JOURNAL OF CATALYSIS **40**, 255–267 (1975)

Methanol Carbonylation Catalyzed by a Polymer-Bound Rhodium (I) Complex

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Received May 27, 1975

The carbonylation reaction of methanol in the presence of methyl iodide promoter was catalyzed by a matrix-bound Rh(I) complex formed by ligand exchange of RhCl(CO)$(PPh_3)_2$ with a styrene-divinylbenzene copolymer containing bound $-CH_2PPh_2$ groups. Infrared spectra of a functioning, 7-μm-thick membrane catalyst were measured simultaneously with reaction rates in a steady-state flow reactor at 1 atm and 90–125°C. Kinetic experiments were also performed with macroporous catalyst beads suspended in a stirred batch reactor operating at conditions of potential industrial interest, 20 atm and 90°C.

Reaction rates of the order of 10^{-5} moles/(sec mole of Rh) were observed at 100°C. The carbonylation product at 1 atm was methyl acetate, and the only side product was dimethyl ether. The reaction was approximately first order in methyl iodide, zero order in each of the reactants, and second order in the Rh(I) complex. The stretching frequency of the Rh(I)-bound carbonyl (1978 cm^{-1}) indicated that the predominant form of the catalyst was the bound analog of $RhCl(CO)(PPh_3)_2$. This complex was converted over tens of hours of operation to a coordinatively saturated and inactive Rh(III) complex, probably an iodine adduct.

The results point to a mechanism involving slow oxidative addition of methyl iodide to a Rh(I) complex followed by methyl migration and subsequent steps in the coordination sphere of Rh. The suggested transition state for methyl iodide addition involves two Rh(I) centers in the flexible polymer network, one acting as a nucleophile attacking the carbon and the other playing a solvent-like role stabilizing the transition state.

INTRODUCTION

The renaissance in inorganic chemistry arising from the understanding of structure and bonding of transition metal complexes has led to a simultaneous renaissance in homogeneous catalysis. Industrial catalysis by transition metal complexes involves solutions which, like solutions of acids and bases, are characterized by corrosiveness and difficulty of separation from fluid-phase products. Consequently, methods have been developed in recent years (*1,2*) for bonding metal complexes to solid polymer matrices to eliminate these disadvantages. The matrix-bound complexes form a class of solids comparable to ion-exchange resins, which were developed several decades ago with the similar objective of providing noncorrosive and easily separated acids and bases.

There is a rapidly growing literature of catalysts formed by bonding transition metal complexes into polymer matrices and onto surfaces of inorganic solids. Most of this literature, reviewed in refs. (*3–6*), consists of patents, with the remainder focused primarily on catalyst synthesis. The catalytic nature of matrix-bound complexes and the effects of anchoring the complexes are in need of systematic investigation.

This research was intended to characterize the performance of a polymer-bound transition metal complex catalyst. Infrared spectroscopy was chosen to complement reaction kinetic studies since infrared spectra of sulfonic acid groups bonded in the matrix of a functioning polymeric catalyst have been obtained and interpreted with little more difficulty than is expected for catalysts in solution (*7,8*). Experiments with vapor-phase reactants were chosen to allow observation of catalytic groups in the absence of solvents and over a wide range of reactant concentrations, especially low concentrations.

Methanol carbonylation was chosen as an appropriate reaction since (a) it is industrially important (*9–11*); (b) it takes place in the presence of Rh-complex catalysts in solution at the conveniently mild conditions of 1 atm and about 150°C (*9*); (c) analogous complexes bonded to poly(styrene-divinylbenzene) matrices have been prepared (*3–6*) and were expected to exhibit catalytic behavior similar to that of the soluble complexes; and (d) the reported soluble catalysts include carbonyl complexes of Rh(I), and the analogous bound complexes were expected to be identifiable by their carbonyl stretching frequencies, which could be determined by methods previously applied to ion-exchange resin catalysts (*7,8*).

Conversion of methanol and carbon monoxide to acetic acid is carried out in a process yielding about 300 million pounds of acetic acid per year; the Rh-complex catalyst in solution, in the presence of a promoter such as CH_3I or HI, allows conversion at about 15 atm and 175°C, with greater than 99% selectivity (*9–11*). In contrast, earlier Co-complex catalysts required pressures of hundreds of atmospheres and gave yields of only about 80% (*10*). There is clear incentive for development of solid catalysts to retain the chemical characteristics of the soluble industrial catalyst and reduce the problems of separation and corrosion (*12*).

The importance of methanol and methanol carbonylation to the chemical industry might be expected to increase with the increased availability of synthesis gas (largely CO and H_2), which may be produced by coal gasification. Since methanol itself is synthesized directly from CO and H_2, all of the constituents required for production of acetic acid are potentially available from coal.

