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Infrared and Kinetics Study of Polymer-Bound Rhodium Cluster Catalysts for Olefin Hydrogenation

M. S. JARRELL[1] AND B. C. GATES[2]

Center for Catalytic Science and Technology, Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19711

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Polymers prepared by ligand exchange of $Rh_6(CO)_{16}$ with poly(styrene-divinylbenzene) membranes containing bound $-PPh_2$ groups were found to be active catalysts for the hydrogenation of cyclohexene and of ethylene at 75°C and 1 atm. The cyclohexene hydrogenation reaction catalyzed by the polymer was second order in cyclohexene and one-half order in hydrogen; the ethylene hydrogenation reaction was 0.8 order in the olefin and 0.2 order in hydrogen. Infrared spectra of catalyst membranes contacted with CO had carbonyl bands which suggested that small metal clusters attached to the polymer were unchanged in structure after use as a catalyst. The polymer-bound cluster had no carbonyl ligands during the steady-state catalytic reaction, and added CO bonded with the metal and acted as a strong reaction inhibitor. The ligands present on the functioning catalyst were inferred to be hydride, hydrocarbon, and polymer-attached phosphine groups. The phosphinated polymer evidently stabilized the unsaturated metal clusters by chelating them and preventing aggregation of the metal; the catalyst maintained undiminished activity for up to 75 hr on stream.

INTRODUCTION

Many transition metal clusters (compounds having metal–metal bonds) have been synthesized and yielded to structural determination in recent years (*1–3*). The clusters present an intriguing new class of catalysts since they have unique structures which are intermediate between those of the frequently applied classes of metal catalysts, mononuclear metal complexes [such as Wilkinson's hydrogenation catalyst, $RhCl(PPh_3)_3$] on the one hand and surfaces of bulk metals on the other. Understanding of reaction mechanisms involving metal complexes has been of some value in the understanding of surface-catalyzed reactions (*4*), but the ties between metal-complex and metal-surface catalysis are still poorly drawn. Further ties might be provided by an understanding of the intermediate metal-cluster catalysts.

Metal clusters are also of potential value as industrial catalysts. Recent patents (*5, 6*) have shown that rhodium cluster carbonyls such as $[Rh_{12}(CO)_{30}]^{2-}$ are present in solutions catalyzing the direct conversion of CO + H_2 (synthesis gas) into a mixture of ethylene glycol, propylene glycol, methanol, and other products. The formation of glycols points to an essential difference between a mononuclear metal complex and a metal cluster, since the cluster, with its metal–metal bonds, may facilitate the bonding of carbon-containing groups on neighboring metal atoms (as on

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[1] Present address: Union Carbide Corporation, South Charleston, West Virginia 25303.

[2] To whom correspondence should be addressed.

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a surface) and allow catalysis of carbon–carbon bond formation.

One of the most thoroughly characterized clusters is the rhodium carbonyl, $Rh_6(CO)_{16}$ (*3*, *7*). This octahedral metal cluster has four bridging CO ligands and 12 terminal CO ligands. Since its metal framework is similar to that of the presumed ethylene glycol synthesis catalyst and since it is a relatively stable and readily available cluster, $Rh_6(CO)_{16}$ was chosen as the starting compound for catalyst preparation in this research, which had the broad objective of determining structure–property relations of cluster catalysts.

Catalysis by metal clusters in solution has been studied for a number of years (*8*, *9*) but only seldom have the investigators determined the state of metal aggregation to ensure that indeed a cluster [rather than a fragment (metal complex) or an aggregate (metal particle)] was associated with catalytic activity (*10*). Recent work has shown, for example, that each of the clusters $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ has slight catalytic activity for CO reduction to CH_4 (*11*), and $Ni_4CNC(CH_3)_3$ is active for conversion of acetylene to benzene (*12*). The literature suggests that both the arrangement of metal atoms in a cluster and the nature and number of attached ligands are important in determining catalytic activity, but there is still almost no evidence to establish the presumed dependencies. The suggestion of the importance of the ligands is supported by the reactivity pattern of the iridium cluster carbonyl $Ir_4(CO)_{12}$ as the CO ligands are individually replaced by phosphines: The reactivity of the cluster for the ligand exchange reaction was found to increase by three orders of magnitude when two of the CO ligands were replaced by phosphines (*13*).

The ligands to be attached to metal clusters to modify their properties can even include solids such as phosphinated poly(styrene-divinylbenzene) (*14*, *15*). Bonding of a cluster to a solid offers the potential advantage of restricting the interactions among clusters which otherwise might lead to aggregation; it also allows study of cluster catalysts in the absence of complicating solvent effects (when gas-phase reactants are used) and offers the processing advantages of ease of separation of catalysts from fluid-phase products. Polymer-bound rhodium clusters were chosen for this research since a method for their attachment to the support has been developed (*14*, *15*) and since operating cluster catalysts in this form were expected to be well suited to characterization by transmission infrared spectroscopy, with simultaneous measurement of catalytic reactions rates (*16*). The reactions chosen for characterization of the polymer-bound catalyst were olefin hydrogenations, which were found to occur rapidly at 75°C and 1 atm; a few experiments were also carried out with benzene hydrogenation.

