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The Use of Solid Polymeric Ligands in a New Oxo Catalyst Recovery and Recycle System

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Solid, poly-2-vinylpyridine polymers are used to complex cobalt carbonyls in a unique and reversible way, which provides the basis for a new oxo catalyst recovery and recycle system. In a hydrogen–carbon monoxide atmosphere, both the $HCo(CO)_4$ and $Co_2(CO)_8$ cobalt species compete for sites within the polymer matrix. However, $Co_2(CO)_8$ is absorbed slowly and to a limited extent while $HCo(CO)_4$ is absorbed rapidly and to a much greater extent. In a carbon monoxide atmosphere (without hydrogen), the absorbed $HCo(CO)_4$ is rapidly released and converted to $Co_2(CO)_8$ which can be carried back into the oxo reaction zone by an olefin feed. Thus, cobalt carbonyls are either absorbed by or released from the solid polymer phase depending only on the presence of absence of hydrogen. This recycle system is one which carries the *active* catalyst through the cycle without consuming chemical reagents or producing unwanted by-products.

INTRODUCTION

A major problem in oxo process chemistry is cobalt recovery and recycle. If the product is not decobalted before the hydrogenation step, cobalt deposits on the hydrogenation catalyst, in heat exchangers, plugs lines, etc. Several methods have been devised for cobalt removal and recycle (*1*). However, most of these methods are expensive, laborious, and generally not too efficient.

Some of the known recovery and recycle schemes include (a) the metal cycle, (b) the oil-soluble organic salt cycle, (c) the water-soluble organic salt cycle, (d) the inorganic salt cycle, and (e) the anionic transfer cycle which have been compared by Lemke (*2*). The anionic transfer cycle has a marked advantage in that the anionic $^-Co(CO)_4$ is not destroyed in the catalyst cycle. The product is decobalted by a carbonate solution. The active catalyst is regenerated with sulfuric acid and carried back into the reaction zone in its active form, thus avoiding an induction period.

$$2HCo(CO)_4 + Na_2CO_3 \rightarrow 2NaCo(CO)_4 + CO_2 + H_2O, \quad (1)$$

$$2NaCo(CO)_4 + H_2SO_4 \rightarrow 2HCo(CO)_4 + Na_2SO_4. \quad (2)$$

The net reaction for this cycle is:

$$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 + H_2O. \quad (3)$$

The $NaCo(CO)_4$ salt is water soluble and stable under recovery conditions. The anionic transfer cycle is perhaps the best all-around cobalt recycling method of those mentioned above (*2*).

All of these catalyst cycles, however, are cumbersome to handle, consume chemicals and produce unwanted by-products. The best catalyst cycle would be one which carries *active* catalyst in the simplest way through the cycle without consuming chemical reagents or producing unwanted by-products. This paper describes just such a process which uses polyvinylpyridine (PVP) polymers to complex cobalt carbonyls in a unique and reversible way.

METHODS

All runs were made in a 500-ml autoclave which was equipped for sample introduction and removal as shown in Fig. 1. Usually 100–200 ml of solvent, $Co_2(CO)_8$ in benzene and 5 g of polymer were initially charged into the autoclave. Liquid phase samples were removed for analyses. The polymer cobalt content was calculated by difference except for periodic checks at the end of a run when the solid polymer phase was removed from the autoclave and analyzed as described below. *n*-Heptane was used as the solvent in most of the decobalting runs (under a 1:1 H_2/CO atmosphere) to avoid a reactive and hence a constantly changing system. However, a multitude of runs have been made in which oxo product phases were decobalted equally well (*3*).

Catalyst removal from the polymer phase was usually done using hexene-2 as the solvent in a carbon monoxide atmosphere. Hexene-2 was introduced after traces of hydrogen had been flushed from the autoclave with carbon monoxide at room temperature. The polymer–catalyst mixture under a carbon monoxide atmosphere was then heated to the desired temperature. In some runs hexene-2 was introduced before the heating step. In others, the olefin was pumped into the autoclave after the desired temperature was reached. In several runs the polymer–catalyst bed was extracted by a series of olefin additions and removals. All runs were at ~2500 psig except as noted.

