Permselectivity of Cellulose Acetate Membranes; Separation of H_2/CO Mixtures and the Effect of Added Transition Metals

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Synopsis

Cellulose acetate membranes permit permeation of H_2 and CO_2 but are relatively impervious to CO and N_2. Permselectivity was demonstrated by effective separation of H_2 from its mixtures with CO. The presence of $RuCl_3$ in the membrane does not result in any appreciable change in permselectivity. The exposure of $RuCl_3$- and $RhCl_3$-modified membranes to H_2/CO mixtures results in the formation of $RuCl_2(CO)_x$ and $[RhCl(CO)_2]_2$, respectively. However, these complexes are not covalently anchored to the cellulose acetate matrix and apparently function only as additives that block access to the pores and channels in the cellulose acetate membrane.

INTRODUCTION

The selective permeation of gases through polymeric membranes or films is a well developed commercial reality. The selectivity is accomplished by the choice of monomer as well as by chemical alteration of the polymeric network structure, usually by crosslinking reactions.[1]

Cellulose acetate (CA) is an inexpensive, readily available versatile polymer, easily cast from tetrahydrofuran solutions into membranes with reproducible permeation properties. It has been reported that when solutions composed of the polymer and an equal weight of $Cu(NO_3)_2$ are cast into membranes, the Cu(II) becomes coordinated to the acyl carbonyl oxygen of the CA. Evidence for the presumed coordination of the Cu(II) to the CA was adduced from infrared spectral studies. These spectra showed shifts to lower frequencies of the acyl carbonyl stretching band and a high frequency shift of the ether oxygen-carbon band. The suggested coordination around the metal ion is shown in Figure 1.[2]
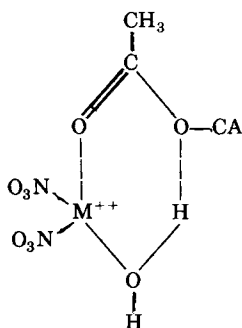

Fig. 1

The source of the water may be adventitious or may be the water associated with the hydrated metal salts.

It occurred to us that a CA membrane into which either a Ru or Rh complex had been incorporated might react selectively with carbon monoxide and that the resulting carbonyl species might show unusual permeability effects with respect to CO in gaseous mixtures containing it.

It is known, for example, that when cobalt complexes that selectively coordinate O_2 are incorporated into membranes, the transport of O_2 is facilitated and the permeate is enriched in O_2.[3]

The anchoring of catalytically active, soluble transition metal complexes of Ru or Rh to polymeric supports has become a subject of much investigation during the past decade.[4] The incentive for such research has been the expectation that the resulting catalysts would combine the advantages of a soluble catalyst (e.g., homogeneity and integrity of the catalytically active species) with those of a solid catalyst (e.g., ease of separation and recycle). The principal barriers to the realization of these expectations has been the problem of slow diffusion of reactants into the pores of these supported catalysts and the slow leaching of the (usually expensive) transition metals by reactants and/or products. Some of these complications could conceivably by minimized by the use of films to support the active metals and there has been at least one report of such a system.[5]

Surprisingly, the possibility of preferentially reacting CO when it is one of the components in a gas mixture with a metal incorporated into a membrane thereby achieving permselectivity (independent of catalytic activity) has not, to the best of our knowledge, been extensively investigated. It has been shown[6] that Ru(III) ions can be incorporated into ion-exchange resins and that films of such modified resins react with carbon monoxide at 400 Torr and 150°C to give a variety of complexes involving carbon monoxide coordination to Ru.

Because of the paucity of information regarding permeation constants of common gases such as H_2, CO, N_2, CO_2, and C_2H_4 through unmodified CA membranes we now have determined such constants. We then prepared Ru- and Rh-modified cellulose acetate membranes and performed similar permeation studies. We were particularly interested in the possibility of separating H_2/CO (synthesis gas) mixtures by the use of such membranes.