NOTATION

k	Reaction rate constant, variable dimensions
P	Partial pressure (atmospheres)
r	Reaction rate [(moles of product formed)/(seconds·gram-atoms of Rh)]

Subscripts

CH	Cyclohexene
E	Ethylene

EXPERIMENTAL METHODS

Catalyst preparation. Brominated, cross-linked polystyrene membranes having an approximate thickness of 7 μm were synthesized by polymerization of a mixture of vacuum-distilled monomers (styrene, divinylbenzene, and *p*-bromostyrene) between glass plates according to the procedures of Zundel (*17*). Divinylbenzene (DVB, 2 mol%) was included in the monomer mixture as a cross-linking agent, and *p*-bromostyrene (5–10 mol%) was in-

TABLE 1

Analysis of the Polymer Catalysts

Sample No.	Form	Cross-linking (mol% DVB)	Elemental analysis (wt%)			P/Rh mole ratio
			Br	P	Rh	
1	Membrane	2.0	1.17	0.92	1.69	1.8
2	Membrane	1.9	0.76	0.44	1.59	0.9
3	Macroporous beads	3	8.45	6.21	0.55	38

cluded to give membranes with the desired degree of functionalization. Attachment of the rhodium to a polymer membrane was carried out according to a procedure analogous to that developed by Haag and Whitehurst for attachment of rhodium complexes to polymer supports (*18*) and later applied with $Rh_6(CO)_{16}$ (*14*, *15*). Treatment of a membrane with a refluxing solution of $LiPPh_2$ in tetrahydrofuran under an atmosphere of N_2 for about 2 days resulted in the replacement of a fraction of the polymer-attached -Br groups with diphenylphosphine.[3] The phosphinated membranes were contacted under a blanket of N_2 with $Rh_6(CO)_{16}$ (Strem) dissolved in benzene. After several days of contact at room temperature, the solution was removed, and the membranes were dried under vacuum and stored in a desiccator until required for reaction studies.

The rhodium-containing membranes were golden brown and translucent. Each membrane was analyzed by Galbraith Laboratories of Knoxville, Tennessee, to determine rhodium, phosphorus, and bromine content. The results of analyses for two membranes, one having twice the P/Rh mole ratio of the other, are given in Table 1.

Reaction rates and infrared spectra were measured with samples of about 5 mg of catalyst containing about 0.08 mg of Rh. Catalyst samples loaded into the reactor/infrared cell were maintained in constant contact with reactants or a helium purge stream.

Brominated macroporous poly(styrene-DVB) beads (Aldrich, 3 mol% DVB, 3–4.5 mmol of Br/g of polymer) were phosphinated and treated with $Rh_6(CO)_{16}$, as described above, to give a solid hydrogenation catalyst. A high P/Rh ratio was obtained in this catalyst by limiting the amount of $Rh_6(CO)_{16}$ equilibrated with the phosphinated beads.

Apparatus and procedures. A flow reactor system described previously (*16*) was used for the simultaneous measurement of steady-state rates of hydrogenation reactions and infrared spectra of functioning catalyst membranes. When catalyst beads were used, spectra were not measured. Reactants contained vaporized cyclohexene or benzene fed from a syringe pump or ethylene fed from a high-pressure cylinder, together with coreactant H_2 and occasionally with CO or He. The gases flowed from cylinders through a bed of supported copper catalyst at 300°C (Harshaw, Cu-0803T, activated in flowing H_2 at 200°C for 2 hr) and then through a bed of zeolite 5A at 25°C (Linde, activated in flowing He at 400°C for 2 hr) to remove oxygen and water impurities, respectively. Reactant vapors contacted the catalyst at approximately 1 atm and temperatures between 68 and 95°C (45 and 102°C for ethylene hydrogenation). The catalyst membrane was mounted perpendicular to

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[3] Phosphination of the brominated polymer is a diffusion-limited process (*16*). The low extent of membrane phosphination reflects the greater homogeneity of bromine distribution in these polymer supports in comparison with those functionalized by a Friedel-Crafts bromination.

the beam of infrared radiation in the reactor, which was a specially designed heated gas cell (*19*) held in the sample compartment of a Beckman IR-12 infrared spectrophotometer. Product vapors flowed from the reactor through a compensating gas cell (conversions were always low, so that resulting infrared spectra were representative of the functioning catalyst membrane) and to a heated gas-sampling valve of a Hewlett-Packard 5750 gas chromatograph equipped with a thermal conductivity detector. Cyclohexene hydrogenation products and benzene hydrogenation products were separated at 100°C in a 0.125-in. o.d. × 20 ft column packed with 10% Carbowax 20M–2% KOH on 80/100-mesh Chromosorb W AW. Ethylene hydrogenation products were separated at 30°C in a 0.125-in. o.d. × 10 ft column packed with 80/100-mesh Porasil C.