Cobalt analyses were done using 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 Beckman DB spectrophotometer to measure the 680 mμ absorption which is a function of cobalt concentration. Cobalt analyses were also done on 10–30-mg samples of the solid polymer–catalyst complex by using 10 ml of diisopropyl ether plus 25 ml of 8 *N* HCl to extract cobalt from the polymer matrix. Cobalt carbonyls deposited in the polymer under a H_2/CO atmosphere were readily removed by this ether–HCl extraction. Cobalt carbonyl deposited in the polymer phase under a carbon monoxide atmosphere was not extracted by the ether–HCl treatment.

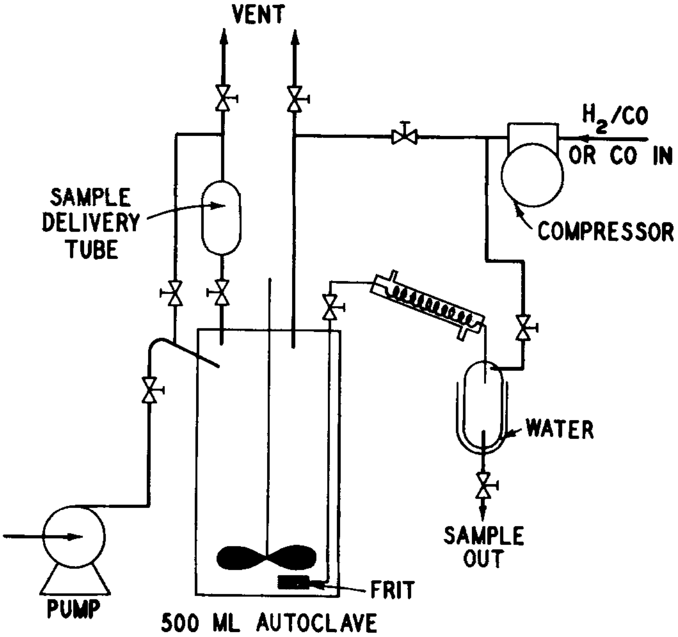


FIG. 1. Apparatus used for cobalt recovery and recycle studies.

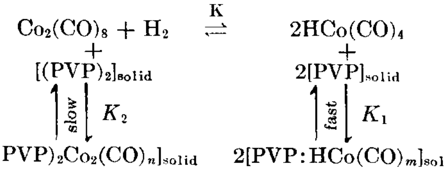
Hexene-2 and *n*-heptane were Phillips pure grade reagents. Dicobalt octacarbonyl (from Alpha Inorganics) was dissolved in benzene under a carbon monoxide atmosphere at room temperature. The resultant catalyst solution was filtered and stored in a capped pop bottle under a carbon monoxide atmosphere. 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.

RESULTS AND DISCUSSION

In a hydrogen–carbon monoxide atmosphere, cobalt carbonyl is rapidly deposited in the solid PVP polymer (*3*). However, in a carbon monoxide atmosphere dicobalt octacarbonyl is only slowly absorbed and the maximum amount of cobalt absorbed is considerably less than when hydrogen is present. These results when coupled with the equilibrium which normally exists between $Co_2(CO)_8$ and $HCo(CO)_4$ (*5*),

$$Co_2(CO)_8 + H_2 \overset{K}{\rightleftharpoons} 2HCo(CO)_4, \tag{4}$$

indicate that the $HCo(CO)_4$ species is the one preferred by the polymer phase. The fact that the absorbed $Co_2(CO)_8$ species is difficult to remove [an HCl–ether media fails to extract any of the dicobalt species from the polymer but readily extracts the $HCo(CO)_4$ species] shows that perhaps the dimer cobalt species may be bound to more than one nitrogen site within the polymer matrix, while the $HCo(CO)_4$ species may require only one of the nitrogen sites. These observations can be illustrated by the following overall equation which seems to govern cobalt carbonyl deposition and release on the solid PVP polymer:



$$\begin{array}{ccc} Co_2(CO)_8 + H_2 & \overset{K}{\rightleftharpoons} & 2HCo(CO)_4 \\ + & & + \\ [(PVP)_2]_{solid} & & 2[PVP]_{solid} \\ \Big\updownarrow \text{slow} \; K_2 & & \Big\updownarrow \text{fast} \; K_1 \\ [(PVP)_2Co_2(CO)_n]_{solid} & & 2[PVP{:}HCo(CO)_m]_{solid}, \end{array} \tag{5}$$

where both cobalt species compete for sites in the polymer matrix. The right hand side of Eq. (5) describes the principal mechanism for decobalting a product stream. This polymer is an effective decobalting system because it has sufficient nitrogen sites to remove a reasonable quantity of cobalt and a large enough equilibrium constant, K_1, to lower the liquid phase cobalt concentration to the desired ppm level. The decobalting of a product stream must, of course, be done in a H_2/CO atmosphere. If hydrogen is removed from the system (i.e., use only a CO atmosphere), the absorbed cobalt hydrocarbonyl is released by the polymer and converted to $Co_2(CO)_8$ for which the polymer has a limited capacity. Hence, the presence or absence of H_2 determines if the cobalt is absorbed by or released from the solid polymer phase.

Equation (5) indicates that a rather complex relationship exists among the various absorbed and liquid phase cobalt species. The equilibrium constant, K, for Eq. (4) may be written as

$$K = \frac{(y/V)^2}{(z/V)P_{H_2}} \tag{6}$$

where (y/V) and (z/V) are the liquid phase $HCo(CO)_4$ and $Co_2(CO)_8$ concentrations, respectively, and P_{H_2} is the pressure of hydrogen. Langmuir type absorption isotherms for $HCo(CO)_4$ and $Co_2(CO)_8$ may be written as

$$(b - y) = \frac{P_1K_1(y/V)}{1 + K_1(y/V)}, \tag{7}$$

and

$$(c - z) = \frac{P_2K_2(z/V)}{1 + K_2(z/V)}, \tag{8}$$

where $(b - y)$ is the polymer phase $HCo(CO)_4$ concentration in mmoles/5 g of polymer, b is the total mmoles of $HCo(CO)_4$ in both liquid and polymer phases, P_1 represents the total mmoles of sites per 5 g of polymer which will absorb $HCo(CO)_4$, $(c - z)$ is the polymer phase $Co_2(CO)_8$ concentration in mmoles/5 g of polymer, c is the total mmoles of $Co_2(CO)_8$ in both phases and P_2 represents the total mmoles of sites per 5 g of polymer which will absorb $Co_2(CO)_8$.

In a carbon monoxide atmosphere (without hydrogen) the only cobalt species available for absorption into the polymer phase is $Co_2(CO)_8$ and an absorption isotherm similar to that described by Eq. (8) can be used to treat the data.

In a hydrogen–carbon monoxide atmosphere where both $HCo(CO)_4$ and $Co_2(CO)_8$ species exist in equilibrium with each other and in equilibrium with the polymer phase, a precise quantitative treatment of the data is difficult to obtain. The total amount of cobalt $(a - x)$ which may be absorbed by the polymer phase is

$$(a - x) = (b - y) + 2(c - z) = \frac{P_1K_1(y/V)}{1 + K_1(y/V)} + \frac{2P_2K_2(z/V)}{1 + K_2(z/V)}. \quad (9)$$