NOMENCLATURE

C	Concentration, moles/liter of reactor volume
k	Reaction rate constant in Eq. (3), moles/{sec mole of Rh [moles of Rh(I)/liter]^2}
$\mathbf{k}$	Reaction rate constant in Eq. (4), liters/{sec mole of Rh [moles of Rh(I)/liter]^2}
k_1	Reaction rate constant in Eq. (1), moles/(sec atm mole of Rh)
k_2	Reaction rate constant in Eq. (2), moles/{sec atm mole of Rh [moles of Rh(I)/liter]^2}
K	Parameter in Eq. (3), atm
L	Ligand
P	(Partial) pressure, atm
r	Carbonylation reaction rate, moles of product/(sec mole of Rh)
$\mathbf{r}$	Carbonylation reaction rate in Eq. (4), moles of product/(sec liter of catalyst)
R	Gas constant, 1.987 Cal/mole °K
[Rh(I)]	Concentration of Rh(I) in catalyst (polymer) phase, moles/liter
	Temperature, °K or °C

EXPERIMENTAL METHODS

Catalyst Preparation

Membranes of poly(styrene-divinylbenzene) having an approximate thickness of 7 μm were synthesized from a mixture of 5 mole% divinylbenzene (DVB) in styrene according to the procedure of Zundel (*7,13*). Catalytic groups were incorporated into the polymer by the synthetic method

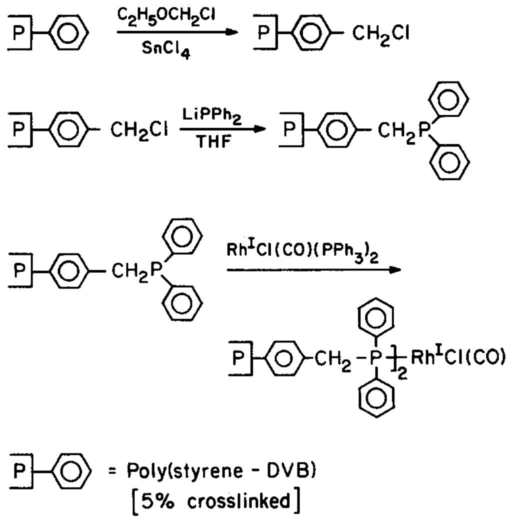

FIG. 1. Summary of catalyst synthesis steps.

of Haag and Whitehurst (*1,14*), which is summarized in Fig. 1.

The chloromethylation of the polymer matrix (*15*) yielded 0.19-CH_2Cl groups/benzene ring, as evidenced by elemental analysis of the polymer.[1] Reaction of the chloromethylated polymer with $LiPPh_2$ (*16*) resulted in the replacement of 82% of the Cl with diphenylphosphine groups. Contacting of the phosphinated polymer with excess $RhCl(CO)(PPh_3)_2$ in benzene for 2 wk at 60°C led to a ligand exchange reaction; this was followed by thorough washing to remove soluble Rh, yielding a solid catalyst containing 3.7% Rh, 3.3% P, and 1.4% Cl. This polymer composition corresponds to about 1 Rh atom/20 benzene rings and an average distance between Rh nuclei of about 25 Å.

The Rh-functionalized membranes were pale yellow and translucent. They exhibited an infrared absorption band at 1978 cm^{-1}, which has been assigned to the stretching mode of a carbonyl group coordinated to Rh in its +1 oxidation state (*17*).

A single catalyst membrane weighing 140 mg and containing 5.0 mg of Rh was used in all the reported steady-state experiments. It was maintained in continuous contact with reactants or a helium purge stream.

The synthesis was performed similarly with styrene-divinylbenzene copolymer obtained in the form of macroporous beads (XAD-2, Rohm and Haas); these were estimated to contain 20% divinylbenzene cross-linking agent (*18*). The functionalized polymer contained 1.4% Rh (*19*).

Apparatus

The flow system described previously (*8,13*) (Fig. 2) was used for the simultaneous measurement of steady-state rates of the methanol carbonylation reaction and infrared spectra of the functioning catalyst membrane. Vapor-phase reactants contacted the catalyst at approximately 1 atm and 90–125°C. The reactor was a heated infrared gas cell (*8*), and the catalyst membrane was held in the cell perpendicular to the infrared beam. Products flowed from the reactor to a reference cell, which was identical to it but contained no catalyst. Both cells were mounted in a Beckman IR-12 infrared spectrophotometer. Since conversions were always low, the compositions of the vapors in the two cells

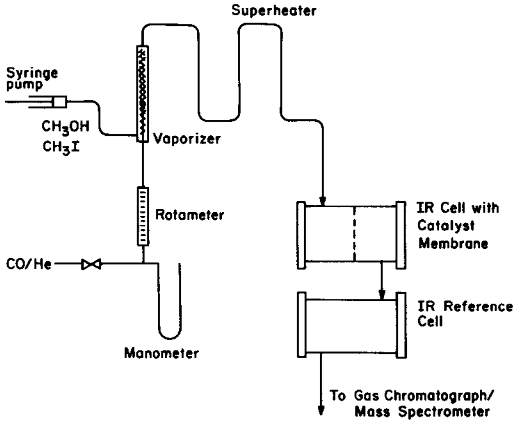

FIG. 2. Schematic diagram of reactor system (*8,13*).