Benzene (Fisher, certified) and cyclohexene (Eastman, $\geq 98\%$) were distilled from lithium aluminum hydride under N_2 before use. Ethylene (Matheson, C. P. grade) was used as received. Research-purity hydrogen, helium, and carbon monoxide cylinder gases were purified to remove traces of oxygen and water, as described above.

During a run, liquid and gas feeds flowed at constant rates, and steady-state conversions were determined by gas chromatographic analysis of the product stream. Precision of the analyses was ±5%. Olefin and benzene flow rates were varied from 9.1×10^{-7} to 1.3×10^{-5} mol/sec, and their partial pressures in the reactor over the course of experiments ranged from 0 to 0.4 atm. Total pressure in the reactor was 1.05 ± 0.05 atm.

Selected portions of the infrared region between 650 and 4000 cm^{-1} were scanned during most runs at 0.67 cm^{-1}/sec. The infrared beam was normally off during operation to prevent heating of the catalyst.

The accuracy of reported infrared bands was estimated to be ±3 cm^{-1}.

Details of the apparatus and procedure are given elsewhere (*20*).

RESULTS

Infrared spectra of polymer membranes had bands at 817, 1008, 1068, and 1403 cm^{-1}, which are not present in spectra of poly(styrene-DVB), confirming the presence of the bromine functionality in the membranes. The presence of polymeric phosphine or of the coordination of that phosphine to the rhodium cluster could not be verified by the assignment of bands in the infrared spectra of the catalysts because of the small amount of phosphine present in all membranes ($<1\%$). Iwatate *et al.* (*15*) assigned the infrared bands of $Rh_6(CO)_{13}(PPh_3)_3$ (including those of coordinated phosphine ligands) in the region of 400–1200 cm^{-1}. Of the bands located near 650 cm^{-1}, only those at 690 and 745 cm^{-1} are strong; these bands would be expected in spectra of phosphinated polystyrene, but would be at least partially obscured by strong absorptions at about 700 and 760 cm^{-1}, indicative of the polymer. Only sample 1 (Table 1), which contained nearly 1% P, showed evidence of a small shoulder on the 760 cm^{-1} infrared band at about 745 cm^{-1}.

The infrared spectra of polymers after equilibration with $Rh_6(CO)_{16}$ and prior to exposure to CO exhibited no absorptions other than those expected for polystyrene or those indicative of membrane bromination and phosphination as described above. The scans showed no new absorptions in the 1700–2200 cm^{-1} region indicative of carbonyl ligands on rhodium (Fig. 1, scan a). This result agrees with results of earlier studies (*14, 15*) and suggests that the carbonyls were displaced from the metal during the catalyst synthesis.

When membranes were contacted with flowing CO at 1 atm and 25°C for 4–5 hr, they developed infrared bands in the region expected for metal carbonyl ligands (Fig. 1,

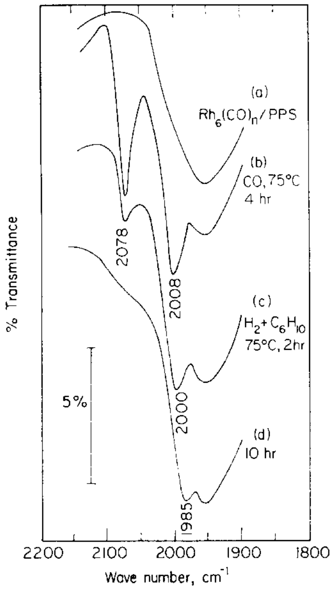

FIG. 1. Metal carbonyl infrared spectra of rhodium-containing polymer (sample 1, Table 1). Spectra were recorded: (a) before carbonylation; (b) following exposure to CO for 4 hr at 25°C; (c) following exposure of the carbonylated sample to reactants at 75°C for 2 hr; and (d) following 10 hr under reaction conditions. The infrared band at about 1960 cm^{-1} arises from the polymer support and not from metal-coordinated carbonyl ligands.

scan b; Table 2). There were two sharp bands, one at 2078 cm^{-1} and the other in the region 2010–1985 cm^{-1}. The position of the lower frequency carbonyl band differed from one catalyst sample to another (2008 cm^{-1} for sample 1, 2010 cm^{-1} for sample 2) and depended on the extent of carbonylation (increasing from about 1985 cm^{-1} with increasing band intensity). At 80°C, carbonylation took place more rapidly than at 25°C, and the bands achieved their maximum intensities in 1–2 hr. The carbonyl spectrum was not appreciably diminished in intensity when the catalyst was exposed to air, He, or H_2 at temperatures up to 80°C. No carbonyl infrared bands were observed at wavenumbers less than 1985 cm^{-1}. Transmission electron micrographs of these polymers showed no evidence of metal particles (the resolution limit of the instrument was 15 Å).

