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RHODIUM ELUTION FROM POLYMER-BONDED HYDROFORMYLATION CATALYSTS

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Summary

The concentration of rhodium in solution over polymer-bonded hydroformylation catalysts was measured, and the factors influencing that concentration were identified. Rhodium dissolution exhibited an equilibrium behavior which decreased with increasing temperature or hydrogen pressure and with decreasing CO pressure. Solvent effects were particularly pronounced with amine resins and the sequential reaction, olefin-aldehyde-alcohol, led to significant redistribution of rhodium within a reactor bed. The implications of these effects in catalysis are noted.

Introduction

In recent years understanding of homogeneous catalysis by transition metal complexes has been characterized by an extraordinary detail. Particularly in the reactions of olefins, reactions such as hydrogenation, hydroformylation, and oligomerization, catalyst selectivities can be markedly influenced by the presence of selected complexing ligands [1—8]. In this regard a detailed picture has developed of the metal complex and of its coordination environment throughout a catalytic cycle. Emphasized in many cycles is the central role of that often-employed ligand, the phosphine, whose stabilizing and dominating influences are to be found throughout the cycle.

It is now well recognized that potentially advantageous effects can be realized if ligands are made a part of an insoluble but accessible "catalyst support"; supports including polymers, resins, and silicas, among others [9—14]. In addition to simply facilitating or eliminating catalyst recovery operations, matrix bonding can afford materials of unusual selectivity, such as a rhodium-based catalyst for the one-step synthesis of OXO alcohols [10] or a selective olefin hydrogenation

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system [14]. It can also stabilize unusual chemical species such as titanocene [13].

Implicit in the use of matrix-bonding techniques is the assumption that the metal catalyst complex remains intact throughout the catalytic cycle, i.e., that the metal ion remains attached (coordinated) to the insoluble ligand. Supporting this assumption are long-term use in continuousflow systems [9], but only limited information exists on the actual rhodium concentration in equilibrium over these catalysts [12,15]. In the following pages data are presented which detail the equilibria involved in the elution of rhodium from one such reacting system, a macro-reticular phosphine resin, and which show the influence of process variables on those equilibria.

Experimental

Materials

Resin-starting materials were obtained from Rohm and Haas and from Ionac. All were porous, macroreticular, styrene-based polymers, cross-linked with divinylbenzene or with ethylene glycol dimethacrylate. Amine resins were polymeric analogs of *N*,*N*-dimethylbenzylamine and contained 5.8% nitrogen (4.1 meq. per gram). Phosphine resins were supplied by Dr. D.D. Whitehurst [9] and were analogs of dibutylphenylphosphine. These latter resins contained 6.6—9.7% phosphorus (2—3 meq. per gram).

Catalyst complexes were prepared by a bridge-splitting reaction between the polymeric ligand and rhodium carbonyl chloride (in hexane or benzene) and initially contained the species, *cis*-$Rh(CO)_2$(polymer)Cl, as evidenced by infrared [16]. Rhodium levels never exceeded 2% (0.2 meq./g) such that the catalysts contained at least a ten-fold excess of ligand.

Procedures

Catalysts were tested in a down-flow, stainless steel reactor, heated by a circulating oil bath (50—120°C, 500—2000 psig). The reactor bed measured 30—50 cm long, 1.2 cm diameter, with a 0.3 cm thermowell in the center, and was preceded by a 20 cm preheater. Provision was made at the preheater inlet for hydrogen, carbon monoxide, and liquid feed. Liquid was metered to the reactor system by a Ruska displacement pump; gases with a Matheson flow meter, gases being present in a 20—100% excess for these experiments. Following the reactor was a dropout receiver from which gas and liquid were removed through separate Annim valves for measurement and analysis. Material balances were 98% or better.

Resins were swelled with methanol prior to loading into the reactor and were removed following a long-term run by washing with hexane and air drying. Reactors operated continuously, 24 hours a day.

Liquid samples (and recovered catalysts) were analyzed spectrophotometrically for rhodium by using a method adapted from Sandell [17]. In a typical analysis, 1 ml conc. HCl and 0.1 g NaCl were added to 15—20 g liquid OXO product containing ~0.1 ppm Rh in a quartz casserole. The sample was taken to dryness, charred, and fused with $K_2S_2O_7$. Absorbance was measured at 475 nm on a 100 ml solution containing 1% $SnCl_2 \cdot 2H_2O$ and 2*N* HCl. Practical limits of the measurements were 0.04 ppm. $Rh_2(CO)_4Cl_2$, sublimed in a CO stream, was used as the reference material.

