Separation of Gas Mixtures by Supported Complexes

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August 1986

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SEPARATION OF GAS MIXTURES
BY SUPPORTED COMPLEXES

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RESEARCH SUMMARY

This final report covers research performed during the period 1 October 1984 to 30 September 1985 by the Pacific Northwest Laboratory (PNL) for the Department of Energy, Morgantown Energy Technology Center.

The goal of this program is to determine the feasibility of solvent-dissolved coordination complexes for the separation of gas mixtures under bench-scale conditions. In particular, mixtures such as low-Btu gas will be examined for CO and H₂ separation.

Two complexes, Pd₂(dpm)₂Br₂ and Ru(CO)₂(PPh₃)₃, were examined in a bench-scale apparatus for the separation of binary (CO-N₂ or H₂-N₂) and quinary (H₂, CO, CO₂, CH₄, and N₂) mixtures. The separation of CO-N₂ was enhanced by the presence of the palladium complex in the 1,1,2-trichloroethane (TCE) solvent, especially at high gas and low liquid rates. The five-component gas mixture separation with the palladium complex in TCE provided quite unexpected results based on physical solubility and chemical coordination. The complex retained CO, while the solvent retained CO₂, CH₄, and N₂ to varying degrees. This allowed the hydrogen content to be enhanced due to its low solubility in TCE and inertness to the complex. Thus, a one-step, hydrogen separation can be achieved from gas mixtures with compositions similar to that of oxygen-blown coal gas.

A preliminary economic evaluation of hydrogen separation was made for a system based on the palladium complex. Direct comparison to pressure swing absorption (PSA) can't be made since the palladium system can extract hydrogen from mixed gases containing very low H₂ content; whereas, water-gas shift catalysis is generally used to increase the hydrogen content to about 90% prior to PSA separation. Further, PSA normally removes CO₂ prior to the shift. Realizing these differences, the palladium system has a separation cost of 50-60¢/MSCF with an assumed capital investment of \$1.60/MSCF of annual capacity charged at 30% per year. This assumes a 3-4 year life for the complex. Starting with a 90% hydrogen feed, PSA separation costs are in the range of 30-50¢/MSCF.

The ruthenium complex was not as successful for hydrogen or carbon monoxide separation due to unfavorable kinetics. Minor modification of the complex should improve the reversibility for both H_2 and CO .

The palladium complex was found to strip hydrogen gas from H_2S . The complex could be regenerated with mild oxidants which removed the sulfur as SO_2 .

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PROGRAM OBJECTIVE AND PURPOSE

The objective of this research is to determine the feasibility of solvent-dissolved coordination complexes for the separation of gas mixtures under bench-scale conditions. In particular, mixtures such as low-Btu gas will be examined for CO and H₂ separation. The engineering and economic information gained from this research will be applicable to facilitated transport membrane systems.

MILESTONE SCHEDULE

The milestones of each task are shown below and in Figure 1. A full discussion of each task follows this section.

Task A. Examination of Less Costly Coordination Complexes

- A.1 Complete selection of a less costly complex for H_2 binding and determine gas uptake, 3/85.
- A.2 Complete selection of two lower cost complexes for CO and CO_2 binding and determine gas uptake of each, 6/85.

Task B. Gas Binding Under Flow Conditions

- B.1 Design and construct a bench-scale apparatus, 12/84.
- B.2 Select solvents and determine solvent properties, 2/85.
- B.3 Conduct operation of bench scale system, 8/85.
- B.4 Calculate economics for the separation system, 8/85.

Task C. Examination of Reversible H_2S Binding

- C.1 Complete synthesis of complexes to bind H_2S , 3/85.
- C.2 Determine kinetics of H_2S binding, 8/85.

FIGURE 1. Milestone Schedule

PROGRAM TASKS

The individual tasks and subtasks are discussed below. Although not identified as a distinct task, there will be a considerable effort needed to coordinate research activities with the subcontractor and report the research results to DOE-METC. Monthly letter reports, quarterly technical reports, and a final technical report will be forwarded to DOE-METC during the normal reporting periods. Meetings will also be attended for reporting purposes as requested by DOE. Such coordination and reporting will be performed by Pacific Northwest Laboratory.

