New Oxo Chemistry Via Solid Polymer–Cobalt Carbonyl Complexes

A. J. MOFFAT

Phillips Petroleum Company, Bartlesville, Oklahoma 74003

Solid poly-2-vinylpyridine polymers were used to complex cobalt carbonyls to form a unique hydroformylation system. This solid, polymer–cobalt carbonyl system serves as a catalyst reservoir which reversibly and rapidly releases enough cobalt carbonyl to override and/or destroy olefin feed poisons and to cause the homogeneous oxo reaction to proceed at a predictable rate without an induction period. Hence, oxo reactions may be run on either pure or impure olefin feeds at low cobalt concentrations. The soluble catalyst concentration was found to be a function of temperature and the polymer cobalt carbonyl concentration. Thirty to 40% of the nitrogen atoms within the polymer matrix are available for complexing cobalt carbonyls in a H_2/CO atmosphere

INTRODUCTION

The complexing of cobalt carbonyls with various ligands to form oxo catalysts is well known (1). Even the soluble pyridine and phosphine (2, 3) complexes are oxo catalysts at elevated temperatures. However, no information is available on the behavior of insoluble, polymeric ligands as oxo catalyst modifiers or cobalt carbonyl complexing agents. The purpose of this research was to see what effect solid poly-2-vinylpyridine (PVP) has on oxo chemistry and perhaps to find a heterogeneous, oxo catalyst system.

A polymeric ligand–cobalt carbonyl complex can be markedly altered via cross-linking. For example, with little or no cross-linking of the polymer phase, the complex may be soluble under oxo reaction conditions. With a high degree of cross-linking, very little cobalt carbonyl is absorbed by the polymer phase. At intermediate degrees of cross-linking, the polymer phase can swell (yet be insoluble) and thus make a high percentage of nitrogen sites within the polymer matrix available for complexing cobalt carbonyl. Hence, PVP polymers with 4–8% divinyl benzene (cross-linking agent) were used in this study to provide the needed ligand, insolubility, and swelling characteristics.

METHODS

Runs were made in a stirred 500-ml autoclave which had been equipped for sample introduction and removable and gas circulation as shown in Fig. 1. This apparatus was used to test the PVP–cobalt carbonyl catalyst for heterogeneous catalytic activity by comparing conversions as a function
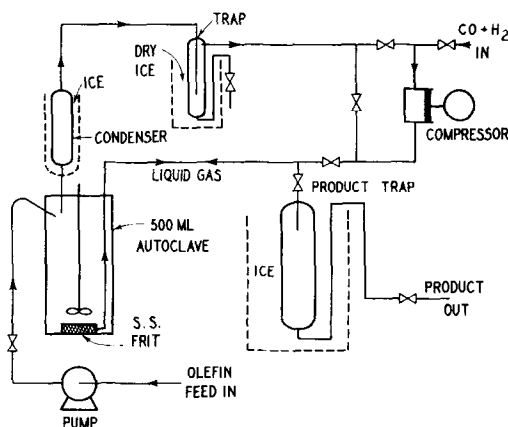

FIG. 1. Apparatus for studying the homogeneous or heterogeneous character of the PVP–HCo(CO)₄ catalyst system.
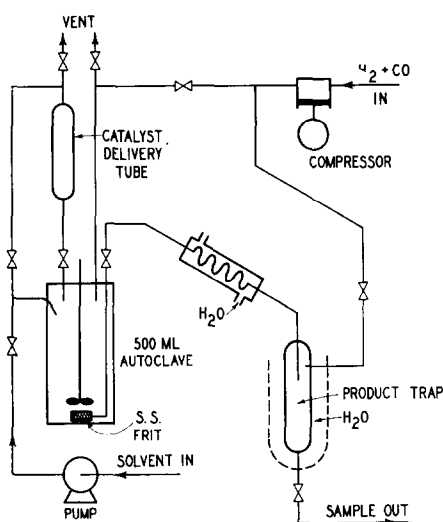
FIG. 2. Apparatus for PVP–HCo(CO)₄ equilibrium studies.

of olefin feed volume at constant residence or reaction times. Phillips pure grade hexene-2 diluted to 50 vol % with pure grade cyclohexane was used as the feed in these runs.

