). For example, the water-soluble catalyst $HRh(CO)(TPPTS)_3$(TPPTS = trisodium tris (*m*-sulfonatophenyl)phosphine) with excess of the water soluble ligand is used commercially for the hydroformylation of propylene (7, 8, 9). The metal complex and excess ligand are insoluble in the organic phase and separation is achieved because the majority of the substrates (propylene) and products (*n*-butyraldehyde and isobutyraldehyde) are only very slightly soluble in the water phase. Efficient conversion of the olefin is reported.

Recently, supported aqueous phase catalysts (SAPCS) (10, 11, 12) have been reported to solve the separation problem for the hydroformylation of higher olefins. These systems cover an inert porous support, such as porous glass, with a thin aqueous film containing a water-soluble catalyst, $HRh(CO)(TPPTS)_3$, and a water-soluble phosphine, TPPTS. Hydroformylation of higher olefins such as 1-octene and oleyl alcohol occur at moderate rates and a selectivity of linear to branched chain aldehydes of 2.3 : 1 is reported (12) at 75°C and 700 psig.

The rate of hydroformylation with the SAPC catalysts is independent of the size of the olefin, whereas in biphasic systems the rate is highly dependent on olefin size (13). It has been suggested (13) that the water phase evaporates from the surface and leaves the insoluble rhodium complex weakly bound to the support via hydrogen bonding of the hydrated sodium-sulfonate groups.

In this article, a new class of heterogeneous catalysts, supported homogeneous film catalysts (SHFCS), is described to achieve separations. Soluble catalysts are dissolved in hydrophilic polymer films or hydrophilic, high-boiling liquids to cover solid supports. The disadvantage of water loss in the SAPC is overcome by using a nonvolatile solvent. In hydroformylation, the insolubility of the hydrophilic film and catalyst in the hydrophobic substrate prevents the leaching of the homogeneous catalyst system into the substrate solution (14). Alternatively, a SHFC catalyst could involve a hydrophobic film and catalyst and either a hydrophilic substrate in water or a gaseous substrate reacting to produce gaseous products (14). The approach in effect involves heterogenizing biphasic systems by dispersing the catalyst-containing phase as a film on the solid.

EXPERIMENTAL

Chemicals

Water was purified by nanopore filtration and stored under nitrogen. Carbon monoxide and hydrogen were premixed. The substrates 1-hexene, 1-octadecene, and 1-octene were purchased from Aldrich Chemical and filtered through acidic alumina before use. Valeraldehyde was filtered through acidic alumina and freshly distilled before use. Silica gel (grade 62, mesh 60–200, surface area 700 m^2 g^{-1}, pore volume 1.1 ml/g) was purchased from Davison, dried at 100°C under vacuum overnight, and sealed under nitrogen. The following were used without any further purification: $Rh(acac)(CO)_2$ (Strem Chemical); polyvinyl alcohol (Fluka); absolute ethanol (Florida Distillery Co.); formamide (Aldrich Chemical); polyethylene glycol

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(MW = 600 and 8000) (Aldrich Chemical); polyvinyl pyrrolidinone (Polysciences Inc.); and polyethylene oxide (MW = 600,000) (Aldrich Chemical).

Apparatus and Instrumentation

Catalysis was carried out in a 300-ml Parr stirred minireactor. Nuclear magnetic resonance spectra were obtained using a Varian VXR 300-MHz or a General Electric QE300 nuclear magnetic resonance (NMR) spectrometer. Gas chromatographs were obtained using a Varian 3300, a Perkin–Elmer 900, or a Hewlett–Packard 5890 with a DEGS packed column. GC-MX were obtained using a Varian 3400 equipped with a Finnagan MAT ion trap detector.

Syntheses

All manipulations were carried out under an atmosphere of nitrogen.

The preparation of TPPTS was carried out using a previously reported procedure (12). Recrystallization from methanol with ethanol removed most of the phosphine impurities. If any HTPPTS remained it could be removed by washing the solid with methanol.

The preparation of the supported homogeneous film catalysts, SHFC, were carried out by adding TPPTS (0.98 g, 1.73 mol) to water (30 ml). To this solution Rh(acac) $(CO)_2$ (0.0098 g, 3.72×10^{-5} mol) is added and stirred until completely dissolved. At this time an atmosphere of H_2/CO (1 : 1) is introduced and stirring is continued for 3 h to produce HRh(CO) $(TPPTS)_3$. Excess TPPTS is present in solution as evidenced by P^{31} NMR. Liquid polymer and/or high-boiling liquid was added to the stirred solution. Silica gel was then added in the amounts specified. Water is evaporated under reduced pressure and the resultant yellow solid is dried under vacuum at 40°C overnight. Phosphorous NMR of the complex prepared by ligand substitution of the acetylacetonate (acac) ligands on $Rh(acac)_2(CO)$ with TPPTS in the presence of the carbon monoxide and hydrogen in polyethylene glycol showed that the product was HRh(CO) (TPPTS) (Fig. 1).