Analysis of reaction products by gas chromatography showed that the polymers catalyzed the conversion of cyclohexene and hydrogen into cyclohexane. For some catalysts, well in excess of 10^4 molecules of product per rhodium atom were formed without significant changes in the rate of reaction. Catalysts maintained stable activities for up to 75 hr on stream, and used catalysts showed no evidence of metal particles by transmission electron microscopy. When catalysts were contaminated

TABLE 2

Metal Carbonyl Spectra of $Rh_6(CO)_{16}$ and Substituted $Rh_6(CO)_{16}$

Sample	Treatment	Carbonyl stretching frequency, (cm^{-1})		Reference
		Terminal	Bridging	
$Rh_6(CO)_{16}$		2073, 2026	1800	*(23)*
$Rh_6(CO)_{13}(PPh_3)_3$		2079, 2005	1850, 1780	*(15)*
$Rh_6(CO)_{10}(PPh_3)_6$		1984, 1965, 1938	1779	*(24)*
$Rh_6(CO)_{16}/Al_2O_3$	Dried in air,	2080, 2000	—	*(25)*
	+CO, 1 atm	2060, 2010	1805	
$Rh_6(CO)_{16}/SiO_2$	Heat, +CO	2095, 2060, 2035	1860	*(26)*
$Rh_6(CO)_{16}$/PPS[a]	Dry, air,	—	—	*(15)*
	+CO, 1 atm	2080, 2000	1855	
$Rh_6(CO)_{16}$/PPS	Dry, air,	—	—	This research
	+CO, 1 atm	2078, 2008	—	

[a] Phosphinated poly(styrene-DVB).

with oxygen under reaction conditions, changes in activity for olefin and benzene hydrogenation were observed. The changes were associated with oxidation of the phosphine ligands and subsequent agglomeration of the rhodium into crystallites containing hundreds of atoms. These results are discussed elsewhere (*20, 21*).

The observed conversion of cyclohexene was generally limited to less than 4%. The conversions were demonstrated experimentally to be in the differential range, determining reaction rates directly (*20*); the effects of heat and mass transport on reaction rates were shown to be negligible (*20*), and therefore the rates reported in the following pages represent intrinsic kinetics of the hydrogenation reactions.

Cyclohexene was hydrogenated at a rate of about 10^{-1} mol/s·g-atom of Rh at 75°C in the presence of a 5-mg membrane containing 1.5% Rh with a reactant stream of cyclohexene at a partial pressure of 0.1 atm and hydrogen at a partial pressure of 0.9 atm. Cyclohexane was the only product observed within the limits of chromatographic detection; correspondingly, the selectivity of the catalyst for formation of cyclohexane was estimated to be >99%. Experiments with the flow reactor lacking added catalyst confirmed that uncatalyzed reaction and reaction catalyzed by the reactor walls and lines were negligible.

Reaction rate data were collected over a range of hydrogen and cyclohexene partial pressures (with and without diluent helium). The results are summarized in Table 3. The kinetics of cyclohexene hydrogenation was found to be

$$r = k_1 P^2_{\mathrm{CH}} P^{\frac{1}{2}}_{\mathrm{H_2}} \qquad (1)$$

at 1 atm of total pressure and 75°C over the full range of reactant partial pressures studied. The good fit of the data for sample 1 (Table 1) to a rate expression of the form of Eq. (1) is illustrated in Fig. 2. The rate of hydrogenation was unaffected by the introduction of either *n*-hexane or benzene into the reaction mixture at partial pressures as high as 0.12 atm.

The apparent activation energy of cyclohexene hydrogenation catalyzed by the polymer-bound catalyst was determined by plotting the hydrogenation rate constants at various temperatures in an Arrhenius fashion. The value is about 7

TABLE 3

Summary of Olefin Hydrogenation Kinetics

$r = kP^m_{\mathrm{olefin}} P^n_{\mathrm{H_2}}$

Catalyst	Sample No.	Cyclohexene hydrogenation at 75°C			Ethylene hydrogenation at 78°C		
		k (mol/s·g atom of Rh·atm^{m+n})	m	n	k (mol/s·g atom of Rh·atm^{m+n})	m	n
Rh cluster attached to poly(styrene-DVB) membrane	1	6.1 ± 0.3	2.06 ± 0.03	0.55 ± 0.10	0.57 ± 0.04	0.92 ± 0.04	0.23 ± 0.09
Rh cluster attached to poly(styrene-DVB) membrane	2	7.4 ± 0.4	2.22 ± 0.05	~0.5[a]	0.57 ± 0.03	0.80 ± 0.03	0.22 ± 0.07
Rh cluster attached to macroporous poly(styrene-DVB) particles	3	—[b]	—[b]	—[b]	0.0048 ± 0.0010	0.61 ± 0.15[c]	0.9 ± 0.4[c]

[a] A value of 0.50 was assumed in calculating k and m.

[b] The catalytic activity was too low to allow measurement of kinetics.

[c] Temperature = 77°C.