EXPERIMENTAL

Preparation of Cellulose Acetate (CA) Membranes

Reproducible membranes were prepared by the following procedure: 4.00 g of cellulose acetate (Aldrich Co.) was dissolved in 90 mL of tetrahydrofuran (THF) (Fisher Scientific) in a 150-mL beaker and the resulting solution warmed to about 70°C in an oil bath and concentrated at this temperature until the volume reached about 33 mL. The concentration of CA at this stage is approximately 12% by weight. After cooling to room temperature, the polymer solution was cast on a glass plate using a doctor's knife (Gardner Co.). The thickness of the membrane was controlled in the range from 0.7 mil to 1.2 mil. After 3 hours in air at room temperature, the cast membranes were annealed at 110°C overnight.

Preparation of Ruthenium-Containing Cellulose Acetate Membranes (CA-Ru)

For the preparation of these modified membranes, before casting the tetrahydrofuran solutions of cellulose acetate described above, 0.40 g of $RuCl_3 \cdot 3H_2O$ (10 wt%) dissolved in 30 mL of THF was added to the solution. After concentrating, the membrane was cast, and the resulting pale brown membrane dried in air at room temperature for 24 h. The thickness was controlled so as to lie in the 0.9 to 1.2 mil range.

The analysis of H_2/CO mixtures was performed by gas-liquid chromatography (GLC) using a 6' × 1/4'' copper tube containing 80/120 mesh molecular sieve 5A at 60°C with a TC detector at 220°C and a helium flow of 40 mL/min. The analysis was programmed with a HP3390A integrator. The polarity of the detector was set to start at a negative value (e.g., − 0.6) for the hydrogen signal and a program in the GLC instructed the polarity to change to positive at 1.20 min corresponding to the time at which all the hydrogen had disappeared. The response of the detector was not proportional to the concentration of hydrogen and thus correction factors which are a function of the signal area must be applied.

The permeation measurements were made with a stainless steel cell modelled after that reported in the literature.[7] Copper tubing was used for most of the gas lines but the tubing carrying the permeate gas to the metering tube was .062 inch inner diameter × 4 feet stainless steel. The cast membranes were cut to appropriate size and placed in the cell and tested for small leaks. Permeation rates were measured several times for each membrane and several times again for another membrane from the same casting solution. The values of the permeation constants, P, for H_2 which ranged, depending on conditions, from 5 to 20 are believed to be accurate to within $\pm 5\%$ but the values of P for CO which range from < 0.1 to about 0.6 are probably only accurate to within $\pm 20\%$.

RESULTS AND DISCUSSION

Permeation Studies with Cellulose Acetate

The permeation results with various pure gases under selected temperatures and pressures are shown in Table I. The most striking feature of these data is the very low permeability of CO compared to H_2 and CO_2. At 24°C and a pressure drop across the membrane of 15 psig, the ratio (α) of the permeation constants for H_2 to CO is greater than 73 and for CO_2 to CO it is greater than 100.

As expected, raising the temperature increases the permeation constants; in the case of H_2 increasing the temperature from 24°C to 50°C almost doubled the value of P. Low rates of permeation were particularly difficult to duplicate but the consistency of our results added to our confidence in them.

The increase of P with increasing pressure drop, especially in the case of H_2, appears to be a genuine effect. That an increase in pressure gives an increase in rate is inherent in the calculation of P values and if this were a simple linear relationship, the value of P should be independent of pressure. The demonstrated effect of pressure on P thus indicates a dependence perhaps related to structural deformations in the membrane.

TABLE I
Membrane Permeation Values (P)[a]

Membrane	psig	24°C						
		H_2	CO	CO_2	O_2	N_2	C_2H_4	H_2:CO
CA[b]	15.0	7.3[c]	< .1	9.0	.92	.28[d]	—	> 73
CA	30.0	9.2	.15	8.5	.85	< .03	—	61
CA-Ru-10[e]	15.0	5.4	< .1	2.0	—	.08	—	—
	22.5	6.2						—
	30.0	6.5	.15	1.6		.03	—	43
		50°C						
CA	7.5	8.4	—	—	—	—	—	—
	15.0	15.4	.57	—	—	—	< .03	
	22.5	19.5					1.9	
	30.0	20.5	.50	9.8	—	.12	1.2	41
CA-Ru-10[e]	15.0	10.6[f]		3.9		.16	—	
	30.0	11.6[f]	.46[f]	4.8			—	25

[a] Units = $10^{16} \times cm^3$ (STP) $cm/cm^2 \cdot s \cdot cmHg$.