The amount of film used relative to the pore volume of the solid is indicated by delta, δ. This is calculated by dividing the volume of film added by the total pore volume (1.1 ml/g) times the grams of silica used.

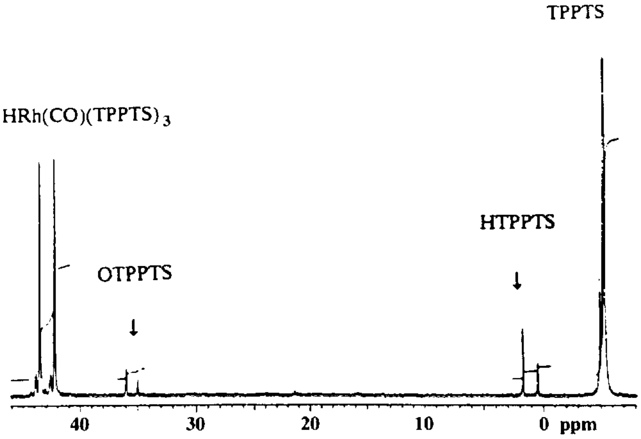

FIG. 1. ^{31}P NMR spectrum of *in situ* generated HRh(CO)$(TPPTS)_3$. (OTPPTS is trisodium tris(m-sulfonatophenyl)phosphine oxide, HTPPTS is the protonated tris(m-sulfonatophenyl)phosphine).

Catalytic Run

The catalyst (2.0 g) and 1-hexene (50 ml) are added to a 300 ml Parr pressure reactor. The reactor is sealed, flushed three times with argon (50 psi), and allowed to stir for 30 min to check for leaks. If no leaks are evident, the argon is bled, the reactor is flushed three times with H_2/CO (1 : 1, 50 psi), and heated to the reaction temperature. This procedure is followed to prevent catalyst decomposition at elevated temperatures. After the 30 min to attain reaction temperature, the reactor is filled to a final pressure of 83 psi, the solution is stirred at 400 RPM and the reaction is monitored by the uptake of H_2/CO gas. The reproducibility of turnover numbers in duplicate runs is 10%.

The activities of the various catalysts were determined by the method of initial rates. The pressure of reactant gases over the catalyst changes as the reaction proceeds, leading to changing reaction conditions during the run. Consumption was followed for at least the first 15 psig of the reaction. Plots of the change in pressure, P, versus time, t, produce results similar to those shown in Fig. 2. Initial rates were calculated using the slope of the first 6 psig of gas uptake. The number of moles of H_2 used in 6 psig of reactant gas was calculated. Every mole of H_2 consumed produces a mole of aldehyde. Dividing the number of moles of products $(n)_p$ by the moles of rhodium catalyst $(n)_c$ yields the turnover number (TON), which divided by time gives TON/min. Gas chromatographic analysis indicated no hexane or any products other than *n*- and *b*-aldehydes that would consume CO or H_2.

Selectivity was calculated from the ratio of the gas chromatographic product peaks and verified by H^1 NMR. The ratio is reported as linear to branched aldehyde, n/b.

RESULTS AND DISCUSSION

PEG Films

Ideal liquid phases for SHFCs are nonvolatile film-forming liquids in which the active catalysts are soluble and which are insoluble in the substrates and products. Low molecular weight hydrophilic polymers possess most of these criteria, making them excellent candidates as films for rhodium hydroformylation catalysts. The main focus of this work will concentrate on polyethylene glycol (PEG)