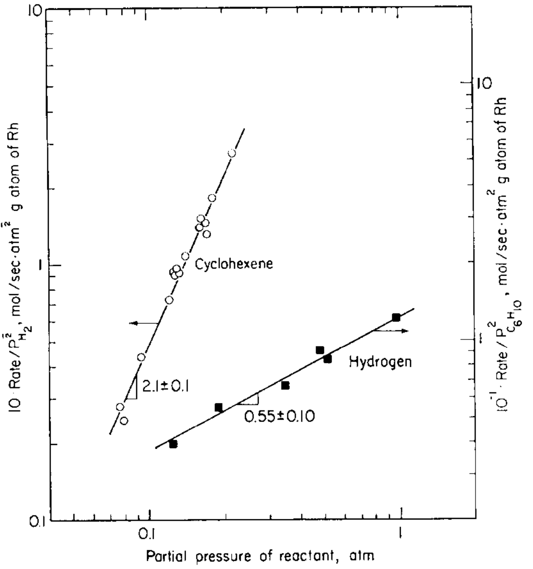

FIG. 2. Kinetics of cyclohexene hydrogenation catalyzed by a rhodium-containing polymer (sample 1) at 75°C.

kcal/mol, which is within the range reported by Bond (*22*) for activation energies of olefin hydrogenation reactions catalyzed by supported metals and determined in a similar manner.

The polymer catalysts were also active for the hydrogenation of ethylene. Conversion of reactants was again differential, and ethane was the only observed product. Ethane was not detected in the absence of added catalyst. In the presence of the polymer-bound rhodium catalysts, reaction rates were typically 10^{-1} mol/s·g-atom of Rh at 78°C in an atmosphere of ethylene at 0.1 atm of partial pressure and H_2 at 0.9 atm of partial pressure. Catalysts maintained a stable activity for as long as 30 hr on stream.

The kinetics of ethylene hydrogenation at 75°C determined for all catalysts listed in Table 1 could be approximated by a rate expression of the form

$$r = k_2 P^{0.8}{}_{\mathrm{E}} P^{0.2}{}_{\mathrm{H}_2}. \tag{2}$$

The agreement of typical rate data for sample 2 (Table 1) with this equation is shown in Fig. 3. The apparent activation energy of the ethylene hydrogenation reaction was 5–6 kcal/mol.

Both the cyclohexene and ethylene hydrogenation reactions were catalyzed at

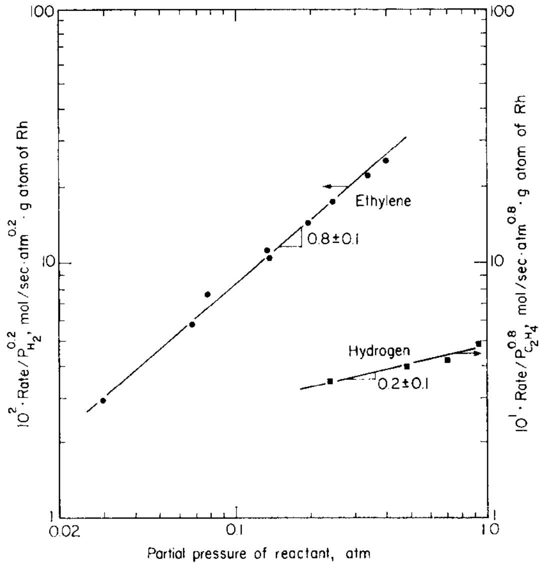

FIG. 3. Kinetics of ethylene hydrogenation catalyzed by a rhodium-containing polymer (sample 2) at 78°C.

higher rates when the phosphine to rhodium ratio in the catalyst was reduced, and the dependence of rate on this ratio was less with ethylene than with cyclohexene (Fig. 4).

When a stream of benzene and hydrogen contacted the polymer-bound catalyst at 75°C and 1 atm, trace amounts of product cyclohexane were formed. The conversion data showed that the catalysts were about 70 times less active for benzene hydrogenation than for cyclohexene hydrogenation, but the activity was too low to allow measurement of the kinetics of benzene hydrogenation.

The rhodium-containing polymers which were used as catalysts without prior carbonylation by flowing CO were found to be immediately active as olefin hydrogenation catalysts. Upon exposure to CO, the catalysts lost activity. Upon removal of CO from the vapor and recontact with reactants, they regained activity, and the process was fully reversible.

The infrared spectra show that activation of catalysts occurred by loss of carbonyl ligands from the rhodium. Infrared spectra of a functioning membrane catalyst which had become fully active for cyclohexene hydrogenation indicate the absence of metal carbonyls (e.g., Fig. 1, scan a); in contrast, the carbonylated catalyst (scan b) had an immeasurably low activity for cyclohexene hydrogenation.

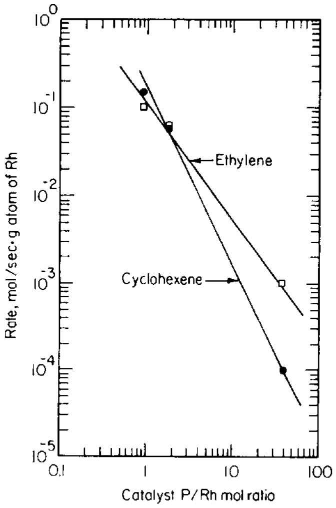

FIG. 4. Dependence of hydrogenation activity on polymer P/Rh ratio at 75°C.