Cobalt analyses made on the liquid phase were not designed to differentiate between $HCo(CO)_4$ and $Co_2(CO)_8$ but to measure the total liquid phase cobalt concentration. To avoid cobalt loss via deposition in lines, etc., the liquid samples were withdrawn and cooled to room temperature while under a H_2/CO atmosphere. Hence the $HCo(CO_4/Co_2(CO)_8$ ratio could change after the sample was isolated from the polymer phase. Also, dimer sites can probably be used by both $HCo(CO_4)$ and $Co_2(CO)_8$ species whereas most monomer sites will not accommodate the $Co_2(CO)_8$ species. Thus the evaluation of P_1 and P_2 in a H_2/CO atmosphere would be rather complex. To provide a practical (if not precise) way to handle the data, the total mmoles of cobalt absorbed (both species) per 5 g of polymer was assumed to be related to the total mmoles of available sites, P_T, a gross equilibrium constant, K_T, and the experimentally measured liquid phase cobalt concentration (x/V) by:

$$(a - x) = (b - y) + 2(c - z) = \frac{K_TP_T(x/V)}{1 + K_T(x/V)}. \quad (10)$$

In a H_2/CO atmosphere at low cobalt concentrations where c and z are small compared to b and y, Eq. (10) reverts to Eq. (7). Also in a carbon monoxide atmosphere (no hydrogen) where b and y equal zero, Eq. (10) becomes identical to Eq. (8).

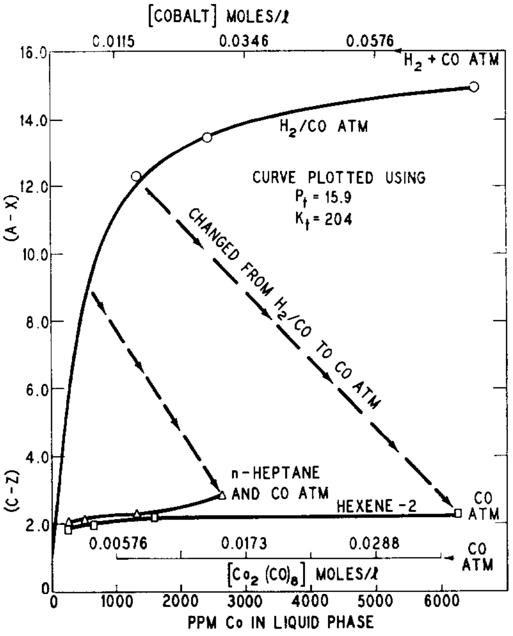


FIG. 2. Cobalt deposition and removal characteristics for PVP-6 at 350°F; comparison of hexene-2 with n-heptane in the cobalt removal step.

In Fig. 2, the three data points obtained at 350°F in a H_2/CO atmosphere were used to calculate K_t and P_t from which the curve was plotted. This plot shows that when $(a - x)$ is 6 mmoles/5 g of polymer, the liquid phase cobalt concentration will be 200–300 ppm, which is too high to be practical in decobalting a hydrocarbon feed. Hence a lower temperature must be used in the decobalting step. Hexene-2 and n-heptane were compared as solvents in the cobalt release step (CO atmosphere) shown in Fig. 2. Both solvents were comparable in their ability to remove cobalt from the polymer matrix except that hexene-2 appears to do so more rapidly.

A comparison of Figs. 2, 3, and 4 shows the effect of lowering the temperature from ~350 to ~300 to ~250°F, respectively. The two cobalt deposition cycles in Fig. 4 show that from 11 to 12 mmoles (0.65 to 0.71 g) of cobalt can be deposited in 5 g of PVP-6 (6% divinyl benzene) at 250°F

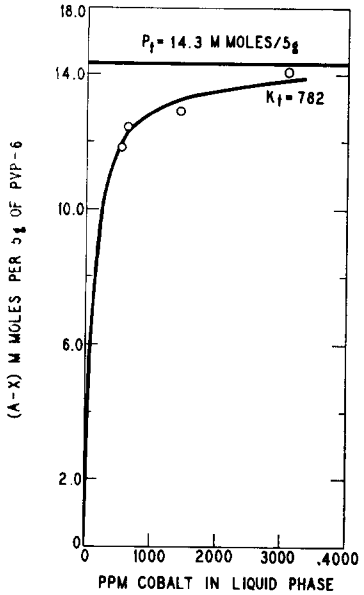


FIG. 3. mmoles of sites in PVP-6 polymer at 300–310°F and 2500 psig in a H_2/CO atmosphere.