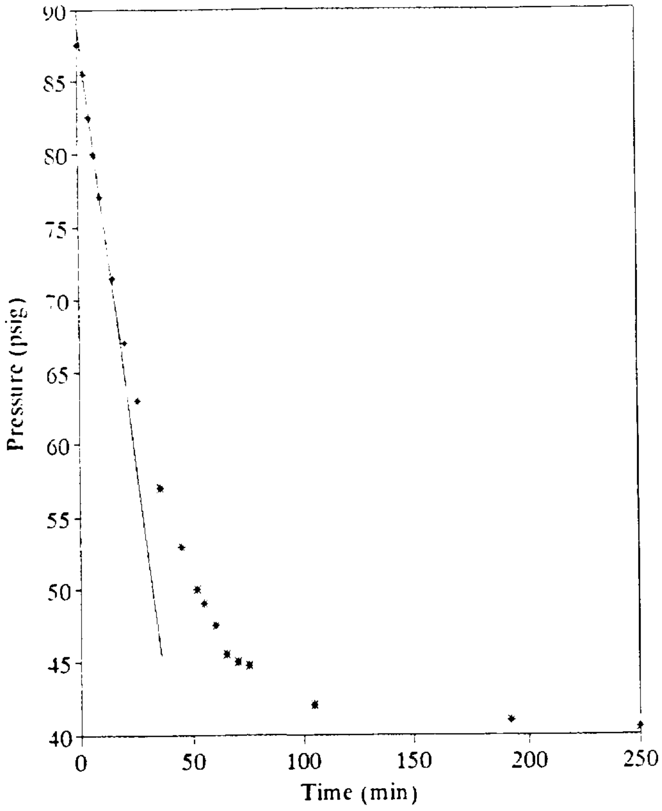

FIG. 2. Change in total pressure in a batch reactor with reaction time.

as the liquid phase. Polyethylene glycol 600 is a low molecular weight polymer that dissolves the rhodium complex $HRh(CO)(TPPTS)_3$. It is hydrophilic and is a liquid at reaction temperatures. We have investigated the influence of several variables, e.g., pore filling and the addition of water and additives, with this film. The results of all our experiments for the hydroformylation of 1-hexene are summarized in Table 1.

A catalyst prepared by supporting the catalyst on silica with no film gave an activity of 1.3 TON/min (moles of product per mole of catalyst per minute) at 100°C and 90 psig total pressure (Run 1). The addition of PEG as a film to the catalyst (Run 2) doubled the activity (2.6 TON/min), with little change in selectivity. A similar catalyst was prepared containing 50% PEG and 50% water (Run 3) to decrease the viscosity of the film. The activity of this catalyst increased to 8.3 TON/min.

In order to make a direct comparison of a homogeneous catalyst and our supported thin film catalyst, we determined the activity of a homogeneous catalyst ($HRh(CO)(PPh_3)_3$ and excess phosphine under our reaction conditions (Run 27). The stirred (440 RPM) solution of the homogeneous catalyst showed an activity of 68 TON/min and an *n*/*b* ratio of 3:1 at 100°C and 85 psig. The addition of excess phosphine to the PEG film produces results similar to those of the homogeneous reaction. A catalyst containing the supported polymer system polyethylene glycol (MW = 600), $HRh(CO)(TPPTS)_3$, and excess TPPTS supported on silica gel in which the pores were totally filled (degree of pore filling, $\delta = 1.4$) (Run 4) showed an activity of 24.7 TON/min and an *n*/*b* ratio of 6:1 at 100°C and 85 psig. Thus, the advantage of heterogenizing the catalyst can be achieved with only a slight loss of activity with SHFC.

Comparison of the SHFC (Run 4) and a biphasic system, $HRh(CO)(TPPTS)_3$, and excess TPPTS in water and 1-hexene (Run 28) demonstrates the superiority of the SHFC catalyst. The biphasic catalyst showed an activity of 0.09 TON/min and a selectivity of 35:1 at 100°C and 85 psig. The advantage of the SHFC arises from increasing the area of contact between the catalyst phase and the substrate solution.

TABLE 1

Activities for the Hydroformylation of 1-Hexene with SHFC[a]