TASK A. EXAMINATION OF LESS COSTLY COORDINATION COMPLEXES

Subtask A.1. Hydrogen Carriers

Although metals such as Ir and Ru can be recovered from degraded or irreversibly oxidized complexes, the cost of large quantities of precious metals may contribute to overwhelming capital expenditures for gas separation. Some of the ligands of these complexes are expensive and difficult to use under aerobic conditions. Thus, there is a need to examine complexes containing less costly metals and ligands, but yet reversibly bind H_2 . Examples of candidate complexes which are known to form hydrides include $Co(N_2)(PPh_3)_3$ and $CoH(N_2)(PPh_3)_3$. One complex will be examined which uses a more available metal center. If the uptake studies are favorable, solution kinetics will be determined.

Subtask A.2. CO/CO₂ Carriers

Due to the cost of the dpm ligand in $Pd_2(dpm)_2Cl_2$ another complex with an inexpensive ligand capable of CO binding will be examined under solution conditions. Although there are several Fe and Co porphyrins which reversibly bind CO, most also bind O_2 at equivalent or faster rates. A complex such as $Mn(MeCp)(CO)_3$, where MeCp is methylcyclopentadienyl, may require further examination.

The binding of CO_2 is considered more difficult than CO due to the need of a very basic metal center. However, bifunctional group activation or the use

of insertion reactions may provide an alternate route to reversible CO_2 binding. For instance, $\text{Mo}_2(\text{OCHMe}_2)_6$ and $\text{Cu}(\text{OMe})_2$ are examples of complexes which may be examined.

A minimum of two complexes will be examined for the uptake of CO and CO_2 . If the uptake studies are favorable, solution kinetics will be determined.

TASK B. GAS BINDING UNDER FLOW CONDITIONS

Subtask B.1. Equipment Design and Construction

The previous work done at PNL with complexes involved binding of gas under static conditions. A bench scale system with regeneration capability must be prepared in order to examine the complexes under more exacting conditions. The equipment will be sized to accommodate a 20-100g sample. Glass and stainless steel are the likely materials of construction. The system will consist of an absorber and elution (regeneration) column. It is presumed at this time that packed columns will be used.

Subtask B.2. Solvent Determination

Several solvents will be examined which can be used to prepare solutions of the complexes. These must be relatively nonvolatile solvents which allow binding and desorption to occur, yet do not contribute drastically to cost or later engineering problems (corrosion as an example). The solubilities of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$, and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ as well as CO , CO_2 , and H_2 will be determined in the selected solvent. The vapor pressure of the solvent will also be determined at operating conditions. The viscosity and gas diffusivity may also have to be obtained at temperatures in the operating range.

Subtask B.3. Bench Scale Operation

The complexes $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$, $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ or less costly substitutes will be examined in the dual column system to determine the efficiency of gas separation. The mass balance and calculated energy requirements will be determined with each complex. The feed gas will approximate either a low or a medium-Btu type. The mass transfer coefficient and rates will be determined. Since this will be a multi-component system a computer

program may be necessary for these latter calculations. Data necessary to determine the equilibrium of the binding/desorption will be obtained.

Subtask B.4. System Economics

Although Task A was concerned with obtaining less costly complexes, improved performance may not be achievable. Thus, a metal recovery step may be included in the economic calculations. The information from Task B should allow determination of the column height necessary for various gasification plant sizes. These economics will be compared to information available on comparable cryogenic and pressure-swing adsorption systems.

TASK C. EXAMINATION OF REVERSIBLE H₂S BINDING

Subtask C.1. Preparation of Complex

Only one coordination complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, has been found which coordinates H₂S in such a manner that desorption is possible [A. M. Mueting, et al. Inorg, Chem. 23:44(1984)]. We will prepare this complex and at least two analogs with differing ligands which could enhance the desorption of H₂S.

Subtask C.2. Kinetics of H₂S Binding

The solution kinetics will be determined so that the conditions of reversibility can be established for the complexes of Subtask C.1. The complex with the best binding desorption characteristics will be examined to determine the equilibrium constant.

DISCUSSION

EXAMINATION OF LESS COSTLY COORDINATION COMPLEXES

The complexes examined as possible substitutes for $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, and $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ are discussed below in relation to the respective gases which they selectively bind.

HYDROGEN

$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ had been examined in our previous work,⁽¹⁾ and was found to be a candidate complex for the reversible binding of hydrogen. However, the cost of ruthenium (\$80/troy oz. in June 1985) may be a burden to the initial cost of a gas separation system. Thus, the literature was reviewed to determine if there were any hydrogen binding complexes which could be prepared with less expensive metals and ligands.