before the liquid phase concentration exceeds 50 ppm. The cobalt release step at 250°F is quite similar to the 350°F release step except that the polymer retains a little more cobalt at 250°F. In the second cobalt release step shown in Fig. 4, a pressure drop and a 10–15% conversion to aldehyde products were noted. This behavior was caused by a trace of H_2 being present in the system. A new source of CO was used with the effect noted in Fig. 4. Thus, H_2 in the cobalt release step has an effect on cobalt removal. At higher temperatures, however, traces of hydrogen would be used up rapidly via reaction with the olefin feed and have little overall effect upon the cobalt release step.

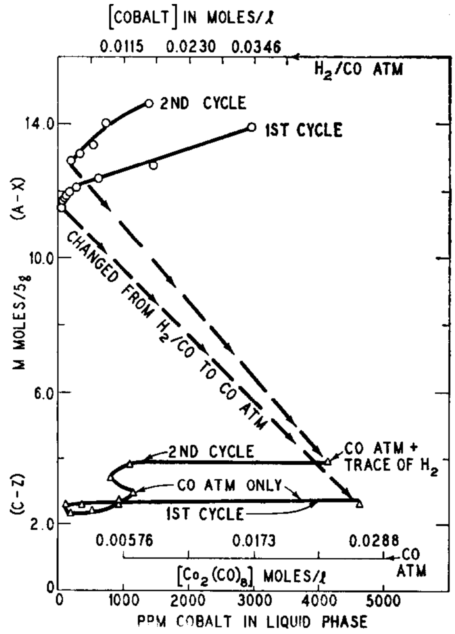


FIG. 4. Cobalt deposition and removal using PVP-6 at 250–260°F and 2500 psig; both runs 1 and 2 were made on the same 5-g polymer sample.

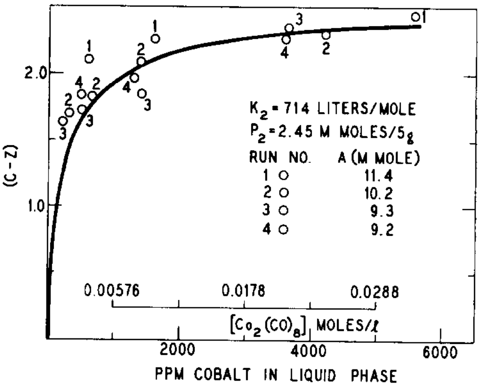


FIG. 5. The $Co_2(CO)_8$ and PVP-4 equilibria in a CO atmosphere at 350–360°F and 2300–2700 psig; the first three data points from run 2 were used for calculating K_2 and P_2 and for plotting the curve.

Figure 5 summarizes four recycle runs which were made on one 5-g sample of PVP-4 (4% divinyl benzene) at 350°F. The polymer appearance after these four cycles was no different than after single cycles and no significant differences were noted among the four runs. In each cycle a total of 9–11 mmoles of cobalt was deposited on the polymer at 350°F from a *n*-heptane solvent in a H_2/CO atmosphere. After cobalt deposition, the autoclave was cooled and the solvent and gaseous atmosphere were replaced by hexene-2 and carbon monoxide. The autoclave was then heated to 350°F where the data shown in Fig. 5 were collected by repeated extractions with hexene-2 for each run. The cobalt release step of each cycle brought the cobalt level back to the same base line of approximately 2 mmoles of $Co_2(CO)_8$/5 g of