[b] Cellulose acetate from Aldrich Co., acetyl content of 39.8%, cast from THF.

[c] A value of 3.5 is reported by Y. Ito, cited in *Polymer Handbook*, J. Brandup and E. H. Immergut, Eds., John Wiley & Sons, New York, 1975.

[d] Reported for a plasticized cellulose acetate at 30°C, R. Waack, N. H. Alex, H. L. Frisch, V. Stannett, and M. Swarc, *Ind. Eng. Chem.*, 47, 2524 (1955). This article also reports values of P for O_2, and CO_2 equal to .78, and 22.7, respectively.

[e] Cellulose acetate plus 10 wt% $RuCl_3 \cdot 3H_2O$.

[f] At 40°C.

As the data of Table I illustrate, the permeation of CO through the CA membrane is very slow; so slow in fact that only careful attention to experimental detail demonstrates any permeation at all. Thus it was of considerable interest to incorporate into these membranes a transition metal such as Ru or Rh which are known to form metal carbonyls under rather mild conditions. The expectation was that such reactive membranes would facilitate CO permeation.

Permeation Studies With $RuCl_3$-Treated CA Membranes

The exact nature of the chemical bonding, if any, between $RuCl_3$ and CA has not been investigated. The structure of $RuCl_3 \cdot 3H_2O$ is probably octahedral and on reaction with CA it is possible that the coordinated H_2O is replaced in whole or in part by acetyl groups coordinated to the metal through the oxygen of the carbonyl group somewhat analagous to the Cu(II) complex of Figure 1. The stoichiometry of the reactants should lead to a glucose unit : Ru atom ratio of about 10. After incorporation of the $RuCl_3$ into the membrane it is not certain whether the complex remains Ru(III) or has been reduced to Ru(II) or whether two or three chlorine atoms are associated with each Ru atom. Analysis[8] indicates a ratio of Cl : Ru of 2.3.

The permeation measurements were conducted similarly to those performed with the untreated CA membrane and the results obtained with these mem-

branes are also listed in Table I. In general it appears that the incorporation of Ru into the membrane results in a *decrease* in the permeability of all the gases studied. Thus there appears to be no advantage, with respect to selectivity, of incorporating this transition metal in the membrane in the form of its trichloride. As will be shown below, it is unlikely that the metal is chemically bonded to the acetyl groups of the CA membrane; it appears to behave as an unreactive additive blocking or reducing accessibility of pores or channels.

Infrared Studies of CA–RuCl$_3$ Membranes

Our experience in metal carbonyl chemistry made it difficult for us to believe that CO was not reacting with the metal to generate ruthenium carbonyl species. In order to determine whether such species were indeed
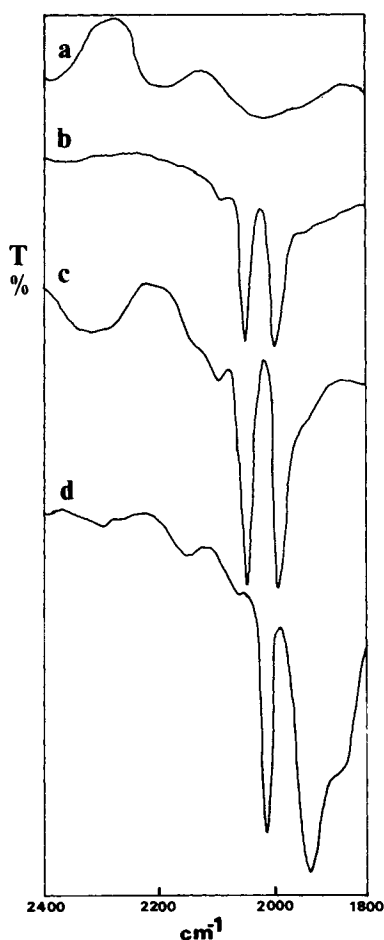

Fig. 2. Infrared spectra of CA membranes: (a) CA only; (b) CA + 5 wt% RuCl$_3$ · 3H$_2$O after treatment with CO at 40°C; (c) same as b but with 10 wt% RuCl$_3$ · 3H$_2$O; (d) CA + 10 wt% RuCl$_3$ · 3H$_2$O after treatment with [13]CO at 110°C for 24 h.

formed, the infrared spectra of the CA-RuCl$_3$ membranes before and after CO exposure were examined.