Most complexes capable of the oxidative addition of H_2 contain Rh, Ir, Pt, Ru, or Pd.⁽²⁾ There are a few examples of complexes which contain Cr,⁽³⁾ Mo,⁽⁴⁾ Fe,⁽⁵⁾ and Co.⁽⁶⁾ Either little is known about the reversibility of hydrogen with these metal centers^(3,4) or a ligand such as nitrogen must be removed prior to H_2 addition.^(5,6) An example is shown below:

The equilibrium of this reaction does not favor reformation of $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$. Although $\text{Co}(\text{N}_2)(\text{PPh}_3)_3$ has been shown to bind hydrogen,⁽⁵⁾ it was found to be extremely sensitive to small amounts of oxygen. Our experience with similar cobalt complexes suggests that irreversible oxidation occurs even with oxygen levels <50 ppm.

Two cobalt complexes which may be of use for the reversible binding of hydrogen are $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and $[(\text{CN})_4\text{Co}(\mu\text{-en})\text{Co}(\text{CN})_4]^{4-}$, where en is ethylenediamine. Both complexes have been examined in aqueous systems.^(7,8) The

pentacyanocobaltate(II) anion attains a d^6 octahedral configuration via a net H_2 addition to two cobalt centers as shown.

However, there is a slow degradation (or aging) in aqueous systems since water also adds to the cobalt center to give both hydroxyl and hydride products. These complexes might be stabilized by miscellular incorporation or by the use of biphasic systems.

We pursued an alternative complex, $[(C_5H_5)Cr(CO)_3]_2$, which is reported to reversibly react with hydrogen to form $(C_5H_5)Cr(CO)_3H$ ⁽⁹⁾ (Equation 3). The forward reaction was first carried out at 70°C and 150 atm H_2 . Further, this reaction was reported to react slowly and incompletely at room temperature and 1 atm H_2 .⁽⁹⁾ We presumed that the chromium dimer could be made to react nearly quantitatively under a moderate pressure of H_2 (<10 atm) at room temperature.

Our studies were conducted at 25°C in a small tubing bomb at a H_2 pressure of 10 atm. Samples were contained in 5 mm tubes and solution volumes were less than 1 ml. In pentane, in which the dimer is only slightly soluble, and without stirring, no hydride could be detected by infrared spectroscopy. The dimer is more soluble in tetrahydrofuran (THF). In this solvent (again without stirring) an appreciable amount of hydride was detected, but the reaction was incomplete. A method was devised to efficiently stir the reaction mixture with a magnet. Under these conditions nearly quantitative conversion in THF was noted.

The hydride, $(C_5H_5)Cr(CO)_3H$, easily liberates H_2 to reform the dimer complex by heating to 80°C in the solid state under vacuum. We expect this regeneration to be facile in solution as well. Hydrogen gas was detected by gas chromatography, and an infrared spectrophotometric analysis of the remaining material indicated that only $[(C_5H_5)Cr(CO)_3]_2$ was present.

This complex shows promise as a hydrogen transfer agent in an immobilized liquid membrane (ILM) system. To be used effectively in an ILM a more detailed knowledge of the effects of temperature and pressure on the position of the equilibrium in Equation 1 is necessary. At the optimal temperature the hydride should form rapidly on the high pressure side of the membrane, but will decompose to liberate H_2 on the low pressure side.

CARBON MONOXIDE

Although $Pd_2(dpm)_2Cl_2$, where dpm = bis(diphenylphosphino)methane, was shown to possess favorable kinetics and specificity for reversible CO binding,⁽¹⁰⁾ it would be desirable to obtain a complex with similar characteristics but possessing a less costly metal center and ligand. Phthalocyanatoiron(II) has been shown to bind CO reversibly.⁽¹¹⁾ Prior work has also indicated the reversible interaction of O_2 and NO with phthalocyanatoiron(II) or Fe(pc). There does not seem to be a dimerization of Fe(pc) in the presence of O_2 with an irreversible loss of gas binding ability. This irreversible reaction has been well noted for most other iron(II) porphyrins whereupon μ -oxo-iron(III) dimers are formed.⁽¹²⁾ Sterically hindered macrocycles must be constructed to prevent such undesirable reactions. Some Fe(II) porphyrins reversibly bind O_2 without irreversible oxidation, but temperatures less than $-60^\circ C$ are required.