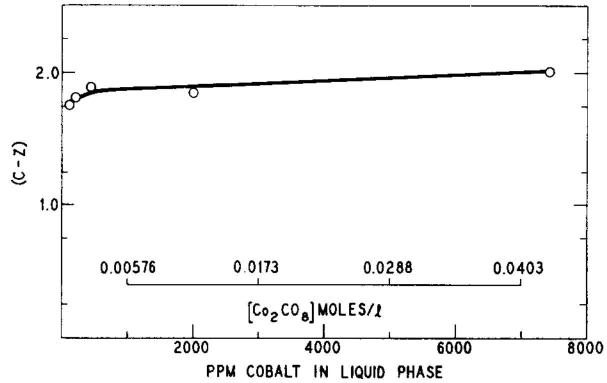


FIG. 6. Equilibration of PVP-4 with $Co_2(CO)_8$ in a CO atmosphere at 350–360°F and 2500–3000 psig using hexene-2 as a solvent.

polymer. There was no evidence of polymer degradation at the end of the four cycles.

In all the cobalt release steps shown in Figs. 2, 4, and 5, the cobalt was initially deposited in the polymer from a H_2/CO atmosphere. In the run shown in Fig. 6, $Co_2(CO)_8$ was equilibrated with PVP-4 in a CO atmosphere to see if $Co_2(CO)_8$ could be deposited directly in the polymer without first going through the $HCo(CO)_4$ deposition step. A comparison of Figs. 5 and 6 shows that in both cases the polymer will accommodate $Co_2(CO)_8$ to about the same extent and is independent of the initial method of deposition.

For the PVP–cobalt recycle system to be commercially acceptable, the rates of cobalt deposition and release must be reasonably fast. Table 1 shows that when 15.9 mmoles of cobalt is equilibrated with the 15.9 mmoles of sites on 5 g of PVP-6, equilibrium is reached in less than 5 min at 300°F. Table 2 shows that at 250°F, PVP-6 with 6.1 mmoles of cobalt/5 g will add an additional 5.8 mmoles of cobalt and reach equilibrium in approximately 20 min.

The cobalt release step in CO atmosphere was examined at 350, 295, and 250°F. At 350°F, cobalt was released and equilibrium was reached too rapidly to measure. The 295 and 250°F runs are shown in Fig. 7. These runs were made by rapidly pumping (2–4 min) 200 ml of hexene-2 into the autoclave which contained the polymer–cobalt sample at the desired temperature in a carbon monoxide atmosphere. As soon as the hexene-2 was introduced the stirrer was turned on (time zero in Fig. 7) and samples were collected at various times as noted. Figure 7 shows a semilog plot of [(a —

TABLE 1

RATE OF COBALT DEPOSITION ON 5g OF PVP-6 POLYMER AT 300°F IN A H_2/CO ATMOSPHERE AT 2500 PSIG

Time (min)	$(a - x)$ (mmoles/5 g)	a^a (mmoles)
0	0.0	15.9
1	10.5	15.9
3	11.8	15.6
5	12.2	15.5
9	12.1	15.3
25	12.1	15.1

[a] a, the total mmoles of cobalt in both phases decreases because of sample withdrawal.

TABLE 2

RATE OF DEPOSITION OF 5.8 MMOLES OF COBALT IN 5 g OF PVP-6 POLYMER WHICH INITIALLY CONTAINED 6.1 MMOLES OF DEPOSITED COBALT (250°F; 2500 PSIG; H_2/CO)

Time (min)	Cobalt ppm in Liquid Phase
0	2500 (calc)
1	1490
4	768
9	298
14	164
17	128
60	90
156	84

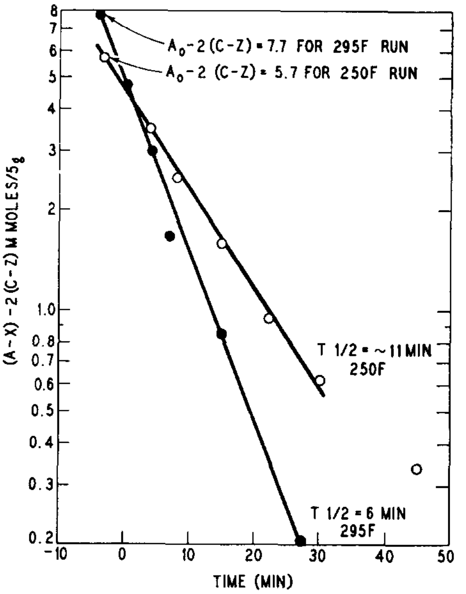


FIG. 7. Rates of cobalt carbonyl removal from PVP-6 at 250 and 295°F in a CO atmosphere at 2500 psig.