Reaction products were analyzed by gas chromatography by using tricresylphosphate and Carbowax 1000 columns. The olefins, 1-hexene and 1-octene (Humphrey), were percolated over alumina prior to use.

Results

Reaction of 1-hexene with CO and H_2 over these rhodium catalysts can be described by the scheme in Fig. 1. Under the mild conditions of these experiments, characteristics of the various catalysts have been published and can be summarized as follows [9—10]: (*a*) Except in the presence of certain tertiary amine ligands ($pK_b = 3$—7), aldehyde formation dominates with little further hydrogenation to alcohol; (*b*) Olefin isomerization is inhibited by phosphine to yield products high in linear aldehyde; and (*c*) Soluble $Rh_2(CO)_4Cl_2$ alone (or Rh carbonyl clusters) produce aldehyde and internal olefin. Indeed the high aldehyde linearity obtained over phosphine resin catalysts provides the strongest evidence that rhodium is attached to such polymers during reaction [9]. Direct measurement of the polymer—solution equilibrium is detailed below.

Phosphine resins

An orientation to the transport properties of rhodium on phosphine resins is

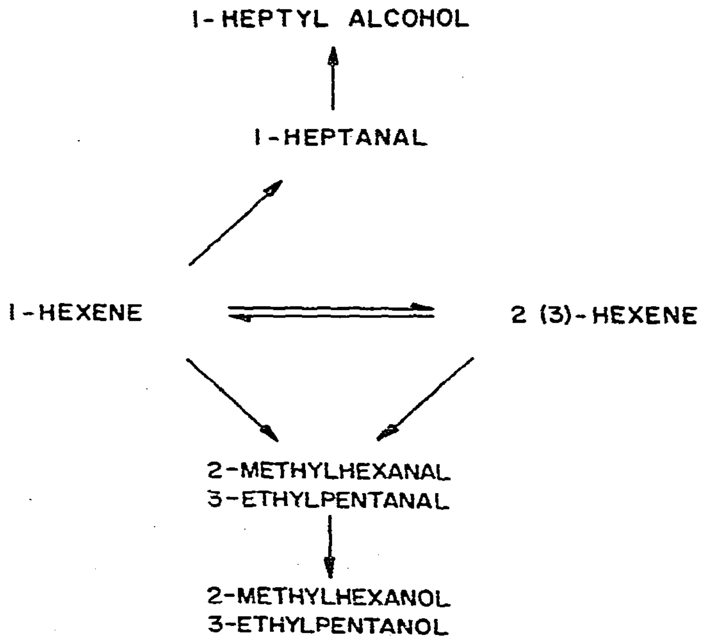

Fig. 1. Reaction sequences in the hydroformylation of 1-hexene.