With membranes having low RuCl$_3$ loading, the infrared spectra of the CA–Ru membrane shows little change from the pure CA membrane. However, as the metal loading is increased to 10 wt%, two significant changes are observed. The acetyl carbonyl band ν(C=O) at 1750 cm^{-1} gradually broadens and a shoulder at 1725 cm^{-1} appears. This shift to lower frequency is similar to that reported for the CA–Cu membrane[2] and is consistent with the lowering of the C=O bond order on coordination to the metal at the oxygen atom. The other change involves the ν(C—O) of the ester group linking the glucose unit to the acetyl group. Incorporation of Ru broadens this 1230 cm^{-1} band and a shoulder band gradually appears at 1260 cm^{-1}. Again this shift to higher frequency has also been reported for the CA–Cu case and is attributed to an increase in (O)C—O bond order of the C—O bond by participation of the lone pair electrons in bonding with the acyl carbon. As expected for CA—RuCl$_3$, a band at 320 cm^{-1}, ν(Ru—Cl) is also observed.

When CA membranes containing RuCl$_3$ are treated with CO, typical coordinated C≡O stretching bands ν(C≡O) appear in the infrared spectra (Fig. 2). Two strong bands at 2068 and 2003 cm^{-1} characterize these spectra as well as two weak bands on either side of these bands, namely at 2130 and 1980 cm^{-1} (shoulder). The intensities of these four bands increase as the metal loading increases. These bands are similar to those reported for silica- and alumina-supported ruthenium carbonyl catalysts[9] and are most compatible with the pure octahedral Ru(II) complexes, L$_2$Ru(CO)$_2$Cl$_2$ (L = PR$_3$) reported in the literature.[10] The *absence* of certain bands in the spectra of the CA–Ru–10 membranes after CO treatment is also significant. Thus no bridging carbon monoxide bands ν(—Ru—C(O)—Ru) are present. Furthermore, on treatment with H$_2$, no ν(Ru—H) band is observed and the four terminal ν(C≡O) bands are unaffected by H$_2$ permeation at 40°C, indicating the integrity of the metal carbonyl bonding under reducing conditions. However, it should be pointed out that the formation of metal carbonyls does not required the metal to be coordinated to the cellulose acetate matrix of the membrane, and can be independent of such bonding.
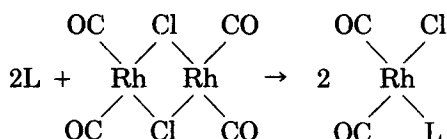
INFRARED AND [13]CO EXCHANGE STUDIES

The infrared spectral studies reported above showed unequivocally that treatment with CO of CA membranes containing RuCl$_3$ · 3H$_2$O produces ruthenium carbonyls in the membrane. It was not clear, however, whether the formation of the carbonyl was a stoichiometric reaction and that once formed, the coordinated CO would or would not exchange with additional CO. In order to answer this question the carbonyl containing CA—Ru—10 membrane was treated with [13]CO at 110°C for 24 h. The infrared spectrum of this membrane showed the same features of the analagous [12]CO membrane [Fig. 1d] but with all four ν([12]C≡O) bands (2130, 2068, 2003, 1980 cm^{-1}) shifted an average of about 52 cm^{-1} to lower frequency (2080, 2015, 1960, 1930 cm^{-1}). When the [13]CO-treated membrane was exposed to [12]CO the isotopic ^{13}C carbonyl band intensities decreased gradually and the expected ν([12]C≡O) bands grew back in.