FeTPP, meso-tetraphenylporphyrin iron(II), has also been examined for CO binding.⁽¹³⁾ However, it is extremely sensitive to oxygen, and can endure only three oxygenation-deoxygenation cycles at $-78^\circ C$ before irreversible oxygenation is apparent.⁽¹⁴⁾

Due to the low solubility of phthalocyanato-iron(II) in favorable solvents, and the low temperature requirements of several other porphyrin complexes, laboratory studies were not pursued.

CARBON DIOXIDE

Our previous work had also involved $Rh(OH)(CO)(PPh_3)_2$ as an agent to reversibly bind CO_2 . Reduction of cost could be achieved if the metal center were a cheaper transition element. One candidate showing potential was cupric dimethoxide. A suspension of this polymeric compound in pyridine reacted with

CO₂ to form cupric methylcarbonate.⁽¹⁵⁾ The inserted CO₂ was quite labile and could be removed by heating at 80°C under a stream of nitrogen to regenerate cupric dimethoxide.

Copper (II) dimethoxide was carefully prepared and isolated as a blue precipitate from methanol. The solid (3.6×10^{-4} mole) was suspended in a hanging basket above pyridine saturated with CO₂. The solubility of CO₂ in pyridine is 3.28 ml/g. Release of the solid into the pyridine caused an uptake of 5.5×10^{-4} mole of CO₂. This indicated that 1.6 mole of CO₂ was bound to 1.0 mole of copper complex. A previous report⁽¹⁵⁾ suggested that 2.0 moles of CO₂ should be taken up by the complex. The discrepancy of results may be due to an impure sample of copper dimethoxide. However, during the freeze-thaw degassing of pyridine, while the complex was in the hanging basket, some pyridine could have condensed on the solid which may have initiated the CO₂ uptake prematurely.

One disturbing characteristic of the copper complex was its sensitivity to water. Samples of the complex were exposed to air then examined by infrared spectroscopy. Large OH absorbances were noted by IR within minutes of air exposure. It is assumed that hydrolysis of the methoxy groups occurs under these conditions.

GAS BINDING UNDER FLOW CONDITIONS

This section shall follow the subtasks, but will combine some information which could be presented within two or more of the respective subtasks. For instance, the mathematical model used to design the bench-scale apparatus will be discussed below, while kinetic and equilibrium data for the complexes will be presented separately. Experiments were performed with dissolved complexes circulated between absorber and stripper columns. The resulting data and experience should be useful for designing membrane separators as well as scaled up absorber/stripper systems.

EQUIPMENT DESIGN AND CDNSTRUCTION

Preliminary calculations showed that the absorption-desorption process can be treated as two steps in series; i.e., mass transfer occurs through a liquid film in which a negligible amount of reaction occurs while most reaction occurs between dissolved gas and complex in the bulk liquid. The dissolved gas concentration in the bulk liquid at any point in an absorber or stripper falls between physical equilibrium with the gas and chemical equilibrium with the complex. The concentration balances the rates of mass transfer and reaction.

The mass transfer process can be represented by:

$$K_1 a (x_i - x) = -G \frac{dy}{dh} \quad (4)$$

where K_1 = overall liquid phase mass transfer coefficient in cm/s,
 a = interfacial area per unit volume (cm^{-1}),
 x = dissolved gas concentration (g-moles/ cm^3),
 x_i = dissolved gas concentration in physical equilibrium with gas,
 G = superficial molar velocity (g-moles/ cm^2/s),
 y = mole fraction of transferring component in the gas phase, and
 h = distance through the column (cm).

The physical equilibrium expression for Henry's law coefficient H ($\text{atm-cm}^3/\text{g-mole}$) at total pressure P (atm) is;

$$y_P = Hx_i \quad (5)$$

The concentration of complex-bound gas in the liquid can be represented as w (g-mole/cm³), while the superficial velocity of the circulating liquid is L (cm/s) and the subscript "o" in Equation 6 describes those terms at a column terminus. With these definitions the material balance expression can be presented in Equation 6.

$$L(x + w) + G_o y_o = L_o(x_o + w_o) + G y \quad (6)$$

For an absorber-stripper operating at steady state, the rates of mass transfer and chemical reaction in any volume element must be equal as shown in Equation 7.

$$K_1 a(x_i - x) = l_f R(x, w, z) \quad (7)$$

where l_f = the volume fraction liquid holdup and
 $R(x, w, z)$ = reaction rate (g-moles/cm³/s) which is a function of w, x
 and the total concentration of dissolved complex, z
 (g-moles/cm³).