$x) - 2(c - z)]$ vs time where $[(a - x) - 2(c - z)]$ represents the mmoles of cobalt/5 g of polymer which must be released before equilibrium is attained. Since $(c - z)$ is the equilibrium $Co_2(CO)_8$ concentration in the polymer, any cobalt in excess of this amount will be released and diffuse into the liquid phase. The value of $(c - z)$ was measured by difference after the system had approached equilibrium. Figure 7 shows the rate of $Co_2(CO)_8$ removal to be first order with respect to the excess cobalt concentration in the polymer and to have $t\frac{1}{2}$ values of ~6 and 11 min at 295 and 250°F, respectively. The —4 to 0-min section of Fig. 7 shows that even during the nonstirred, 2–4-min period used for hexene-2 introduction, $Co_2(CO)_8$ was being released about as fast without stirring as with stirring. These results indicate that the rates of both cobalt deposition and release are high enough to make the PVP–cobalt carbonyl recycle system commercially practical.

There seems to be a rather complicated interrelationship between cross-linking and swell index factors, availability of sites, polymer cobalt concentration, etc. For example, with too little cross-linking the polymer may be too soluble or swell so much that the original particulate structure is broken down into a gelatinous mass and/or agglomeration occurs. With too much cross-linking, too little swelling occurs which results in poor cobalt carbonyl uptake. Most of the polymers used in this study have swell indices between 2 and 3; i.e., individual polymer particles swell from 2 to 3 times their original size under reaction conditions. PVP-6 polymer containing 18.8% styrene (PVP-6, 18.8 S) only swells slightly but readily complexes with cobalt carbonyls as shown in Fig. 8. Perhaps this is because its bulk density is approximately ½ that of other PVP polymers which were tested; hence, it already has an expanded structure with approximately 30–35% of the total nitrogen sites available for complexing cobalt carbonyls. A comparison of Figs. 2 and 8 shows that the PVP-6, 18.8 S, copolymer has a little less capacity for $HCo(CO)_4$ with a near identical $Co_2(CO)_8$ capacity.

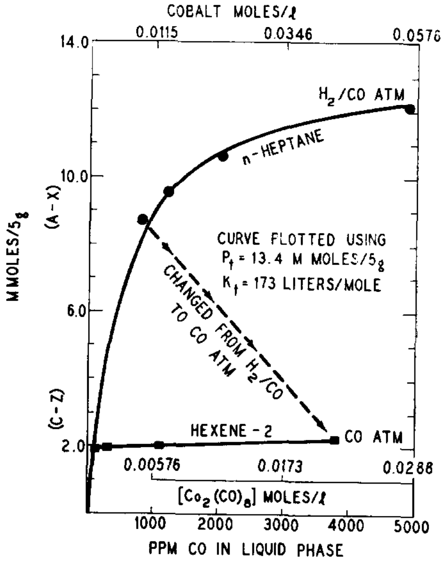


FIG. 8. Cobalt carbonyl deposition and removal characteristics for the PVP-6, 18.8S, polymer at 350–360°F.

CONCLUSIONS

Poly-2-vinylpyridine polymers and poly-2-vinylpyridine–styrene copolymers crosslinked with divinyl benzene can be used to decobalt oxo process streams and to recycle the cobalt in the octacarbonyl form. Cobalt carbonyls which are readily deposited in the solid polymer matrix using a H_2/CO atmosphere, are readily released by a CO atmosphere. This recycle system is one which carries active catalyst through the complete cycle without consuming chemical reagents or producing unwanted by-products.

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