Another series of runs were made using Phillips pure grade n-heptane to extract cobalt carbonyl from the PVP–cobalt carbonyl solid in a CO/H₂ atmosphere at various temperatures. The purpose was to measure equilibrium constants and nitrogen site availability. These equilibrium studies were made in the 500-ml autoclave equipped as shown in Fig. 2. n-Heptane was used in place of an olefin feed to avoid a reactive and hence a constantly changing system. All oxo reactions and equilibrium studies were done in a 1:1 H₂/CO atmosphere at 2000–3000 psig except as noted.

Cobalt analyses were done following a procedure similar to that of Singlier and Reckova (4). A 1- to 20-ml sample was mixed with 10 ml of diisopropyl ether and extracted with 25 ml of 8 N HCl. The aqueous phase was then analyzed for cobalt using a Beckmann DB spectrophotometer to measure the 680-mμ absorption which is a function of cobalt concentration.

Dicobalt octacarbonyl (from Alpha Inorganics) was dissolved in benzene under a CO atmosphere at room temperature. The resultant catalyst solution was filtered and stored in a capped pop bottle under a CO atmosphere.

PVP polymers were prepared by the copolymerization of 2-vinylpyridine with 4–8 wt % divinyl benzene in a precipitation polymerization system in aqueous methanol using AIBN as an initiator.* A 2-vinylpyridine–divinyl benzene–styrene polymer was also prepared and used in this study.

Oxo product analyses were done via glc (thermal conductivity detector) using a 5-ft × ¼-in. column packed with 16.6% Carbowax 20M on 60–80 mesh, acid washed Chromosorb P. Helium was used as a carrier gas.

RESULTS AND DISCUSSION

Several runs by the author and others in our laboratory demonstrated that oxo reactions can be carried out at reasonable rates using the PVP–cobalt carbonyl catalyst system at temperatures from 300 to 400°F to obtain oxo products containing less than 10 ppm cobalt. In each of these initial runs the product was separated from the PVP–cobalt carbonyl catalyst after the reactor had been cooled.

Percentage conversion per unit time and hence reaction rate for a heterogeneous reaction is inversely proportional to the hourly space velocity in a flow reactor. This same relationship should be true for a stirred, batch reactor with a constant catalyst weight and reaction time. Thus the reaction rate, $-dA/dt$ (if the reaction is heterogeneous) should be inversely proportional to the feed volume, V, and proportional to some power, n, of the olefin concentration A.

$$-\frac{d(A)}{dt} = \frac{k_2}{V} (A)^n. \qquad (1)$$

If the reaction is homogeneous and is catalyzed by soluble cobalt carbonyl of low concentration, then there would be no significant change in the solid polymer cobalt concentration and the reaction rate should be

$$-\frac{d(A)}{dt} = k'_1[Co](A) = k_1(A), \qquad (2)$$

TABLE 1

THE EFFECT OF FEED VOLUME ON REACTION RATE AT 330–335°F USING THE PVP–HCo(CO)$_4$
CATALYST SYSTEM

Run no.[a]	Feed	Feed vol (ml)	Conversion (%)	$t_{1/2}$ (min)	Decobalting Temp (°F)	Decobalting Time (min)	Soluble cobalt (ppm)[b]	Reaction time (min)
1[c]	50% Hexene-2	200	51	44	200	15	14	45
2		100	50	45	170	75	7	45
3		50	47	49	200	25	8	45
4		50	44	54	200	25	8	45
5		100	44	54	190	25	7	45
6		200	52	42	170	35	26	45
7		200	50	45	250	15	11	45
8		100	50	45	235	15	13	45
9		50	51	44	250	20	10	45
10		50	51	44	250	20	10	45
11		100	49	47	235	15	14	45
12		200	55	39	240	15	17	45
13	Hexene-2	200	56	38	250	90	8	45
14		100	53	41	250	15	14	45
15		100	55	26	250	30	10	30
16[c]		100	41	59	250	90	9	45

[a] H$_2$/CO = 1.0 for runs 1 through 14; Run 15, H$_2$/CO = 2.0; Run 16, H$_2$/CO = 0.5.