Run no.	Film[b]	Mass of film (g)	% poly.	[Rh] × 10^6 (mol/g cat)	Delta	Activity (TON/min)	*n*/*b*
1	None	0.00	0	7.9	0.2	1.27	10.3
2	PEG 600	2.83	100	3.8	0.5	2.58	7.4
3	PEG/water	5.70	50	3.6	1.4	8.31	6.5
4	PEG 600	5.70	100	3.6	1.4	24.7	6.0
5	PEG 600/hex[c]	5.70	100	3.6	1.4	0.19	2.0
6	PEG 600/val[d]	5.70	100	3.6	1.4	7.58	5.5
7	PEG 600/water	5.70	0	3.6	1.4	15.4	15.6
8	PEG 600/water	5.70	25	3.6	1.4	1.18	25.5
9	PEG 600/water	5.70	49	3.6	1.4	7.93	5.3
10	PEG 600/water	5.70	75	3.6	1.4	15.6	6.5
11	PEG 600	5.70	100	84.0	0.06	2.74	4.1
12	PEG 600	5.70	100	29.5	0.2	18.6	6.3
13	PEG 600	5.70	100	10.9	0.5	7.05	7.4
14	PEG 600	5.70	100	7.7	0.7	9.96	6.5
15	PEG 600	5.70	100	1.2	2.0	2.89	5.5
16	PEG 8000	5.70	100	3.6	1.4	4.80	6.0
17	PEG 8000	5.70	80	3.6	1.4	15.6	6.0
18	PVP	5.70	100	3.6	1.4	0.44	7.2
19	PEO[e]	5.70	100	3.6	1.4	0.00	0.0
20	PVA	5.70	100	3.6	1.4	0.00	0.0
21	Formamide	5.70	100	3.6	1.4	0.63	17.0
22	Formamide	5.70	100	3.6	0.05	1.19	9.2
23	Formamide	5.70	100	3.6	0.7	0.67	9.2
24	Formamide	5.70	100	3.6	1.4	0.58	12.4
25	PEG 600/formamide	5.70	50	3.6	1.4	2.81	9.4
26	Glycerol	5.70	100	3.6	1.4	0.03	21.7
27	Homogeneous	0.00	0	3.7	0.0	68.0	3.0
28	Biphasic[f]	0.00	0	3.7	0.0	0.09	35.9

[a] Conditions: temperature 100°C; pressure 50 psig (1:1 hydrogen/carbon monoxide); 4.08 g support except in Run 2, where 6.16 g was used, and Runs 27 and 28, where none was used. The ratio of phosphine to rhodium was 44 to 1. Neat solvent was used unless indicated otherwise with a footnote. The variable *n*/*b* is the ratio of linear to branched aldehyde. The degree of pore filling δ is calculated by dividing the volume of the film by the pore volume of the solid.

[b] PEG is polyethylene glycol and PVP is polyvinylpyrrolidinone.

[c] Solvent is cyclohexane.

[d] Solvent is 1-hexane/valeraldehyde.

[e] PEO molecular weight 600,000.

[f] Solvent is 50 ml 1-hexene and 10 ml water.

TABLE 2

Activities for Hydroformylating Higher Olefins[a]

Run no.	Film	Mass of film (g)	% poly.	[Rh] × 10^6 (mol/g cat)	Delta[b]	Activity (TON/min)	n/b[c]
1′	PEG 600	5.70	100	3.60	1.40	2.47	5.0
2′	PEG 600	5.70	100	3.60	1.40	20.02	5.4
3′	PEG 600	5.70	100	3.60	1.40	1.35	4.0
4′	PEG 600/surfynol 485	5.70	80	3.60	1.40	4.59	5.1

[a] Reaction temperature is 100°C except in Run 2′, where it is 125°C. Substrate is 1-octene except in Run 3′, where octadecene was used.

[b] Delta is calculated by dividing the volume of the film used by the available volume of pores in the solid (total pore volume is 1.1 ml/g).

[c] The ratio of linear to branched aldehyde.

The hydroformylation of liquid substrates such as 1-hexane by homogeneous catalysts requires the use of inert solvents, such as cyclohexane or toluene, to obtain optimal activity. The activity of the rhodium catalyst decreases dramatically at high olefin concentration (15). In the supported catalyst film, the polymer or liquid phase is equivalent to the solvent (1-hexene is slightly soluble in PEG) and the need for a solvent is eliminated. Both the activity and the selectivity of the SHFC catalyst in cyclohexane were lower than the same catalyst in neat 1-hexene (compare Runs 4 and 5). The external solvent (cyclohexane) hinders the activity of the catalyst by slowing mass transfer of the substrate into the film and to the interface. When toluene was used as a solvent the liquid polymer film dissolved in the solvent leaving a solid rhodium catalyst supported on silica. The activity of this system was low.

Increasing the chain length of the substrate from 1-hexene to 1-octene led to lower activity as expected. However, the hydroformylation of 1-octene with the PEG film catalyst (Run 1, Table 2) showed a considerable increase in the rate as the reaction proceeded. The activity during the early stages of the reaction was 2.5 TON/min, and 2 h later the rate had increased to 5.1 TON/min. This increase in activity is attributed to the retention of some of the product aldehyde in the film, which acts as a surfactant increasing the solubility of 1-octene in the film. The H^1 NMR spectrum of the washed film from the 1-hexene hydroformylation reveals the presence of aldehydes in the film. This proposal is supported by experiments with film additives, vide infra.