Initial experiments with the bench-scale apparatus used reversible absorption of CO by $\text{Pd}_2(\text{dpm})_2\text{X}_2$ for which solution kinetics are represented by:

$$R = k_f(z - w)x - k_r w \quad (8)$$

The forward and reverse reaction rate coefficients k_f (cm³/g-mole/s) and k_r (s⁻¹) are functions of temperature as shown in Table 1.

Equations 5, 6, 7, and 8 can be solved simultaneously; by eliminating x_i and obtaining $x + w$ and x as functions of y, G , and L . For a solvent of molar density (D_M) and vapor pressure (P_{sat}) operating at total pressure (P), G and L can be calculated for any y . The fraction of the liquid flow vaporized in the column is small. Treating L as a constant simplifies the mathematics. Table 2 lists the resulting sequence of formulae used to relate y to h by numerical integration with a LOTUS(") spread sheet.

TABLE 1. Solution Kinetics for $\text{Pd}_2(\text{dpm})_2\text{X}_2$

Definitions: $k_r = k_f/K$

$$k_f = k_f^0 \exp(-\Delta H_f/RT-1)$$

$$k_f^0 = k_f^{297} \exp(\Delta H_f/RT+1)$$

$$K = \exp[-(\Delta H/T-\Delta S)/R]$$

Data: (10)

X	ΔH_f	k_f^{297}	ΔH	ΔS
(units)	(kJ/mole)	($\text{M}^{-1}\text{s}^{-1}$)	(kJ/mole)	(J/mole-deg)
NCO	26	3150	-48	-55
Cl	15	6600	-57	-88.9
Br	15	6000	-61	-118.4
I	23	4200	-48	-102

TABLE 2. Sequence of Spread Sheet Formulae to Calculate Column Height from Incremented Gas Mole Fraction of CO

```

Q32: 'G
Q35: +$GO*(1-$YO)/(1-$PSAT/$P-Y)
R32: 'xi
R35: +Y*$P/$H
S32: 'x+w
S35: +G/$L1*Y+$X&WO-$GO/$L1*$YO
T32: 'x
T35: (-$KL*$A-$LF*$KF*($Z-X&W)-$LF*$KR+((($KL*$A
+$LF*$KF*($Z-X&W)+$LF*$KR)^2+4*$LF*$KF*($KL*$A*XI
+$LF*$KR*X&W))^0.5)/2/$LF/$KF
W32: 'h
W35: +H0+(Y*G-YO*GO)*(-2/$KL/$A/(XI0+XI-XO-X))

```

Experiments demonstrated the validity of the model and determined K_1a as a function of experimental variables. Once mass transfer coefficients have been determined at the benchscale, standard correlations can be used to size a commercial scale gas separation plant.

The bench-scale apparatus was designed for the smallest practical liquid holdup consistent with obtaining reliable absorption/reaction data for scale-up. The entire system fit inside a bench top fume hood (see Figure 2) with the exception of temperature control and analytical equipment. Figure 2 shows the system before addition of insulation. A variable speed pump (lower left)

FIGURE 2. Bench-Scale Test Apparatus

delivered solution to the absorber (upper right) from which solution flowed by gravity through a stainless steel packed heater (center) into the stripper (left of center) and back to the pump through a cooling coil (in polyethylene container behind the pump). Liquid and gas flows were monitored by flow meters (left and right). Fuel gas and diluent flowed through the absorber. Nitrogen was fed to the stripper through another packed heater (below absorber). Gas and solvent vapor flowed from the stripper to a two-pass cooler-condensor which returned solvent to the top of the stripper. Gas and liquid sample points were strategically located throughout the system and manometers monitored pressure drop across the columns.

In the experimental system, nitrogen or helium stripped absorbed CO or H₂ from the solution while a commercial system would use a pressure change and/or steam stripping. The use of an inert gas allowed accurate metering and analyses of both inlet and outlet streams to obtain reliable data. A Hewlett-Packard multi-column gas chromatograph was set up next to the system for rapid analysis.

Glass, stainless steel and Teflon were used as materials of construction throughout the system. Figure 3 is a close-up view of the stripper. The absorber and stripper were similarly constructed with 30 mm (i.d.) glass columns of 25 cm length packed with 3 mm glass spheres. The dry packing had a void fraction of 0.4 and a total surface area of 2400 cm² per column. The Teflon support plate had four nozzles (not visible) and a downcomer (tube in liquid pool) to facilitate counter flow of both gas and liquid. The column temperature was monitored by thermocouples at three points. A data logger recorded all 19 system temperatures on demand or on a timed cycle. Automatic controllers regulated power supplies for the gas and solution heaters to control their outside wall temperatures.