[b] Liquid phase cobalt concentration after decobalting at reduced temperature.

[c] The initial polymer cobalt concentration declined from 5.86 mmoles/10 g of PVP-4 to 5.52 mmoles/10 g at the end of run 16.

which is independent of feed volume. The results of a series of runs at constant temperature and reaction time obtained by varying feed volume are shown in Table 1. A 50% 2-hexane-cyclohexane feed was used to aid in temperature control since the oxo reaction is very exothermic. Although temperature control was not as good, the neat hexene-2 runs gave substantially the same results. The reaction was first order with respect to olefin concentration and within experimental error was independent of feed volume. Thus, it was concluded that the reaction is catalyzed by soluble cobalt carbonyl which is removed reversibly from the solid PVP–cobalt carbonyl polymer. A drop in temperature from the 330–335°F reaction temperature to 170–250°F caused most of the soluble cobalt to be redeposited back in the polymer matrix leaving ∼10 ppm of soluble cobalt in the product. The soluble cobalt concentration at reaction temperature was approximately 100 ppm. When runs were made with 50, 100, and 150 ppm cobalt (without PVP), the rates were comparable to those where the polymer–catalyst released cobalt in the same concentration range.

In the absence of H$_2$ (i.e., in a CO atmosphere) only a limited amount of cobalt is absorbed by the polymer phase. Thus the HCo(CO)$_4$ species is the one which is preferentially absorbed into the polymer matrix.

A series of runs were made using the apparatus shown in Fig. 2 to establish the equilibrium relationships which exist between soluble and absorbed cobalt. It was necessary to use a nonreactive solvent since use of an olefin feed in a H$_2$/CO atmosphere results in a continuously changing reaction media. The principal equilibrium which seems to control the liquid phase cobalt concentration is:
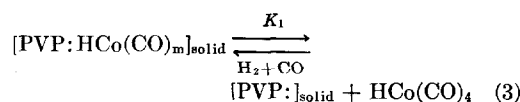
$$[\text{PVP}:\text{HCo(CO)}_m]_{\text{solid}} \underset{\text{H}_2+\text{CO}}{\overset{K_1}{\rightleftharpoons}} [\text{PVP}:]_{\text{solid}} + \text{HCo(CO)}_4 \quad (3)$$

TABLE 2

THE EQUILIBRIUM BETWEEN HCo(CO)₄ AND PVP-4 AT VARIOUS TEMPERATURES

Sample no.	$(X/V)^a$		A^b (mmoles)	$(A - X)^c$ (mmoles)	Temp (°F)	Equilibration Time (hr)	$K_1 \times 10^3$ (mmoles/ ml)	$K_1 \times 10^3$ av
	(mmoles/ml)	(ppm)						
1	0.00178	153	5.85	5.66	315	3	2.62	
2	0.00162	141	5.71	5.50	318	5	2.51	2.6
3	0.00158	137	5.56	5.36	320	2	2.55	
4	0.00249	216	5.42	5.10	355	2	4.35	
5	0.00228	198	5.19	4.90	357	2	4.23	4.2
6	0.00204	177	4.95	4.69	358	5	4.05	
7	0.00273	237	4.78	4.43	376	3	5.90	
8	0.00220	191	4.53	4.25	375	2	5.05	5.5
9	0.00220	191	4.32	4.04	375	3	5.42	
10	0.00248	215	4.12	3.80	400	4	6.64	
11	0.00175	152	3.92	3.73	407	4	4.82	
12	0.00119	103	3.81	3.66	405	6	3.36	
13	0.0086	75	3.70	3.58	400	6	2.52	
14	0.00073	63	3.62	3.53	350		2.17	

^{a} Room temperature cobalt concentrations.