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[1] This synthesis step required the precautions due to the carcinogenic nature of the reactant chloromethylethyl ether.

were nearly the same, and the resulting infrared spectra were characteristic of the catalyst membrane and the reactants chemically bonded to it.

Products flowed from the reference cell to the heated gas sampling valve of a Hewlett-Packard 5750 gas chromatograph. Products were separated at 140°C in a 0.125-in. o.d. column packed with 80–100 mesh particles of Porapak N. Products were detected by flame ionization; alternatively, the separated products were occasionally introduced into an interfaced Hewlett-Packard 5930A mass spectrometer for qualitative identification.

Measurement of Rates and Spectra

Liquid feeds were methanol (Fisher, 99.9% pure) mixed with methyl iodide (Fisher, bp, 40.4–42.4°C) in molar proportions ranging from 1:1 to 9.3:1. These were prepared immediately before use to minimize formation of iodine impurity in feedstocks, which resulted from reaction of methyl iodide, methanol, and oxygen. The liquid feed was vaporized in the flow system and mixed with a metered gas stream of carbon monoxide occasionally diluted with helium.

Methanol flow rate varied from 1.7×10^{-6} to 6.3×10^{-6} moles/sec. Methanol partial pressure varied from 0.11 to 0.41 atm, methyl iodide partial pressure from 0 to 0.62 atm, and carbon monoxide partial pressure from 0 to 0.91 atm. Total pressure was 1.05 ± 0.03 atm. Reaction temperatures between 90 and 125°C were measured with a precision of ±0.5°C.

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 ±10%.

Infrared absorption spectra of the catalyst between 650 and 4000 cm^{-1} were obtained during most runs at a scanning rate of 1.33 cm^{-1}/sec. The infrared beam was normally off during operation to prevent heating of the catalyst.

Experiments with liquid-phase reactants and macroporous catalyst beads were performed in a glass-lined batch reactor (Autoclave Engineers, Model ABP-300-DC) at 85–95°C and carbon monoxide partial pressures of about 20 atm. The methanol to methyl iodide molar ratio in the reactant mixture was typically greater than 15:1. Liquid samples were withdrawn periodically for product analysis as the reaction proceeded. After reaction, the catalyst was recovered in a filtration step in which it was exposed to air.

Details of the apparatus and procedure are given elsewhere (*19*).

RESULTS

Methanol carbonylation proceeded at rates typically of the order of 10^{-5} moles of product/(sec mole of Rh) at 1 atm and 100°C. No conversion was observed when either the catalyst or the promoter methyl iodide was absent. The carbonylation product at these conditions was methyl acetate, whereas in the analogous solution reaction the principal product was acetic acid (*9*).[2] Traces of dimethyl ether were the only observed side product, in agreement with results for the solution reaction (*9*).

Steady-state conversions of methanol in the flow reactor were demonstrated to be differential (<0.1%), so that reaction rates were measured directly. Mass transfer influence on reaction rates was negligible as shown by results of standard experimental tests and by estimation of intramembrane diffusion resistance (*19*).

Methanol carbonylation in the presence of macroporous catalyst beads and liquid-phase reactants was observed at conditions estimated to be those of possible industrial interest, 90 ± 5°C and 20 atm.

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[2] The ester product normally predominates in the presence of excess alcohol(*11*).

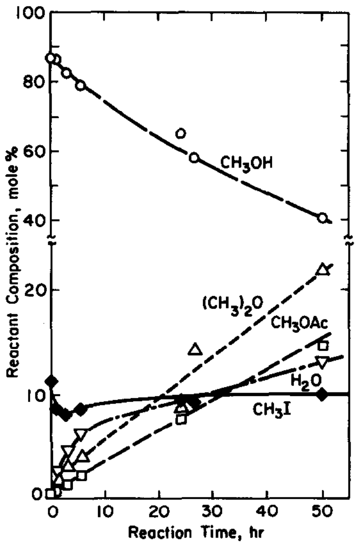


FIG. 3. Product distribution in a batch reactor operating at $T = 95°C$ and $P = 20$ atm; the reactor contained 0.81 g of beads of polymer catalyst (incorporating 0.11 mmole of Rh); the liquid reactant initially contained 0.52 moles of methanol and 0.845 moles of benzene. The reactant composition is given on a benzene-free basis.

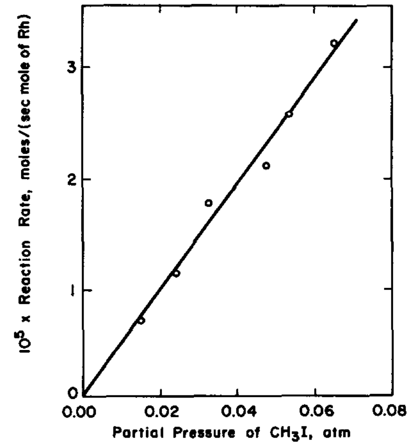


FIG. 4. First-order dependence of methanol carbonylation rate on methyl iodide partial pressure at 125°C.