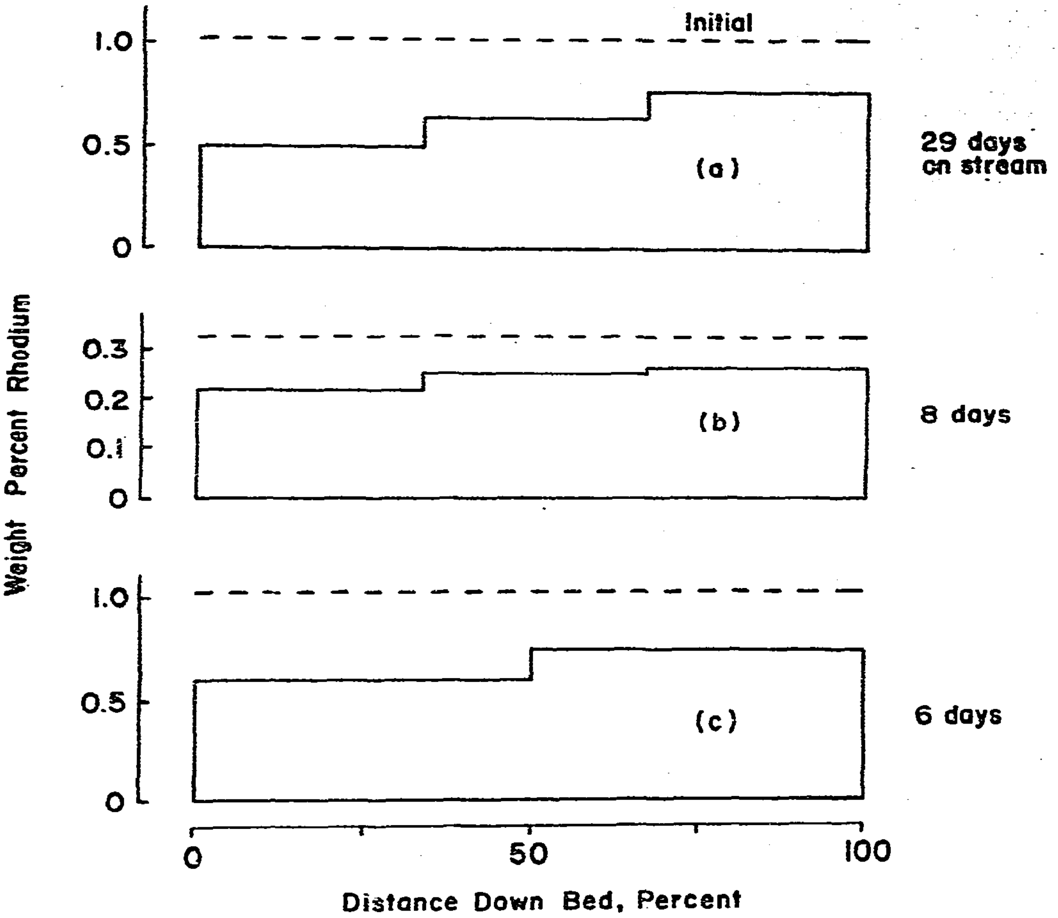

Fig. 2. Rhodium distribution in recovered phosphine resin catalyst beds.

provided by the data in Fig. 2. In this Figure are plotted the rhodium distribution in recovered, sectioned reactor beds following extended processing of olefins. Hexenes had been processed over 2a; propylene over 2c; and mixed olefin feeds over 2b. Although reaction conditions were varied almost daily in these runs, all three reactor beds showed a similar rhodium distribution. Depletion was greatest at the top of the bed, where the resin—solution equilibrium was established.

As shown in Table 1, rhodium concentrations in benzene and in ethylhexanal solution over phosphine resin catalysts were approximately proportional to percent loading, indicating that equilibrium is indeed established in these two solvents. Since the phosphine ligand was in at least a 20-fold excess over rhodium in these examples, the ratio of rhodium concentration in solution: rhodium concentration in resin (bound) is a good approximation to an equilibrium constant.

TABLE 1

POLYMER—SOLUTION EQUILIBRIA FOR RHODIUM OVER PHOSPHINE RESINS

Feed	Conversion	H_2 (psig)	CO (psig)	Temp. (°C)	Loading (%)	[Rhodium] (*M*)	Ratio [a]
Benzene		1000	1000	100	0.08	0.15×10^{-5}	1.9×10^{-5}
		1000	1000	100	0.64	0.8×10^{-5}	1.2×10^{-5}
2-Ethylhexanal		1000	1000	100	0.08	0.4×10^{-5}	5.0×10^{-5}
		1000	1000	100	0.64	2.3×10^{-5}	3.6×10^{-5}
90% 1-Hexene, 10% methanol	36	1000	1000	85	0.08	0.6×10^{-5}	7.5×10^{-5}
	94	1000	1000	85	0.59	1.9×10^{-5}	3.2×10^{-5}
1-Hexene	25	750	750	85	0.06	0.4×10^{-5}	6.6×10^{-5}
	80	750	750	85	1.02	1.3×10^{-5}	1.3×10^{-5}

[a] Rhodium concentration in solution: weight percent rhodium loading.

For convenience the resin concentration is expressed as weight percent loading.

The equilibrium values reveal that rhodium concentrations are strongly dependent on solvent and hence, where olefins are involved, on conversion. As solvent polarity or as olefin content of the liquid increased, rhodium concentration in solution increased. Under practical conditions of high (80—95%) conversion, solution concentrations were described by the ratios 1.3×10^{-5} (1-hexene) and 3.5×10^{-5} *M*: percent loading (propylene) both determined at 85°C, 1500 psig, $1:1\ H_2:CO$.