^{b} Total cobalt in both phases.

^{c} Cobalt deposited on 5 g of polymer.

The equilibrium constant for this reaction is:

$$K_1 = \frac{(X/V)[P - (A - X)]}{(A - X)}, \qquad (4)$$

where (X/V) is the liquid phase cobalt concentration (mmoles/ml); $(A - X)$ is the polymer phase cobalt concentration (mmoles/5 g of polymer); $[P - (A - X)]$ is the concentration of available but unoccupied sites (mmoles/5 g of polymer); V is the liquid phase volume (ml) and A is the total (mmoles) cobalt in both liquid and solid phases. P, the concentration of available sites was determined by using high cobalt carbonyl concentrations and loading the polymer with as much cobalt as could be absorbed (see Fig. 3). P values were calculated using Eq. (4). The PVP-4 polymer was found to contain 14 mmoles of available nitrogen sites/5 g of polymer. Hence, 31% of all nitrogen in the polymer is available for complexing cobalt carbonyls in a H_2–CO atmosphere. The values for K_1 which were calculated at these high cobalt concentrations varied between 2 and 5 $\times$ 10^{-3} moles/liter.

The data in Table 2 was collected in the low cobalt concentration range to see the effect of temperature on the equilibrium constant, K_1. These results seem to be consistent with the expected behavior described by Eqs. (3) and (4). For example, using $K_1 = 4.2 \times 10^{-3}$ (from Table 2) and $P =$

TABLE 3

APPROXIMATE VALUES OF K_1 AND P FOR PVP POLYMERS AT VARIOUS TEMPERATURES

Polymer	Temp (°F) (av)	P (mmoles/ 5 g)	$K_1 \times 10^3$ (mmoles/ ml)
PVP-4	318	—	2.6^a
	357	14.0	4.2^a
	375	—	5.5^a
PVP-6	300	14.3	1.3^b
	355	15.9	4.9^b
PVP-6-18.8S^c	350	13.3	5.6^b

^{a} Measured in the low cobalt range $A = 3$ to 6 mmoles/5 g of polymer.

^{b} Measured in the high cobalt range $A = 12$ to 24 mmoles/5 g of polymer.

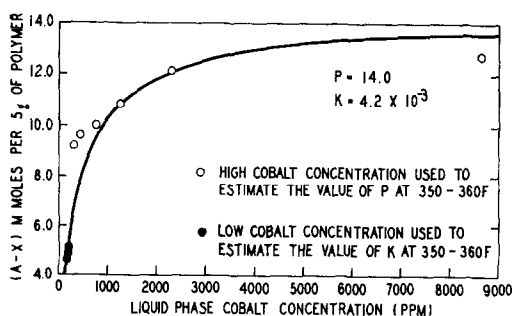^{c} This polymer was prepared from 18.8% styrene, 6% divinyl benzene, and 75% 2-vinylpyridine.

FIG. 3. The Cobalt–PVP-4 equilibria at 350—360°F in a H_2/CO atmosphere ($\sim$2500 psig).

14.0 for the PVP-4 polymers at 350–360°F, the curve shown in Fig. 3 was obtained. At 400°F and above, the value of K_1 dropped from $>6.64 \times 10^{-3}$ to 2.52×10^{-3} during a 20-hr test period. The appearance of the $HCo(CO)_4$–PVP-4 catalyst was not visibly different when compared with those used at lower temperatures, and the sample readily picked up additional $HCo(CO)_4$ which was introduced into the system. It is not known whether the polymer was slowly degraded above 400°F or whether there was insufficient CO partial pressure ($CO/H_2 = 1.0$ at 2500 psig) to prevent cobalt carbonyl degradation.