Data were obtained for conversions to carbonylated products as high as about 20%, as shown in Fig. 3. Analysis of catalyst samples before and after use showed that Rh was lost during reaction or during the subsequent filtration; consequently, decreased catalyst activity was observed when the catalyst was reused (*19*).

The membrane catalyst measurably lost activity over tens of hours of operation, but the deactivation was so slow that kinetics were determined accurately during periods of negligible deactivation. Data showing the dependence of reaction rate on methyl iodide partial pressure are given in Fig. 4. The first-order dependence is the same as that reported for the analogous solution reaction (*9*). The reaction rate was found to be nearly independent of the partial pressures of methanol and of carbon monoxide over almost the entire ranges investigated; these results also agree with those for the solution-phase carbonylation. The temperature dependence of the pseudo first-order rate constant defined by the equation

$$r = k_1 P_{\mathrm{CH_3I}} \qquad (1)$$

indicates an activation energy of 13.2 ± 1.0 kcal/mole (Fig. 5).

Deactivation of the membrane catalyst is shown by the data of Fig. 6, indicating the decrease of the pseudo first-order rate constant k_1 as a function of the time of contact with reactants and promoter methyl iodide. No deactivation occurred in the absence of catalytic reaction.

The infrared spectrum of the working

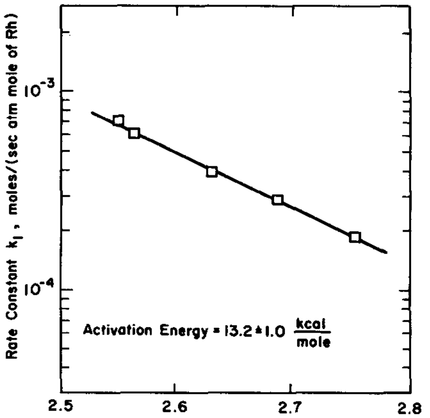


FIG. 5. Arrhenius plot: temperature dependence of the pseudo first-order rate constant k_1.

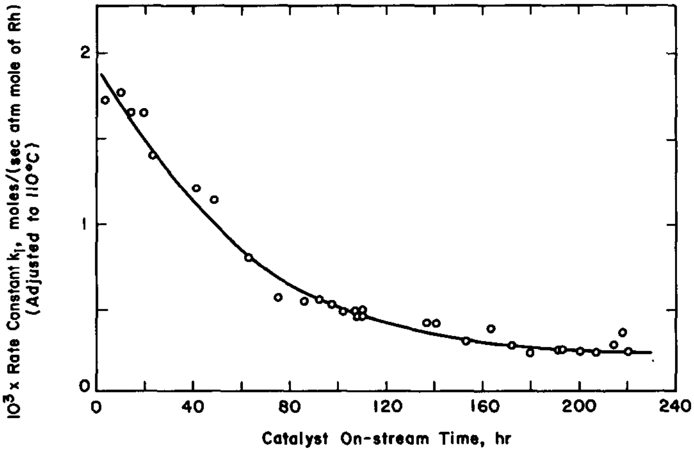


FIG. 6. Catalyst activity loss in operation with vapor-phase reactants at 1 atm and temperatures between 100 and 125°C.

catalyst initially contained no bands significantly different from those of the originally prepared catalyst. The identity of the bound complex has been inferred from the frequency of the stretching mode of Rh-coordinated carbonyl of the analogous soluble complex (*20*) and the polymer-bound complex (*17*). The spectrum was always independent of reaction conditions over periods short enough to exclude significant catalyst deactivation. Therefore the predominant form of the catalyst during reac-

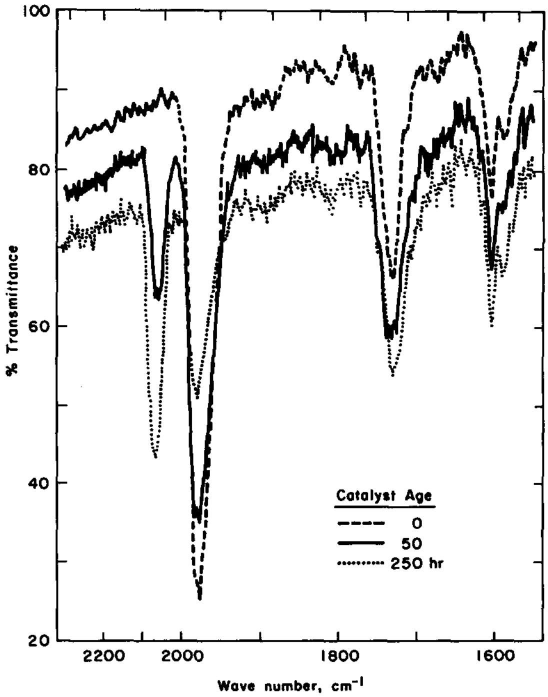


FIG. 7. Infrared spectra of functioning polymer membrane catalyst: conversion of a Rh (I) carbonyl complex (1978 cm^{-1}) to a Rh (III) carbonyl complex (2063 cm^{-1}) during operation.

tion is concluded to have been the species shown in Fig. 1, the matrix-bound analog of chlorocarbonylbis(triphenylphosphine)rhodium(I).