Pressure and temperature have an equally pronounced effect on rhodium elution. In an only partially successful attempt to minimize the effects of solvent and of conversion, rhodium concentrations were monitored with a 10% 1-octene, 10% methanol in hexane feed as shown in Table 2. The data show three

TABLE 2

PRESSURE AND TEMPERATURE EFFECTS ON RHODIUM EQUILIBRIA (10% 1-octene, 10% methanol in hexane)

Temp. (°C)	CO (psig)	H_2 (psig)	Ratio [a]
At high temperature and conversion			
120	200	750	1.3×10^{-5}
	750	750	7.4×10^{-5}
	250	250	5.7×10^{-5}
	250	1000	2.0×10^{-5}
85	250	1000	5.0×10^{-5}
At low temperature and conversion			
50	200	750	12×10^{-5}
	750	750	39×10^{-5}
	250	250	22×10^{-5}
	250	1000	20×10^{-5}

[a] Moles per liter: percent loading.

significant trends: (*a*) As expected, an increase in CO pressure effects a marked increase in rhodium concentration in solution; (*b*) Rhodium elution is sharply reduced by an increase in temperature; and (*c*) At higher temperatures, an increase in H_2 pressure retards the loss of rhodium.

The effects of CO and of temperature can be readily understood in terms of a shift in equilibrium from phosphine to carbonyl complex, increased temperature favoring the more stable phosphine. The effect of hydrogen, particularly pronounced at the highest temperature, is similarly rationalized, the hydrido phosphine complex being well known and stable in contrast to the hydrido carbonyl. There was no evidence of rhodium metal deposition in any of these experiments.

Amine resins

With the amine resin catalysts, rhodium was redistributed during use such

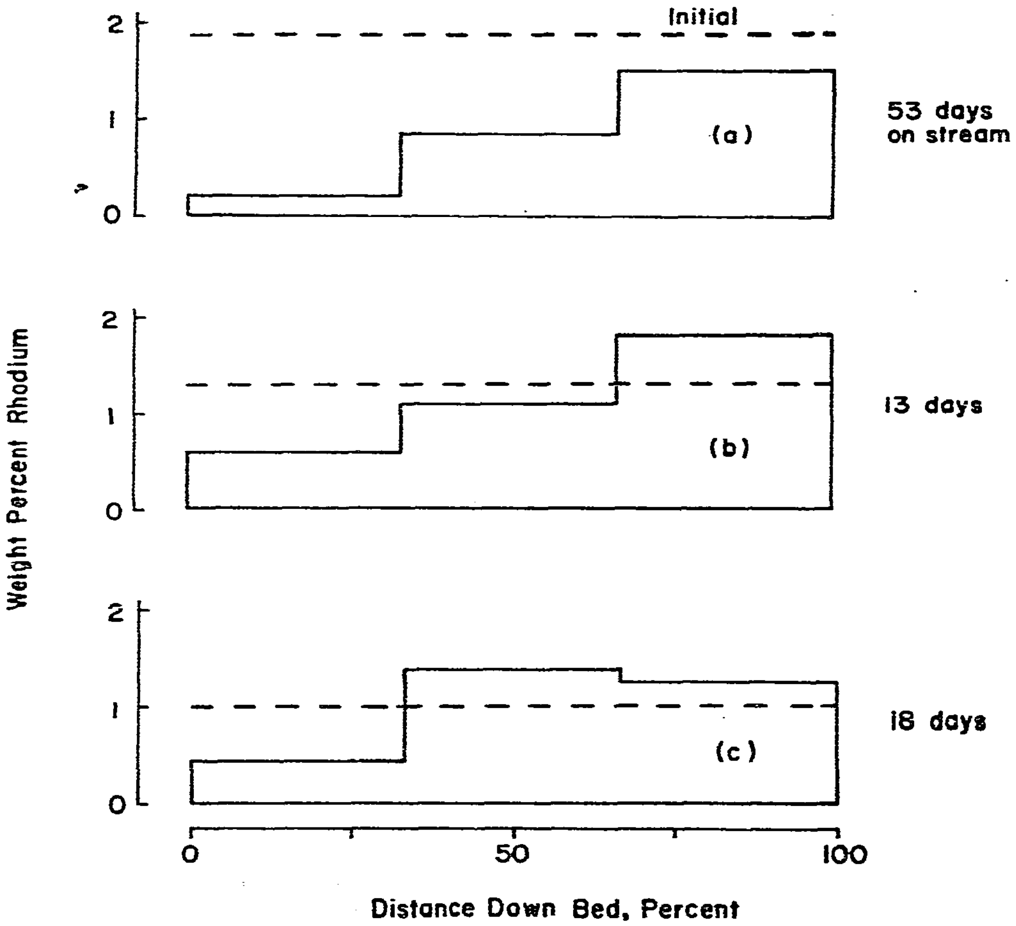

Fig. 3. Rhodium distribution in recovered amine resin catalyst beds.