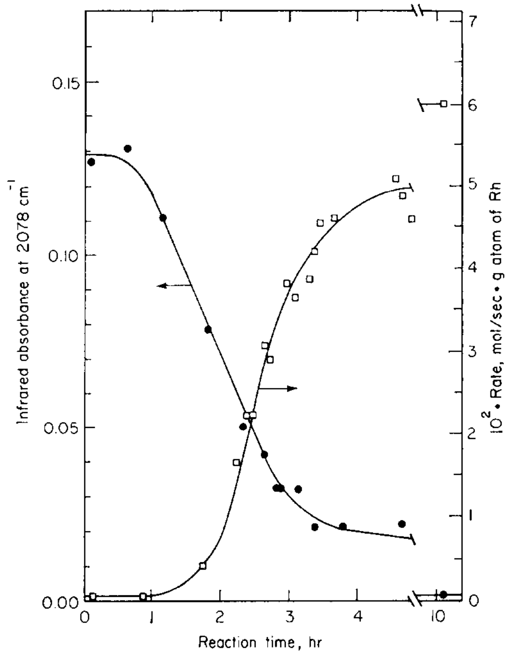

FIG. 5. Results of a transient kinetics experiment at 75°C: The fully carbonylated catalyst (sample 1) contacted CO until zero time, when flow of cyclohexene (0.12 atm) and H_2 (0.91 atm) was begun.

Experiments were performed in which the flow over the catalyst, after a steady state had been reached, was switched from CO to a mixture of cyclohexene and H_2. The results are summarized in Figs. 1 and 5. The carbonylated catalyst (Fig. 1, scan b) slowly lost its carbonyl spectrum (scans c and d), the lower frequency band shifting from 2008 to about 1985 cm^{-1} before disappearing from the spectrum. The catalyst returned after 10–15 h on stream to its uncarbonylated form (Fig. 1, scan a, and Fig. 5), which had full activity for the cyclohexene hydrogenation reaction. The data show that CO in the reactant had a simple, strong inhibiting effect on hydrogenation activity for all catalysts. Introduction of CO in the reactant stream at a

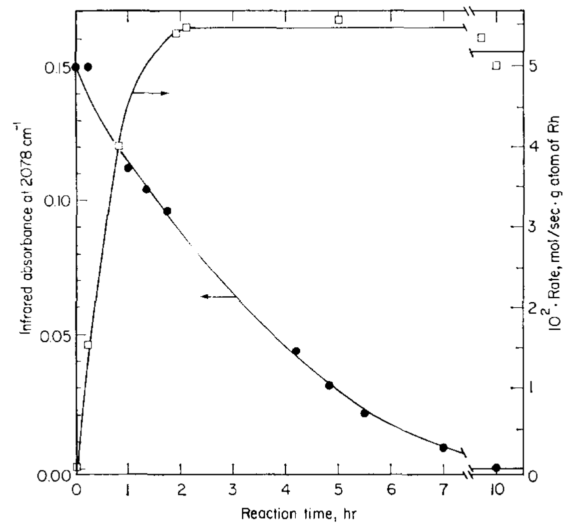

FIG. 6. Results of a transient kinetics experiment at 45°C: The fully carbonylated catalyst (sample 2) contacted CO until zero time, when flow of ethylene (0.14 atm) and H_2 (0.91 atm) was begun.

concentration of about 2 mol% gave the infrared spectrum indicative of the fully carbonylated catalyst and caused the rate to fall to an undetectably low value. The products of olefin hydroformylation were not observed under a flow of olefin, H_2, and CO at temperatures as high as 95°C.

In contrast to cyclohexene hydrogenation, ethylene hydrogenation proceeded in the presence of a partially decarbonylated polymer catalyst at a rate equivalent to that achieved with the fully decarbonylated catalyst (Fig. 6). In all other respects, loss of the carbonyl spectrum during ethylene hydrogenation was as described above for cyclohexene hydrogenation.

The infrared spectrum of a polymer recarbonylated after it had experienced long periods of use as a hydrogenation catalyst was indistinguishable from the spectrum of the freshly synthesized carbonylated catalyst shown in Fig. 1 (scan b). The catalysts experienced no detectable change in activity for cyclohexene or ethylene hydrogenation as long as this characteristic metal carbonyl spectrum could be regenerated.

Infrared spectra of functioning catalysts contained no bands indicative of ligands other than CO bound to the metal species during the catalytic reaction. The concentrations of any reaction intermediates bound to the catalyst might be expected to be quite low, and since infrared absorptions indicating such species are expected to be less intense than absorptions indicating metal carbonyls, the intermediates are evidently not detectable in experiments like those reported here.