Over a period of on-stream time sufficient for measurable catalyst deactivation, there was a significant change in the intensity of the band indicating the carbonyl stretch (Fig. 7). The loss in intensity of this 1978 cm^{-1} band was accompanied by the growth in intensity of a new spectral band at 2063 cm^{-1}. The position of this new band indicates a Rh(III)-coordinated carbonyl species (*20,21*).

The rate of loss of carbonyl groups indicated by the 1978 cm^{-1} band was equal to the rate of formation of groups indicated by the 2063 cm^{-1} band (*19*). Therefore the change in the spectrum resulted from the conversion of the Rh(I) carbonyl complex to a Rh(III) carbonyl complex. This change was accompanied by catalyst activity loss, and an analysis of the kinetics (*19*) led to the conclusion that the Rh(I) complex was catalytically active and the Rh(III) complex was not.

The change in concentration of the catalytically active Rh(I) complex caused by the deactivation process provided an opportunity for determining the dependence of carbonylation rate on the concentration of the Rh(I) species. The data of Fig. 8 show that the reaction was second order in the concentration of the Rh(I) complex bonded within the polymer matrix. The kinetics are therefore represented as follows:

$$r = k_2\,[\text{Rh(I)}]^2\,P_{CH_3I} \qquad (2)$$

where $k_2 = 6 \times 10^8\ e^{-13{,}200/RT}$ moles/{sec atm mole of Rh [moles of Rh(I)/liter]^2}.

This equation provides a good representation of almost all the data, as shown in Figs. 4–6, but clearly the rate cannot be independent of the reactant partial pressures over their entire ranges. As expected, the data taken at the lowest partial pressures of methanol and carbon monoxide indicated more complex kinetics. The results are analyzed elsewhere (*19*) and lead to the following rate equation:

$$r = \frac{kP_{CH_3I}P_{CO}P_{CH_3OH}[\text{Rh(I)}]^2}{(K_{CH_3I} + P_{CH_3I})(K_{CH_3OH} + P_{CH_3OH})(K_{CO} + P_{CO})} \qquad (3)$$

This equation was selected from a number of equations of similar form, since it was the one giving the best fit to the complete set of rate data. The best values of the parameters were determined by a least-squares criterion with the algorithm of Marquardt (*22*). The parameter values are collected in Table 1, and the goodness of fit is illustrated in Fig. 9. The data were insufficient to allow a precise determination of the parameters in Eq. (3) for temperatures other than 125°C. The observed carbonylation rate was nearly independent of methanol partial pressure at the lower temperatures, however, indicating that $K_{\text{CH}_3\text{OH}}$ was smaller at the lower tempera-

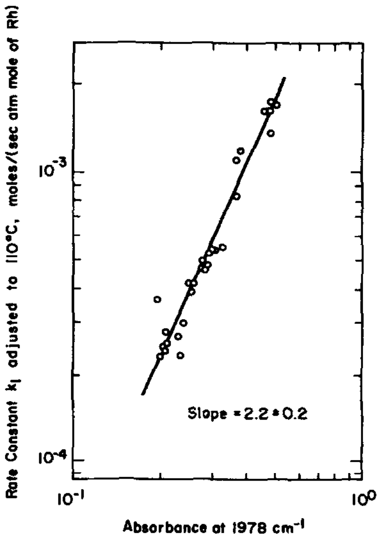


FIG. 8. Second-order dependence of carbonylation rate on the concentration of the polymer-bound Rh(I) complex.

TABLE 1
PARAMETERS FOR RATE EQUATION, EQ. (3), AT 125°C

k (moles/{sec mole of Rh[moles of Rh(I)/liter]^2})	$(9.6 \pm 0.7) \times 10^{-2}$
K_{CH_3OH} (atm)	0.40 ± 0.04
K_{CH_3I} (atm)	0.08 ± 0.01
K_{CO} (atm)	~0.01

tures, and that Eq. (2) was a good approximation to almost all these data.

The rates of carbonylation in the batch reactor were also consistent with the simple kinetics of Eq. (2), as shown by the data of Fig. 3, which demonstrate a nearly constant carbonylation rate even though the methanol concentration changed significantly during the experiment.

DISCUSSION

Reaction Mechanism

The matrix-bound Rh(I) catalyst and the analogous soluble catalyst can be compared by the kinetics of the respective carbonylation reactions. For both the matrix-phase and liquid-phase reactions, the methanol carbonylation was first order in methyl iodide and approximately zero order in methanol and in carbon monoxide.