TABLE 3

RHODIUM CONCENTRATIONS IN SOLUTION OVER AMINE RESINS (1-hexene, 100° C, 1000—2000 psig, 2 : 1 H_2 : CO)

[Rhodium (*M*)]	Loading (%)	Conversion (%)	[Rh]: loading [a]
1.3×10^{-5}	0.23	40	5.7×10^{-5}
4.0×10^{-5}	0.72	15	5.6×10^{-5}
5.5×10^{-5}	0.92	30	6.0×10^{-5}
14.0×10^{-5}	1.4	35	10.0×10^{-5}
12.0×10^{-5}	2.0	20	6.0×10^{-5}
17.0×10^{-5}	2.0	25	8.5×10^{-5}
			7.0×10^{-5}

[a] Moles per liter/Weight percent loading.

that an actual increase in metal content occurred in the middle or lower sections of a reactor bed. Fig. 3 shows the results for three such catalyst beds recovered after extended use. Hexene was the primary feed to reactors 3a and 3c, mixed feeds to 3b.

Since conversion over the amine resin catalyst produces first aldehyde, then alcohol, rhodium equilibria were determined first at low conversion, where aldehyde was the overwhelming product. These data are shown in Table 3 across a 10-fold range in Rh loading with effects of conversion shown in Table 4. As indicated, equilibrium ratios are $\sim 7 \times 10^{-5}$ at low conversion (where aldehyde is the product) and decrease to $\sim 1.2 \times 10^{-5}$ as conversion increases and as alcohol is formed. The sharp decrease in equilibrium ratio as the liquid phase shifted from olefin to aldehyde to alcohol neatly explained the down-stream rhodium accumulations observed in recovered catalysts.

Two factors were considered as possible causes for the changing equilibrium ratio: decreasing olefin content (as found with phosphine) and changing solvent (aldehyde vs. alcohol). The plot in Fig. 4 favors the latter explanation. In this Figure rhodium concentrations are shown to decrease sharply with decreasing aldehyde in a system containing no olefins.

As with the phosphine, pressure and temperature had an additional influence on rhodium concentrations in solution, an influence generally obscured by the effects of changing conversion (and solvent). Using pure benzene as the feed it was shown that both increased temperature and decreased CO pressure lead to reduced rhodium concentrations. At 1000 psig H_2, 100° C, an increase in CO pressure from 250 to 1000 psig effected an increase in equilibrium ratio from

TABLE 4

RHODIUM ELUTION AND PRODUCT COMPOSITION FROM AMINE RESIN CATALYSTS (1-hexene, 1500 psig, 100° C)

[Rhodium]	Loading (%)	Conversion (%)	Alcohol [a] (%)	[Rh]: loading
1.3×10^{-5}	0.23	40	5	5.7×10^{-5}
0.5×10^{-5}	0.23	65	25	2.2×10^{-5}
1.5×10^{-5}	1.25	80	65	1.2×10^{-5}

[a] In the effluent stream.