Table 3 compares P and K_1 values for three different PVP polymers as a function of temperature. These polymers are comparable in most respects except for PVP-6-18.8S (18.8% styrene) where P is lower (as expected) and K_1 is higher.

The rates of cobalt release from and uptake by the polymer matrix are important considerations. Any equilibrium shifts caused by catalyst poisons, temperature changes, etc., should occur rapidly for the system to function properly. At 300°F, starting with 15.9 mmoles of cobalt and 5 g of PVP-6 polymer, it took less than 4 min to reach equilibrium (i.e., to add 12 mmoles of cobalt to the polymer). Rapid temperature changes from 350–370 to 250–260°F showed that the equilibrium concentrations were reestablished in 1 to 3 min. When n-heptane was pumped into an autoclave containing 13 mmoles of cobalt on 5 g of PVP-6 polymer at 375°F, equilibration occurred before the first sample was removed at 1.5 min. Equilibration rates appear to be

fast enough to meet any demands which catalyst poisons, etc., may place on the polymer–catalyst system.

An unusual characteristic of the polymer–catalyst is its ability to override and destroy catalyst poisons. Several refinery streams of questionable composition (made up of from 30 to 70% olefins) under normal oxo conditions required from 500 to 1500 ppm cobalt just to initiate an oxo reaction and then only after an induction period. Apparently enough cobalt carbonyl must be added to exceed that which is temporarily complexed by dienes or other catalyst poisons. After the oxo reaction begins, these catalyst poisons are destroyed (at least in part) perhaps via hydrogenation thereby releasing cobalt carbonyl which further accelerates the reaction (sometimes beyond control). When the polymer–cobalt catalyst system is used on these impure feeds, little or no induction period is observed and the reaction rates are as fast as those expected for cleaner feeds of the same olefin types. The polymer–catalyst seems to function as a catalyst reservoir, releasing enough catalyst to override poisons and yet maintain the equilibrium $HCo(CO)_4$ concentration which is necessary for the oxo reaction. As catalyst poisons are destroyed, the excess $HCo(CO)_4$ is redeposited in the polymer matrix. In all these runs, the polymer cobalt concentration was sufficient to provide several thousand ppm Co, if needed. However, the liquid phase cobalt concen-
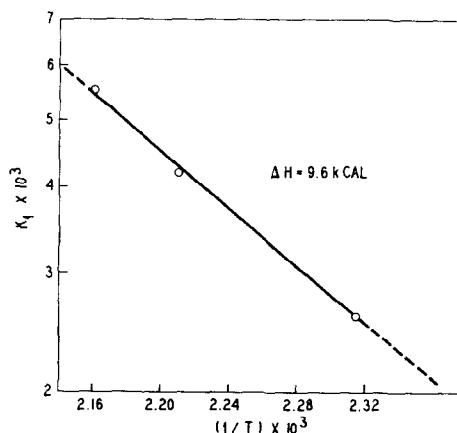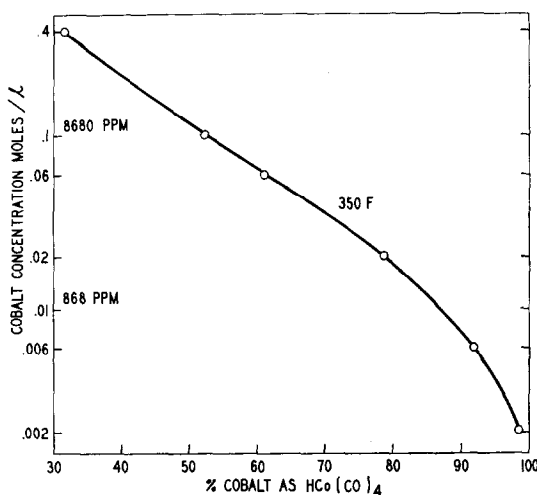

FIG. 4. The temperature dependence of K_1.