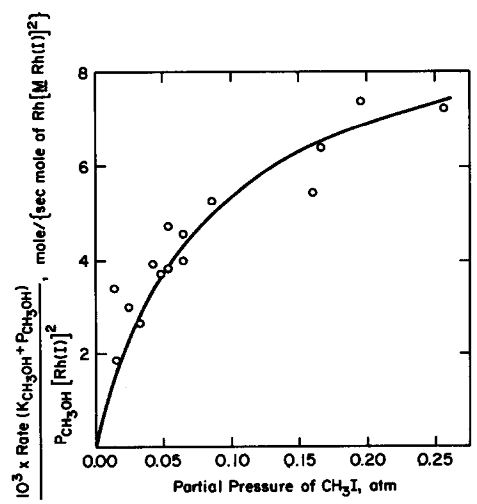


FIG. 9. Rate of methanol carbonylation at 125°C; the curve is predicted by Eq. (3) with the parameters of Table 1.

Consequently, the reaction mechanism inferred by Roth *et al.* (*9*) from the solution-phase reaction kinetics is concluded to be similar to that prevailing in the polymer matrix. The Roth mechanism (Fig. 10) involves the oxidative addition of methyl iodide to a Rh(I) complex with unidentified ligands *L* in an elementary step that is rate determining at all but the relatively low concentrations of reactants. This step is followed by the well-known methyl migration (or *cis*-insertion) step (*23*), bonding of carbon monoxide to give a coordinatively saturated Rh(III) complex, and subsequent decomposition of this complex in the presence of methanol to yield a carbonylated product and regenerate the pro-

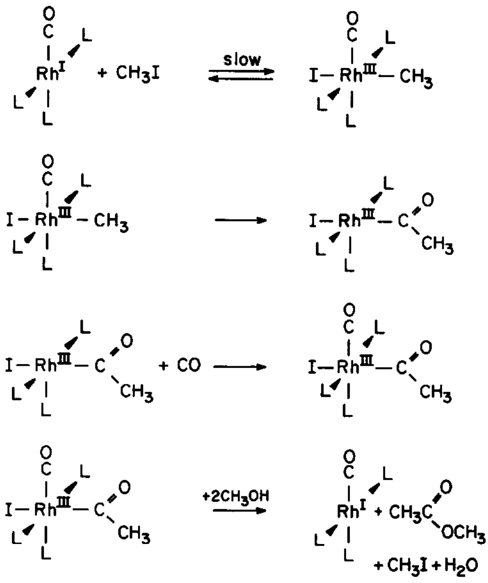


FIG. 10. Mechanism of Roth *et al.* (*9*) for methanol carbonylation catalyzed by a soluble Rh(I) complex. The ligands *L* in the active form of the complex are undetermined.

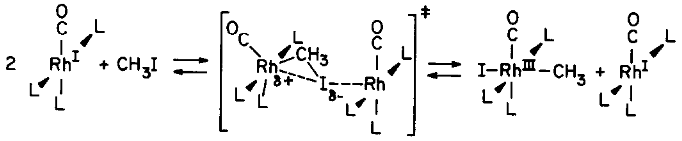


FIG. 11. Proposed first step in the mechanism of methanol carbonylation catalyzed by a polymer-bound Rh (I) complex; the subsequent steps are those given in Fig. 10.

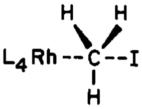
moter and catalyst. This last step (or steps) is poorly characterized.

The kinetics [Eq. (3)] indicate that at the relatively low partial pressures of methanol or of carbon monoxide, the steps subsequent to the oxidative addition are no longer so fast as to be considered in equilibrium, and the assumption of a single rate determining step breaks down. The present results therefore demonstrate the participation of the reactants in steps taking place in the coordination sphere of rhodium, consistent with the second and third steps shown in Fig. 10.

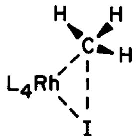
The infrared spectra confirm the occurrence of a mechanism like that of Fig. 10. The presence of the Rh(I) complex shown in the first step and the virtual absence of any Rh(III) species in the undeactivated functioning catalyst point to the first step as rate determining.[3]

Although the matrix-bound Rh(I) complex catalyst bears the aforementioned strong resemblance to the analogous soluble species, it differs in one significant respect: the reaction in the resin matrix in the absence of solvent was second order in the Rh(I) complex, whereas the solution reaction was first order in the soluble complex. Therefore, the mechanism of the resin-phase reaction is suggested to involve two Rh(I) species in the first step, which is usually rate determining, as shown in Fig. 11. According to this interpretation, the carbon of methyl iodide undergoes nucleophilic attack by a Rh(I) complex acting as a Lewis base, and the second Rh(I) complex acts as a Lewis acid to stabilize the transition state. Instances of transition metal complexes acting as both Lewis acids and Lewis bases are well known (*23*).

The possibility of a transition state for this oxidative addition involving two Rh complexes was recognized by Douek and Wilkinson (*24*). The configuration of the transition state is suggested to be intermediate between a linear S_N2-type transition state



and a nonpolar triangular one



as inferred by analogy from the results of Ugo *et al.* (*25*) for the oxidative addition of methyl iodide to Vaska's complex $[IrCl(CO)(PPh_3)_2]$ in solution.