Cyclohexene hydrogenation was carried out with liquid-phase reactants charged with dissolved $Rh_6(CO)_{16}$ at 25°C and 1 atm. An induction period of about 2 hr preceded the onset of hydrogenation. The catalytic activity changed over the course of the reaction, and rhodium metal was present in the product mixtures. Introduction of trace amounts of oxygen into the reaction flask decreased the induction time to 30 min but increased the rate of agglomeration of the metal. Benzene hydrogenation also took place, but it could not be attributed to homogeneous rhodium species because of the metal agglomeration. The agglomeration problems prevented the measurement of quantitative kinetics.

DISCUSSION

The spectra show that the polymer-bound rhodium had no carbonyl ligands immediately after synthesis and before contact with CO, in agreement with earlier results (*14*, *15*). Collman *et al.* (*14*) attributed the apparent loss of carbonyl ligands from the rhodium to a light-accelerated oxidation, in air, and it is considered probable that traces of oxygen introduced during the synthesis or handling of the catalyst caused by decarbonylation in the experiments described here. Exposure of freshly prepared catalysts to flowing CO at 1 atm was sufficient to generate strong metal carbonyl bands. The positions of these bands at about 2008 and 2078 cm^{-1} are characteristic of carbonyl ligands bound to a single rhodium atom, i.e., terminal carbonyls (Table 2). The metal carbonyl spectra of these catalysts differ from those of supported rhodium crystallites (*21*) and closely resemble the spectra of phosphine-substituted rhodium carbonyl clusters such as $Rh_6(CO)_{13}(PPh_3)_3$ (Table 2). The bridging carbonyl ligands observed in the infrared spectra of other rhodium carbonyl clusters at wavenumbers <1900 cm^{-1} (Table 2), including $Rh_6(CO)_{16}$ contacted with a phosphinated polymer (*15*), either were not present or were obscured by absorptions arising from the polymer support (*17*). Although the sharp carbonyl spectra suggest some homogeneity of metal species in the phosphinated polymer, the suggestion that these species retain the octahedral metal framework of $Rh_6(CO)_{16}$ [postulated by Iwatate *et al.* (*15*)] cannot be confirmed. The failure to observe metal crystallites in catalysts by transmission electron microscopy is, however, consistent with the presence of very small metal particles, possibly having some well-defined metal framework structure.

The infrared scans of functioning catalysts showed that the metal species were decarbonylated to form the active catalytic species for hydrogenation and that the original metal carbonyl spectrum of the attached cluster could be regenerated by exposure of the membrane to CO, even after many hours of use as a catalyst. The spectra are consistent with the suggestion that the rhodium clusters originally bound to the polymer matrix were present during catalysis in their decarbonylated forms, but alternatively, the clusters might have formed rapidly in the presence of CO from other metal species present during the catalytic reaction.

A comparison of Figs. 5 and 6 indicates that about half of the metal sites providing bonding sites for CO and contributing to cyclohexene hydrogenation activity did not have ethylene hydrogenation activity. This result suggests that, because of a heterogeneity of metal species in the polymer matrix or differing extents of interactions of the metal species with phosphine ligands, certain polymer-bound metal clusters (or alternatively, metal sites on the same metal cluster) had different catalytic activities.

Although it follows from the infrared spectra of functioning catalysts that the active metal species contained few carbonyl ligands, the spectra provide no direct information about the other ligands bound to the cluster during catalysis. The very occurrence of the hydrogenation reaction, however, is sufficient to suggest the presence of: (i) metal hydride ligands formed from the reactant hydrogen by dissociative bonding; (ii) olefins [presumably π bonded (*4*)]; and possibly (iii) partially hydrogenated hydrocarbon intermediates. Infrared bands indicative of the latter two types of species were detected by Erkelens (*27*) on Ni/SiO_2 catalyzing olefin hydrogenation, but the bands had low intensities and would be expected to be obscured by the background spectrum of the polystyrene support used in the present study.

Since it has been concluded that the rate expressions are reflections of the intrinsic kinetics of the reaction, without polymer swelling effects and mass transfer limitations, the results are consistent with a mechanism of cyclohexene hydrogenation involving dissociative bonding of H_2 (since the reaction order in H_2 is $\frac{1}{2}$) and the interaction of two olefin molecules with the cluster (since the reaction order in cyclohexene is 2).

Evidence of such interactions of olefin reactants with a metal cluster during olefin hydrogenation has been provided by the results of studies with triosmium cluster compounds. $H_2Os_3(CO)_{10}$ reacts with two molecules of ethylene to yield one molecule of ethane and one of $HOs_3(CH{=}CH_2)(CO)_{10}$ (*28*). The stoichiometric hydrogenation is proposed (*29*) to proceed through the intermediate structure $HOs_3(CH_2{=}CH_2)(CH_2CH_3)(CO)_{10}$; coordination of the second ethylene molecule to the cluster leads to expulsion of ethane and formation of the hydridovinylic cluster. A catalytic hydrogenation cycle would be completed if the resulting vinylic cluster were not formed or were susceptible to reduction by hydrogen. Catalytic hydrogenation is indeed observed for other olefins: 1-Hexene is cleanly converted in the presence of H_2 to hexane without destruction of catalytic activity (*30*). If a mechanism similar to that proposed for hydrogenation in the presence of the triosmium cluster were invoked for catalysis by the polymer-bound rhodium species, then reaction orders in olefin and hydrogen ranging from 0 to 2 and from 0 to 1, respectively, would be predicted, corresponding to the results.