FIG. 5. The percentage cobalt in the HCo(CO)₄ form at 350°F and 2500 psig using a 1:1 ratio of H₂ and CO.

tration at reaction temperatures usually fell in the 100 to 300 ppm range.

Kinetic equations describing oxo reaction rates at constant H_2/CO ratios show the reaction to be first order with respect to both olefin and cobalt carbonyl concentrations (5) as shown in Eq. (2). When the solid $PVP-HCo(CO)_4$ catalyst is used, the soluble cobalt carbonyl concentration is:

$$[Co] = \frac{X}{V} = \frac{K_1(A - X)}{[P - (A - X)]} = \frac{K_1\theta}{(1 - \theta)}, \quad (5)$$

and the reaction rate at constant H_2/CO ratios is described by:

$$-\frac{d(A)}{dt} = k'_1 \frac{K_1\theta}{(1 - \theta)} (A), \quad (6)$$

where θ is the fraction of available nitrogen sites which are complexed with cobalt carbonyl and $(1 - \theta)$ represents the fraction of available nitrogen sites which are unoccupied. Hence, oxo reaction rates, using the polymer catalyst system, are controlled by the temperature dependent K_1 (see Fig. 4) and θ.

Some error is introduced by using the simplified model depicted by Eqs. (3) and (4) because of the equilibrium between $HCo(CO)_4$ and $Co_2(CO)_8$ in a H_2/CO atmosphere:

$$Co_2(CO)_8 + H_2 \overset{K}{\rightleftharpoons} 2HCo(CO)_4. \quad (7)$$

Gankin and co-workers (6) use Eq. (8) to describe K as a function of temperature.

$$\log K = 1.365 - \frac{1900}{T}, \quad (8)$$

where T is °K. Figure 5 shows a plot of percentage cobalt as $HCo(CO)_4$ vs total cobalt at 350°F. At cobalt concentrations below 700 ppm, >90% of the cobalt is in the $HCo(CO)_4$ form, while at concentrations greater than 8700 ppm less than 50% of the cobalt is in the $HCo(CO)_4$ form. Since the range of principal interest is the one below 700 ppm cobalt where $HCo(CO)_4$ is the dominant cobalt species and PVP has a limited capacity for $Co_2(CO)_8$, the principal equilibrium which controls the liquid phase cobalt concentration is described by Eqs. (3) and (4).

In the high cobalt concentration studies which were used mainly to estimate P, the value of θ is rather insensitive to the total liquid phase cobalt concentration, and Eq. (4) was used to estimate P values. However, in this high concentration range, the K_1 values may be unreliable unless the equilibrium between $Co_2(CO)_8$ and $HCo(CO)_4$ is taken into consideration.

It is concluded that the solid $PVP-HCo(CO)_4$ catalyst serves as a catalyst reservoir which reversibly and rapidly releases enough $HCo(CO)_4$ to override and destroy catalyst poisons and to cause a homogeneous oxo reaction to proceed at a predictable rate. This system also allows oxo reactions to be carried out using low cobalt concentrations which should simplify catalyst recovery and recycle problems.

ACKNOWLEDGMENTS

REFERENCES

1. Roos, L., AND Orchin, M., J. Org. Chem. **31**, 3015 (1966).

2. SLAUGH, L. H., *U. S. Pat.* 3,168,553 (1965); *U. S. Pat.* 3,231,621 (1966).

3. SLAUGH, L. H., AND MULLINEAUX, R. D., *U. S. Pat.* 3,239,566 (1966); *U. S. Pat.* 3,239,569 (1966); *U. S. Pat.* 3,239,570 (1966); *U. S. Pat.* 3,239,571 (1966).

4. SINGLIER, M., AND RECKOVA, G., *Chem. Prum.* 16(19), 535 (1966).

5. FERGUSON, G. V., *Chem. Ind. (London)* (Mar. 13) 1965, 451–456.

6. GANKIN, Y. V., *et al.*, *Zh. Fiz Khim* 40(1), 215 (1966).