Since it is desirable to carry out reactions at high conversion, it is important to study the rates of reaction at times longer than the initial stage of the reaction. As the reaction proceeds, the concentration of product aldehydes creates a solvent mixture that is more polar than neat 1-hexene. Changes in the properties of the film and in mass transfer as the solvent changes can influence the activity and selectivity of the catalyst. Extended reaction times were simulated by studying the activity of the PEG catalyst in a cosolvent consisting of valeraldehyde and 1-hexene (1 : 1). This mixture simulates the formation of large amounts of aldehyde products, while allowing measure of the products from hexene hydroformylation by gas chromatography. The PEG catalyst showed an activity toward aldehydes of 7.6 TON/min and a selectivity of 5.5 : 1 in the valeraldehyde/1-hexene cosolvent system (Run 6). The drop in activity is expected due to the decrease in the concentration of substrate in solution. The ^{1}H NMR spectrum of the solution from this reaction showed that some of the polyethylene glycol dissolved in the cosolvent, but there was no evidence that the complex or phosphines were extracted.

The isomerization of 1-hexene to 2-hexene is an undesirable side reaction for rhodium-based hydroformylation catalysts because the hydroformylation of internal olefins is much slower than that of α-olefins. Isomerization reduces the overall activity of the catalyst and leads to loss in selectivity. The isomerization to 2-hexene with the PEG catalyst ($\delta = 1.4$) is low, leading to a selectivity of 94.8% of the desired aldehydes. In the presence of valeraldehyde (heptaldehyde simulant) the isomerization rate increases and the selectivity to aldehydes drops to 86.2%. No change in the *n*/*b* ratio was observed.

An important consideration for heterogeneous hydroformylation catalysts is the leaching of the costly rhodium catalyst from the film into the reaction solution. Leaching was measured by filtering off the SHFC and testing the resulting solution from a hydroformylation reaction for activity in a subsequent hydroformylation reaction. No gas uptake occurred with the product solution over an 18 h period. Homogeneous rhodium catalysts are extremely active and the leaching of ppm levels of catalyst would have resulted in some gas uptake over this period (13). This SHFAC produces biphasic conditions between the film and the substrate solution, it prevents the rhodium from leaching into the product solution, and it provides for facile separation of the catalyst from the reaction medium.

The Film as a Homogeneous Reaction Medium

High resolution ^{31}P NMR supports the proposal that the catalyst forms a homogeneous solution in the polymer film. Supported catalysts with a liquid film of PEG 600 showed a broad resonance at −3 ppm in the ^{31}P NMR, which is assigned to TPPTS. The ^{31}P NMR spectrum of this catalyst after hydroformylation shows the presence of TTPTS and the analogous phosphine oxide, OTPPTS, as well as a resonance at 29 ppm. A solution of TPPTS in PEG gave a ^{31}P signal at −5 ppm, and a solution of OTPPTS in PEG showed a ^{31}P resonance at 29 ppm. This signifies oxidation of some of the excess phosphine ligand during the reaction. The broadening of the ^{31}P resonances can be attributed to the presence of solid silica gel in the sample and to decreased mobility of the solute. The absence of a complex signal is expected in view of the low concentration of rhodium in the film. Catalysts prepared by depositing the phosphine and complex on silica without liquid polymer and/or water films do not show resonances. Similarly a catalyst prepared by dissolving the phosphine in a polyethylene glycol 8000 film, a solid at room temperature, gave no resonances in the ^{31}P NMR spectrum. Clearly, the phosphines in liquid films produce homogeneous solutions and the mobility of the phosphines gives rise to the observed solution NMR for the SHFC catalysts. The reactivity of the SHFC and examination of the solubility of the rhodium complex in neat PEG 600 indicate that the complex is dissolved. Rhodium complexes in a solid matrix have no mobility and catalysis of the substrate would be limited to those complexes at the liquid/solid interface. The behavior of the PEG 600 SHFC described above indicates that dissolved substrate is reacting in the film.

The ^{1}H NMR spectrum of the PEG 600 catalyst on silica showed very broad indistinguishable peaks. After a hydroformylation run, the catalyst was washed with D_2O. The ^{1}H NMR spectrum of the wash solution showed the presence of PEG and resonances in the aromatic region, showing that the phosphine remained in the film. This coupled with the lack of PEG or phosphine resonances in the ^{1}H NMR of the reaction solution demonstrates that the film remained intact throughout the hydroformylation experiment. Finally, a resonance at 9.4 ppm in the wash solution shows that some product aldehyde remains incorporated in the film.