Rhodium–CA Membranes

The studies with Ru-containing membranes show that the failure of such membranes to facilitate CO transport is not due to the failures of the Ru to react reversibly with CO, but with the intrinsic lack of permeability of CO in a CA matrix. Even though the Ru reacts with CO, the resulting carbonyl complex does not alter the structure of the matrix CA; indeed the results shown in Table I indicate that the incorporation of Ru acts as an impediment to the permeation of all gases, and simply adds to the tortuosity[11] of the membrane. One may presume from these results that the bonding of the Ru to the CA, if it does occur at all in a structure analogous to structure 1, is very weak indeed and the metal is not anchored to the matrix.

In order to enhance the possibility that CA would bond more strongly to the metal site, the incorporation of Rh was investigated.

The compound chosen as the source of Rh was the complex $[RhCl(CO)_2]_2$. Thus bridging dimer is readily cleaved by attacking ligands, L:

$$
2L \; + \; \underset{\substack{\diagdown \diagup \diagdown \diagup \\ OC \quad Cl \quad CO}}{\overset{\substack{OC \quad Cl \quad CO \\ \diagdown \diagup \diagdown \diagup}}{Rh \quad Rh}} \quad \rightarrow \quad 2 \; \underset{\substack{\diagup \diagdown \\ OC \quad L}}{\overset{\substack{OC \quad Cl \\ \diagdown \diagup}}{Rh}}
$$

CA membranes containing 10 wt% $[RhCl(CO)_2]_2$ were prepared in the same manner as described for the CA—Ru—10 membranes. When such membranes were packed into a reactor tube and treated in a stream of CO/H_2 at 100°C, the unchanged dimer gradually sublimed out of the membrane. Such behavior indicates that no substantial bonding of the Rh to CA occurs.

CA membranes containing the nonvolatile $RhCl_3 \cdot 3H_2O$ were also prepared. On treatment with CO/H_2 at 100°C, the dimer $[RhCl(CO)_2]_2$ was formed and gradually sublimed out of the membrane. This behavior further demonstrates that CA does not bond very strongly if at all to transition metals.

Separation of H_2 / CO Mixtures

Although not designed well for this purpose, the permeation cell was employed to study in a preliminary way the separation of H_2 from mixtures of H_2/CO of known composition. In a static system such as the permeation cell presents, the feed side composition changes as the permselectivity progresses. Accordingly, in our experiments the feed side gas was intermittently exchanged with the feed gas in the reservoir. GLC analysis of known compositions of H_2/CO were performed to validate our analytical techniques. Gas samples were taken from both the feed and the permeate at about the same time. Long permeation times were employed to assure approximate steady-state conditions.

The results of permeation studies with H_2/CO mixtures are shown in Table II. As these data indicate, if one permeates a mixture containing about 55% H_2, the permeate from the one-stage permselectivity results in a permeate composition of about 90-95% H_2. The data also show that there is no advantage to incorporating Ru into the membrane, a result in accordance

TABLE II
Mixed H_2/CO Permeation Studies, 24°C, 15 psi

Membrane	Time, Min[a]	%H_2, Feed[b]	%H_2 Permeate[b]	E.F.[c]
Ca + 10Ru	1500	57	94	11.8
	2700	54	88	6.2
	3900	56	94	12.3
	4000	57	95	14.3
	5175	54	91	8.6
	5280	55	92	9.4
Average·	10.4			
CA	65	56	96	18.9
	120	56	96	18.9

[a]Time after start of permeation of mixed gases at which samples were taken for analysis.
[b]Analysis for CO and H_2 by GLC.
[c]E. F. = enrichment factor = $\dfrac{H_2(\text{Perm.})/H_2(\text{feed})}{CO(\text{Perm.})/CO(\text{feed})}$.

with the data on permeation constants for the treated and untreated membranes shown in Table I. The effectiveness of the membranes for gas separation is expressed in terms of an enrichment factor (EF) which we define as

$$EF = \frac{\% H_2 \text{ in permeate}/\% H_2 \text{ in feed}}{\% CO \text{ in permeate}/\% CO \text{ in feed}}$$

Our results indicate that cellulose acetate membranes may be useful for separating hydrogen from its mixtures with CO and for the adjustment of H_2/CO composition of synthesis gas.

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