The configuration of this transition state depends on the electronic and steric environment of the metal (*25*) and on the Lewis acid character of all species in solution or in the vicinity of the metal (*24*). Consequently, the rate and stereochemistry of the oxidative addition are expected to be sensitive to the environment of the Rh complexes (*25,26*). Clearly, this environment can be designed by incorpo-

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[3] With the lowest applied partial pressures of methanol and carbon monoxide, carbonyl stretching bands indicative of Rh(III) intermediates would be expected in the spectrum. None was discerned, presumably because such experiments were not done early, and catalyst aging produced a Rh(III) species, the bands of which could have obscured the bands indicative of the supposed intermediates.

ration of appropriate functional groups into the polymer matrix.

The existence of a highly structured transition state with two Rh atoms in the polymer, but not in solution, is consistent with the higher concentration of Rh in the polymer. This concentration was about 0.3 *M*, roughly 60 times the concentration attained in solution, as inferred from patent data for the solution reaction (*11*). Although the average separation of the Rh atoms in the polymer was about 25 Å, the 5%-cross-linked matrix was flexible, allowing a metal atom to be coordinated to the polymer network through several bound ligands, as demonstrated by structural determinations of catalysts like the ones used in this work (*27*). The postulated transition state structure is consistent with mechanisms suggested for polymer-phase reactions such as alcohol dehydration (*8*,*28*) and benzene alkylation (*29*) catalyzed by bound $-SO_3H$ groups; orders of reaction in acid groups as high as 7 have been observed (*29*). All these results emphasize that catalysis in a flexible polymer matrix is solution-like catalysis; the catalyst can exert a solvent-like influence on the reactant, bonding to it at more than one position in a manner suggesting the action of an enzyme (*8*).

The absence of solvent in the catalyst operating at 1 atm prevented its complicating the reaction mechanism. We suggest that polar groups added to the catalyst could serve as Lewis acids in the mechanism of Fig. 11, replacing one of the Rh complexes in this function and possibly yielding kinetics first order in the polar groups and first order in Rh. The data of Roth *et al.* (*9*) for reaction in solution are consistent with this suggestion, which is also supported by the results of Chock and Halpern (*26*), who observed large solvent effects in the oxidative addition of alkyl halides to Ir complexes.

The second-order dependence of methanol carbonylation rate on Rh concentration in the polymer matrix suggests that the distribution of Rh in the polymer as well as the amount may affect the reaction rate; restriction of the Rh complex to a small volume of the polymer would be expected to result in increased catalytic activity.

Although chloromethylation of cross-linked polystyrene occurs uniformly throughout the matrix (*15*), phosphination of the chloromethyl groups is a relatively fast reaction dependent on the diffusional resistance offered by the polymer network. Table 2 summarizes data from several sources, indicating that the accessibility of chloromethyl groups to phosphination decreases with increasing polymer particle size, cross-linking, and the concentration of chloromethyl groups in the matrix. These data suggest that it may be possible to design catalysts with Rh groups distributed near a particle surface.

Catalyst Aging

The spectral evidence indicated that aging of the membrane catalyst resulted from conversion of the active Rh(I) complex to an inactive Rh(III) complex. The deactivation is inferred to have resulted from an oxidative addition reaction which was virtually irreversible at the conditions of the experiments (about 100°C and 1 atm). The Rh(III) complex formed by oxidative addition would have no open coordination sites, which explains its inactivity as a catalyst (*21*).

The identity of the Rh(III) species is suggested to be an iodine adduct of Rh(I).[4] Molecular iodine was formed in the feed by reaction of methyl iodide, methanol, and traces of oxygen impurity, as indicated by the formation of iodine deposits in the used catalyst membrane. Studies of similar Rh complexes in solution (*31*) indicate that the iodine adduct of the Rh(I) complex

[4] The formation of a different species such as an oxygen adduct is inferred from the analogous solution chemistry to be improbable (*19*).

TABLE 2
PHOSPHINATION OF CROSS-LINKED POLYSTYRENE MATRICES

Ref.	Bead diam (mm)	% cross-linking of polymer	% of phenyl groups chloromethylated	% of $-CH_2Cl$ groups phosphinated
Evans *et al.* (*17*)	0.1	1	14.3	99
Grubbs *et al.* (*14*)	0.1	2	9.3	94
Capka *et al.* (*30*)	1–2	20	14.4	83
This work				
membrane catalyst	0.01[a]	5	19.3	83
bead catalyst	0.5	20[b]	10.0	67
Haag and Whitehurst (*1*)	—	—	50.0	25

[a] Membrane; dimension is approximate thickness.
[b] Estimated value.

may be stable at low temperatures and unstable at temperatures of industrial methanol carbonylation (about 175°C).

The rate of formation of the Rh(III) species in the oxidative addition is second order in the concentration of Rh(I), as indicated by the results of Fig. 12, showing a linear time dependence of the inverse of the infrared absorbance of the Rh(I)-bound carbonyl. This result suggests that the oxidative addition of iodine to the complex proceeded through a transition state similar to that shown in Fig. 11 for the oxidative addition of methyl iodide to the complex.