It has been reported that the activity of supported aqueous phase catalysts does not change when the substrate is varied, indicating that the active portion of the catalyst lies at the organic/aqueous interface (12, 13). We have studied the hydroformylation of 1-octene and 1-octadecene with the PEG 600 film catalyst ($\delta = 1.40$) at 50 psig of syn gas and 100°C. Table 2 shows that as the chain length of the substrate increases, the activity of the catalyst decreases. This correlates with the solubility of the substrate in the polymer film, and supports our proposal that hydroformylation occurs at the interface and in the homogeneous liquid solution on the support surface.

Davis and co-workers (11) reported that, with their aqueous film catalysts, when the degree of filling the available pore volume, δ, is ~0.06, the best catalyst for the hydroformylation of 1-octene is produced. The activities of these systems drop significantly with increased pore filling. Runs 11–14 and 4 show an increase in activity for hydroformylation as the extent of pore filling increases with the PEG-SHFC catalyst. The same concentration of rhodium in the film is employed in Runs 4 and 11–14. The increased activity from $\delta = 0.06$ to $\delta = 1.40$ is expected for a homogeneous catalyst film that fills the pores and is spread over the surface of the support, providing a high surface area film in which the reaction occurs. At 140% filled pore volume ($\delta = 1.40$) an extremely active catalyst (24.7 TON/min) results. Further loading to $\delta = 2.00$ results in decreased activity. The addition of excess film leads to reduced surface areas and increased solution depth approaching those of spherical droplets. The reaction slows as it becomes mass transfer limited.

Polyethylene glycol 8000, which is a liquid at the reaction temperature (100°C) but more viscous than PEG 600, was used to examine the effects of film viscosity on the activity of the catalyst. PEG 600 has a viscosity of 10.5 g $\sec^{-1}$ cm^{-1} while the viscosity of PEG 8000 is greater than 800 g $\sec^{-1}$ cm^{-1}. A decrease in activity from 24.7 TON/min with the PEG 600 film catalyst to 4.8 TON/min with the PEG 8000 film catalyst resulted at 100°C. The dramatic change in activity supports our claim that catalysis is occurring with the active rhodium catalyst dissolved in the film. Because the concentration of the rhodium complex at the interface should be similar in both cases, little change in activity would be expected if the only active rhodium sites in PEG 600 are located at the 1-hexene/polymer interface. The difference in activity indicates that catalysis is occurring within the polymer film.

Adding water to the PEG 8000 catalyst increased the activity to 15.6 TON/min. The addition of water to this film makes the film less viscous and more mobile. This result further supports catalysis involving a homogeneous film because a less viscous liquid phase should produce a homogeneous catalyst with more facile mass transfer and a higher activity.

Effect of Additives to the PEG Film

A catalyst was prepared with the nonionic surfactant Surfynol added to the polymer film. The hydroformylation of 1-octene with a catalyst that had 20% loading by mass of Surfynol 485 demonstrated an activity of 4.2 TON/min which increased to 5.4 TON/min as the reaction proceeded. The surfactant-modified catalyst showed a higher initial activity at the early stages of the reaction than the standard PEG catalyst (δ for both catalysts was 1.40). The activity after 2 h approaches the highest activity attained with the PEG films in this study. The surfactant increases activity by solubilizing the substrate in the film and increasing the concentration of the alkene available for hydroformylation. The ^{1}H and ^{31}P spectra of the reaction solution were void of resonances that would indicate leaching of the polymer film or its components into the solution.

The film composition was varied by adding water in Runs 3 and 7–10. At 0% PEG (100% water) the activity is 15.4 TON/min and then drops to 1.18 TON/min with the addition of a small amount of polymer. It was noticed that water condenses at the top of the reactor with all aqueous films. At 0% PEG, this evaporation leaves a rhodium complex which is bound to the support by hydrogen bonding of the hydrated sodium sulfonate groups to the support surface (13). Catalysts which contain no water in the film phase showed no condensate in the reactor.

As mentioned previously, the PEG film has some solubility in concentrated aldehyde product solutions. Water, sodium sulfate, aldehydes, sodium nitrate, or surfactants were added to the polymer phase in an attempt to decrease film solubility. Dissolution of the film into concentrated aldehyde solutions occurred in all instances, but not to the same degree. The sodium-sulfate-modified film was less soluble than a film of PEG alone, while the sodium nitrate film showed considerable leaching of the PEG.