When the rhodium clusters were allowed (in separate experiments) to agglomerate and form metal crystallites (*20, 21*), the metal could be characterized by transmission electron microscopy. The micrographs show that the rhodium was bound within the polymer matrices rather than on the surfaces of the membranes. This bonding within the flexible network is quite different from the attachment of a metal crystallite or cluster on the surface of an inorganic solid. The metal catalysts attached within the polymer matrix may resemble metal species in solution; the flexible organic matrix may be capable of influencing the structure and reactivity of the metal by virtue of solvent-like interactions with it. The metal catalysts are expected to be affected both by interactions with the pendent phosphine ligands of the polymer and by the polymer backbone itself, with its aromatic rings.

A comparison of the spectra of $Rh_6(CO)_{13}(PPh_3)_3$ and the carbonylated rhodium species bound to the phosphinated polymer (Table 2) and the decrease in catalytic activity with increasing phosphine content of the catalysts (Fig. 4) indicate that a rhodium cluster was bound into the polymer matrix through replacement of some of its carbonyl ligands with bound phosphines. The number of phosphine ligands coordinated to each bound cluster could not be ascertained directly, but Iwatate *et al.* (*15*) suggested that coordination involved "a few phosphine ligands." Elemental analyses of catalyst samples 1 and 2 (Table 1), prepared with an excess of $Rh_6(CO)_{16}$ relative to available polymeric phosphine groups, showed at least five polymeric phosphines for each rhodium cluster taken up; whether each of these phosphine ligands was coordinated to a cluster was not determined. The number of phosphine ligands coordinated to each cluster may vary with the extent of carbonylation. The shift in position of the lower frequency carbonyl band during carbonylation–decarbonylation cycles (Fig. 1) resembles the shifts in CO spectra noted with changing phosphine substitution on $Rh_6(CO)_{16}$ (Table 2). These spectral changes may alternatively be explained by the existence of clusters in the polymer with differing phosphine substitutions. The foregoing results and the stability of the catalyst suggest that the flexible phosphinated support chelates the attached metal species, forming more than one polymer–metal linkage. There is a mass of evidence supporting the conclusion that cross-linked polymers are capable of this chelation (*14*, *19*).

The metal structures of cluster compounds are highly electron deficient and are stabilized by the coordination of electron-donor ligands (*3*). As a result, the metal clusters most frequently studied are saturated with strongly bonded ligands such as CO. In order to provide an open site for coordination of reactants [a necessary condition for catalysis (*31*)], the cluster must be able to dissociate one or more of these ligands. The difficulty of dissociating ligands from clusters often dictates their use under extreme operating conditions [as in the Union Carbide ethylene glycol synthesis process (*5*, *6*)]. Under these conditions, ligand dissociation may precipitate changes in metal structure which can affect catalytic activity and selectivity.

The results of this research suggest that attachment of the rhodium cluster to the phosphinated support renders it quite susceptible to ligand dissociation, but simultaneously prevents alterations in metal structure [like the metal agglomeration observed in studies with $Rh_6(CO)_{16}$ in solution] that could change the accessibility and activity of the metal atoms of the catalyst. Interaction of the cluster with the pendant phosphine ligands may even serve to labilize the remaining metal carbonyls. This effect is illustrated by results in homogeneous catalysis: $Rh_4(CO)_{12}$ is active for olefin hydroformylation at 50–100 atm and 75°C (*32*), but $Rh_4(CO)_{10}(PPh_3)_2$ catalyzes the same reaction at room temperature and atmospheric pressure (*33*). Unfortunately, the instability of $Rh_6(CO)_{16}$ in solution made comparison of its activity with that of the polymer catalyst impossible.

Solvent-like interactions between the attached rhodium cluster and the polymer support are suggested by results of carbonylation and decarbonylation of the cluster. Considering the stability of metal carbonyl clusters in general, it is surprising that a polymer-bound cluster can experience dissociation of its CO ligands with relative ease. These displaced carbonyl ligands were not completely replaced by polymeric phosphines, since there were only four or five of these ligands for each cluster attached in some of the catalysts. Evidently the clusters were not totally bare in the absence of CO ligands; catalysts contacted with 1 atm of CO only slowly developed a metal carbonyl spectrum, and carbonylation was accelerated by heating the polymer. These results suggest that the decarbonylated metal clusters may have relieved their high degree of unsaturation by interactions with the solvent-like polymer support, particularly the aromatic rings of the backbone. There is, however, no direct evidence of this polymer–metal interaction.

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