In contrast to the membrane catalyst and in contrast to an anologous silica-supported catalyst (*32*), the polymer beads used in the presence of liquid-phase reactants lost activity by loss of rhodium. The mechanism of this rhodium loss is undetermined; it might have proceeded through oxidative cleavage of the rhodium–phosphine coordinative linkage in the presence of oxygen and carbon monoxide (*33*) or through dissociative loss of polymeric phosphine ligands from the Rh(I) complex. Either process would have broken the catalyst–polymer linkage. This rhodium loss might perhaps be prevented by strict ex-

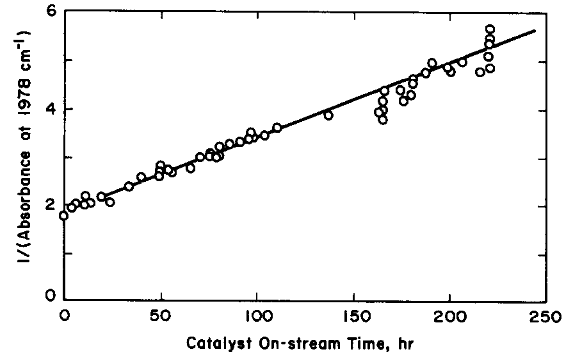

FIG. 12. Catalyst deactivation by conversion of Rh (I) to Rh (III): demonstration of a second-order reaction.

TABLE 3

ACTIVITIES OF SUPPORTED METHANOL CARBONYLATION CATALYSTS[a]

Catalyst	Ref.	[Rh (I)] (moles/liter)	Reactant phase	$10^{-2} \times \mathbf{k}^b$ (adjusted to 100°C)
RhCl (CO) $(P_p)_2$ (membrane)	This work	0.32	Vapor	1.5
RhCl (CO) $(P_p)_2$ (beads)	This work	0.15	Liquid	1.4
RhCl (CO) $(PPh_3)_2$ (supported on carbon)	Schultz and Montgomery (*35*)	0.15	Vapor	1.3

[a] P_p = *p*-(polystyryl) diphenylphosphine ligand.

[b] Values of **k** in [liters/{sec liter of catalyst [mole of Rh(I)/liter]^2} adjusted to 100°C with Eq. (4), assuming activation energies of 13.2 kcal/mole.

clusion of oxygen or by use of a less highly cross-linked polymer.[5]

Process Design

The matrix-bound methanol carbonylation catalyst prepared in the form of macroporous beads and used in a batch reactor at conditions approximating those of possible industrial application exhibited activity roughly the same as that of analogous soluble rhodium complexes (*19*) and carbon-supported complexes (*12,35*). These results suggest that the polymer-bound catalyst may be of value for large-scale processing, providing that catalyst deactivation can be minimized.

Preliminary design estimates can be based on the present results. The approximate rate equation, Eq. (2), can be used conveniently in the following form, which expresses the observed dependence of rate on the concentration of bound Rh(I) in the catalyst:

$$\mathbf{r} = \mathbf{k}C_{CH_3I}[Rh(I)]^2. \qquad (4)$$

The kinetic data for both the membrane and macroporous catalysts were used to calculate the rate constants according to this equation. The values, adjusted to 100°C, are summarized in Table 3, where they are compared with the value for a carbon-supported Rh complex, which was also calculated assuming the same rate equation.

The close agreement among all the rate constants is probably fortuitous, but it leads to the speculative suggestion that there may be a common mechanism of methanol carbonylation in these catalyst matrices; the mechanism (Fig. 11) may require relatively high solid-phase Rh concentrations to allow interaction of two Rh complexes with methyl iodide.

The kinetics suggest that the optimum methanol partial pressure in a fixed-bed reactor using vapor-phase reactants at 125°C might be of the order of 5 atm to give a rate independent of methanol partial pressure, whereas the carbon monoxide partial pressure would be much less [Eq. (3)]. An alternative design to achieve high methanol concentrations, which might be advantageous at higher temperatures (for which K_{CH_3OH} is expected to be greater), would be a trickle-bed reactor, and rough mass transfer calculations (*19*) suggest that a partial pressure of carbon monoxide of the order of 10 atm would be required to preclude gas–liquid mass transfer limitations on the reaction rate. This suggestion is consistent with conditions in processes employing soluble rhodium complexes (*9*),

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[5] Pittman *et al.* (*34*) concluded that the highly cross-linked macroreticular resin is capable of bonding to the rhodium complex through only one phosphine ligand; loss of rhodium might therefore be prevented by use of a more flexible polymer or by use of diphosphine ligands.

for which the carbon monoxide partial pressure might have been chosen to ensure the absence of mass transfer influence.

The foregoing estimates are rough because the temperature variation of the parameters in Eq. (3) is unknown and because catalyst aging is not well characterized.

ACKNOWLEDGMENTS

D. J. Morgan and G. W. Miller performed the preliminary experiments from which this research was formulated. The work was supported by the National Science Foundation.

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