Other Film Catalysts

In addition to low molecular weight PEG, a number of other hydrophilic polymers have been tested as catalytic films. Among these are the known water-soluble film-forming polymers polyvinylpyrolidinone, polyethylene oxide and polyvinyl alcohol. Polyvinylpyrolidinone (PVP) was used as a film (Run 18) and showed low activity, 0.44 TON/min. PVP is solid at 100°C. Catalysts prepared with polyethylene oxide (PEO), a solid at room temperature (Run 19), and polyvinyl alcohol (PVA) (Run 20), were inactive for the hydroformylation of 1-hexene.

Besides polymers, high-boiling liquids can also be used to prepare SHFCs. Formamide, a highly polar liquid with extensive hydrogen bonding, is stable up to 140°C. A formamide film catalyst with a δ of 1.4 had an activity of 0.63 TON/min. This activity was low in comparison to the PEG 600 system. The selectivity was 17:1, approximately three times that of the PEG catalysts. Polar solvents are known to influence the selectivity of hydroformylation catalysts (11). The polar media promotes the more highly substituted rhodium phosphine complex, which is more selective toward linear products but is not as active. Formamide has appreciable volatility under the reaction conditions as evidence by condensate at the top of the reactor that was identified with infrared spectroscopy.

Hydroformylation with a formamide catalyst with a δ approaching zero (Run 22) gave an activity of 1.2 TON/min. Addition of formamide (0.5 ml) to the reaction solution (Run 22) lowered the activity to 0.67 TON/min but again the selectivity rose to 9.2:1. Adding another aliquot of formamide (Run 23) decreased the activity to 0.58 TON/min and the selectivity increased to 12.4:1.

To combine the high activity of the PEG catalyst and the high selectivity of the formamide catalyst, a hybrid catalyst that contained 50% PEG and 50% formamide was made and found (Run 25) to have an activity of 2.8 TON/min. After 2 h the activity increased to 4.3 TON/min. The selectivity, calculated as an average over time, was 9.4:1. Volatilization of formamide was again evident. Evaporation of the formamide leaves a film that is richer in PEG, accounting for the increase in the rate of hydroformylation. The ^{31}P NMR spectrum of the filtered catalyst shows the presence of both OTPPTS and HTPPTS.

Glycerol was chosen as another liquid-phase film, because of its high boiling point (>200°C) and its insolubility in the product aldehydes. The activity of 1-hexene hydroformylation for this catalyst (Run 26) (δ = 1.4), was 0.03 TON/min at 100°C and 85 psig, producing an *n*/*b* ratio of 21.7. The low activity is attributed to the low solubility of the 1-hexene in the glycerol film. The polar nature of glycerol and the low solubility of the substrate contribute to the high selectivity.

CONCLUSIONS

A new class of supported biphasic catalysts are described and shown to be effective for the hydroformylation of liquid substrates. The system utilizes a water-soluble catalyst [HRh(CO)(TPPTS)$_3$] in a hydrophilic polymer covering a silica support. This catalyst relies on the insolubility of the polymer film and complex in the substrate to prevent leaching. We have found that low molecular weight polyethylene glycol produces an effective film for hydroformylation. Three possibilities exist for catalysis in the SHFC. The first involves only rhodium complexes bound to the solid surface of the support. The second possibility involves catalysis with the complex at the solvent/polymer interface. These catalyst sites are probably very active but the quantity is low compared with the amount of rhodium complex dissolved in the bulk film. The third possibility involves a homogeneous catalytic reaction with the polymer film acting as a solvent. The supported PEG thin film catalyst is shown to behave as a supported homogeneous catalyst by: (1) detection of NMR resonances for phosphine in the film; (2) solubility of the rhodium complex in PEG; (3) a decrease in catalyst activity with an increase in the chain length of the substrate; (4) an increase in activity when surfactants are aded to the film; (5) an increase in activity of the PEG 600 catalyst with reaction time when 1-octene is the substrate, as some of the product aldehyde is retained in the film and acts as a surfactant; and (6) a decrease in activity of the PEG 8000 film compared to PEG 600 because of the increased viscosity of the polymer.

The hydroformylation of 1-hexene in the PEG 600 film show activities approaching 25 TON/min with *n*/*b* ratios of 6:1 and little isomerization to 2-hexene. This activity is close to that of homogeneous catalysts under the same conditions. In addition, the hydroformylation of higher olefins (e.g., 1-octene and 1-octadecene) are possible. These catalysts do not leach rhodium into the product solution. The polymer film is insoluble at moderate conversions and has low solubility in aldehyde rich solutions.