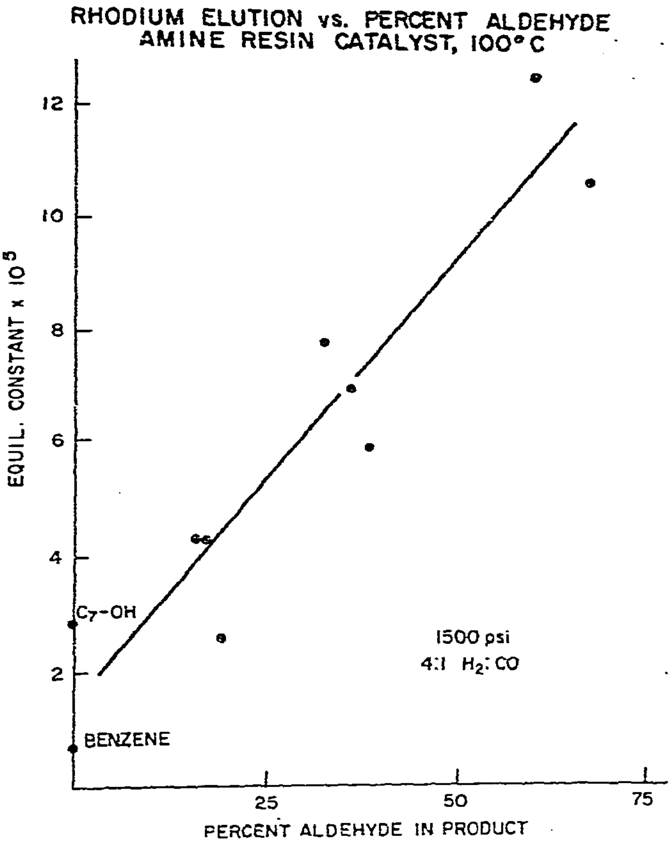

Fig. 4. Rhodium elution as a function of aldehyde content in the effluent.

0.4×10^{-5} to 1.1×10^{-5}. At 2000 psig 1 : 1 H_2 : CO, the ratio decreased from 1.1×10^{-5} to 0.9×10^{-5} when the temperature was raised from 100 to 125°C.

Discussion

Behavior of the phosphine resins can be understood in terms of the coordination chemistry reported by Wilkinson et al. [1,3,4]. Increasing CO pressure shifts the equilibrium to favor free, eluting rhodium carbonyl, carbonyls whose stability relative to the phosphine complexes decreases with increasing temperature. That these eluting species must be of only minor catalytic importance is evidenced by the near absence of the olefin isomerization reaction over these phosphine resins.

Although these present data show a marked dependence of equilibrium rhodium concentrations on solvent and on reaction conditions, some approximate comparison is possible with a value reported for rhodium over silica-bonded phosphine complexes[18]. During the hydroformylation of 1-hexene (650 psig 1 : 1 H_2:CO, 140°C, high conversion), concentration in solution was 10 ppm or about 8×10^{-5} *M*. The catalyst contained 2% rhodium, corresponding to an equilibrium ratio of 4×10^{-5} mols per l/percent loading, but only 2 mols phosphine per mol rhodium (1.2%P). Extrapolating present data with phosphine resins to the same reaction conditions, one would predict an equilibrium ratio for the resins of about 0.9×10^{-5}, the lower value being attributed to the larger excess of phosphine ligand.

Similar comparison is possible with reports for silica-bonded amines, where equilibrium ratios as low as $\sim 2 \times 10^{-5}$ are reported for donors such as triethyl amine analogs [18]. Considering the significantly lower pressure (675 psig vs. 1500 psig) and the strong solvent dependence of the equilibrium, agreement with the values in Table 4 is considered reasonable.

No consensus exists as yet regarding the form of the active catalyst complex in rhodium-amine hydroformylation processes. That facile hydrogenation of aldehydes to alcohols becomes possible in the presence of tertiary amines of specified pK_b and concentration has been reported by two groups [10,19], and it is known that rhodium is predominantly present as carbonyl cluster anions in the amine resin catalysts [10,16]. Distribution and catalytic importance of the species, $NHR_3^+Rh_x(CO)_y^-$, $R_3N—Rh_x(CO)_y(H)$, and $H—Rh_x(CO)_y$, remains however unresolved.

Conclusions

Dominant in the catalytic behavior of rhodium complexes has been the influence of coordinated ligands, ligands retained in the coordination sphere throughout a catalytic cycle [1—8]. The validity of such a concept and its practical utility have been probed by measuring the rates of rhodium elution from phosphine- and amine- resin hydroformylation catalysis.

For both types of resins, rhodium concentrations in solution were proportional to percent rhodium in the resin, (tested in all cases with a large excess of ligand). Rhodium elution from phosphine resins exhibited a pattern in good agreement with the behavior of the monomeric complexes, elution increasing with CO pressure or with olefin content of the effluent and decreasing with increased temperature.

Metal concentrations over amine resins, although they exhibited an equilibrium behavior, were strongly solvent dependent. Elution was particularly enhanced by high aldehyde (as compared with alcohol) in the liquid phase, an effect which obscured any potential contribution from olefin and which led to significant redistribution of rhodium within a reactor bed during use.

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