Unlike homogeneous catalysts, the SHFCs do not need an external solvent for the hydroformylation reaction.

The addition of formamide to the PEG 600 film decreases reactivity and increases selectivity. These results suggest that amide copolymers with PEG or PEG-amide polymer mixtures could afford tuning of selectivity at the expenses of reactivity.

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REFERENCES

1. (a) Rony, P. R., *Chem. Eng. Sci.* **23,** 1021 (1968); (b) Rony, P. R., *J. Catal.* **14,** 142 (1969); (c) Feldman, J., and Orchin, M., *J. Mol. Catal.* **63,** 213 (1990); (d) Hjortkajaer, J., Scerrell, M. S., and Simonsen, P., *J. Mol. Catal.* **10,** 127 (1981); (e) Robinson, K. K., Paulik, F. E., Hershman, A., and Roth, J. F., *J. Catal.* **15,** 245 (1969); (f) Allum, K. G., Hancock, R. D., Howell, I. V., McKenzie, S., Pitkethly, R. C., and Robinson, P. J., *J. Organomet. Chem.* **87,** 203 (1975); (g) Jarrell, M. S., and Gates, B. C., *J. Catal.* **40,** 255 (1975); (h) Pittman, C. U., Smith, L. R., and Hanes, R. M., *J. Am. Chem. Soc.* **97,** 1742 (1975); (i) Davis, M. E., Rode, E., Taylor, D., and Hanson, B. E., *J. Catal.* **86,** 67, (1984); (j) Pittman, C. U., *J. Am. Chem. Soc.* **97,** 1749 (1975); (k) Pittman, C. U., and Hirao, A. *J. Org. Chem.* **43,** 640 (1978); (l) Pittman, C. U., and Lin, C. C. *J. Org. Chem.* **43,** 4928 (1978); (m1) Nuccuche, C., Taarit, Y. B., and Boudart, M., *ACS Symp. Ser.* **40,** (1977); (m2) Corbin, D. R., Seidel, W. C., Abrams, L., Herran, N., Stucky, G. D., Tolman, C. A., *Inorg. Chem.* **24,** 1800 (1985); (m3) Shannon, R. D., Vedrine, J. C., Nuccache, C., and LeFebvre, F., *J. Catal.* **88,** 431 (1984).
2. (a) Nusso, R. G., Hayni, S. L., Wilson, M. E., and Whitesides, J. M., *J. Org. Chem.* **46,** 2861 (1981). (b) Fache, E.; Senocq, F.; Santini, C.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* 1777 (1990).
3. Maviewz, M. K., and Baird, M. C., *Inorg. Chimica Acta* **13,** 95 (1986).
4. Larpent, L., and Patin, H., *J. Organomet. Chem.* **335,** C13 (1987).
5. Larpent, L., Dabard, R., and Patin, H. *Tertrahedron Lett.* **28,** 2507 (1987).
6. LeCante, L., and Sinou, D., *J. Mol. Cat.* **52,** L2 (1989).
7. Kuntz, E. G., *Chem. Tech.*, 570 (1987).
8. Kuntz, E., U.S. Patent Re. 31,812 (1985).
9. Escaffre, P., Thorez, A., and Kalack, P., *J. Chem. Soc. Chem. Commun.*, 146 (1987).
10. Arhancet, J. P., Davis, M. E., Merola, J. S., and Hanson, B. E., *Nature* **339,** 454 (1989).
11. (a) Arhancet, J. P., Davis, M. E., Merola, J. S., Hanson, B. E., *J. Catal.* **121,** 327 (1990); (b) Arhancet, J. P., Ph.D. dissertation, Virginia Polytechnic Institute and State University, 1989.
12. Arhancet, J. P., Davis, M. E., Hanson, B. E., *J. Catal.* **129,** 94 (1991).
13. Horvath, I., *Catal. Lett.* **6,** 43 (1990).
14. Drago, R. S., Barnes, M. J., and Naughton, M. J., U.S. Patent 5,012,008 (1991).
15. Deshpande, R. M., and Chaudhari, R. V., *Ind. Eng. Chem. Res.* **27,** 1996 (1988).
16. Pelt, H. L., Van Der Lee, G., and Scholten, J. J. F., *J. Mol. Catal.* **29,** 319 (1985).