Operability tests were performed to aid in design of the gravity-flow solution heater and the column packing support plates. Calibration, pressure drop and flooding tests were performed with the assembled system.

Figure 4 presents the results of the pressure drop tests. Results are plotted against velocity of nitrogen for dry packing, packing wet with TCE, and three circulation rates of TCE indicated as mass velocities (L). The high reading at L = 0.6 was in the loading zone (incipient flooding). Total

FIGURE 3. Close-Up View of the Stripper Column

FIGURE 4. Column Pressure Drop with Nitrogen and Trichloroethane

operating ing holdup of liquid varied from 200 to 250 cm³ for the system depending upon the circulation rate. The pressure drop data can be used to estimate actual holdup in the packing. Liquid holdup is an essential parameter for determination of mass transfer and reaction kinetic coefficients from the results of the absorption experiment.

SOLVENT DETERMINATION

Several solvents were screened for properties desirable for CO separation by Pd₂(dpm)₂X₂ (X = Br, Cl). Criteria for solvent selection included:

- low volatility,
- high solubility of complex,
- compatibility with complex,
- low cost, and
- UV/VIS spectrum transparent in 310-650 nm range.

The UV/VIS window in the 310-650 nm range was required for determination of equilibrium and kinetic parameters. Previous kinetic work was performed in dimethylacetamide (dma).⁽¹⁰⁾ However, Pd₂(dpm)₂X₂ was only slightly soluble

(10^{-4}M) in this solvent. Further, changes (bandshifts and intensity differences) were noted when $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ remained in dma solution longer than 24 hours. The solubility of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ was also low (10^{-4}M) in dma. Consequently, a different solvent was required to meet the criteria established for the system.

Our previous experience suggested that dichloromethane was an excellent solvent for $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. A maximum concentration of 0.05M $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ in dichloromethane was obtained. However, the boiling point (39.7°C) and vapor pressure (11 torr at 25°C) indicates that dichloromethane would not be a desirable solvent.

In order to determine other solvents suitable for dissolution of $\text{Pd}_2(\text{dpm})\text{Cl}_2$ the concept of solubility parameters (δ) was used. Hildebrand⁽¹⁶⁾ and Hoy⁽¹⁷⁾ used solubility parameters to show why some pairs of materials mix better than others. The solubility parameter is related to the internal pressure or cohesive-energy density:

$$\delta = \left(\frac{\Delta E}{v}\right)^{1/2}$$

where ΔE = energy of vaporization, and
 v = molar volume

Since we could not measure the solubility parameter of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, its value was estimated as approximately 10 since it was quite soluble in dichloromethane ($\delta = 9.8$). Several potential solvents and their physical properties are presented in Table 3.

Tetralin may be a reasonable process solvent, but had to be eliminated from the present study due to conflicting absorbances in the UV/VIS spectrum with $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. Spectra of dibutylphthalate and diphenylether were clear in 310-650 nm region. Diphenylether is not convenient since it is a solid at room temperature, melting at 26°C . Dibutylphthalate met all of the criteria very well except that the solubility of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, measured as approximately $1.6 \times 10^{-3}\text{M}$, is lower than desirable. Both $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ were found to be stable in this solvent at 100°C for 6 hours as determined by UV/VIS spectroscopy. Solutions held at room temperature showed no spectral

TABLE 3. Physical Properties of Solvents Potentially Useful for Dissolution of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$

Solvent	Solubility Parameter	Vapor Pressure at 25°C (torr)	Boiling Point (°C)
dichloromethane	9.80	10.98	39.7
dimethylacetamide	10.80	--	165
diphenylether	10.10	0.01	258
1,2,3,4-tetrahydro- naphthalene(tetralin)	9.50	0.38	205
dibutylphthalate	9.85	0	340
1,1,2-trichloroethane	9.88	22.49	113.8
1,2,3-trichloropropane	10.09	3.33	156

changes for one week. The solubility of CO was established by plotting the uptake of CO in dibutylphthalate versus various partial pressures of CO. Thus, the solubility of CO in dibutylphthalate was determined to be $4.39 \times 10^{-3} \text{ M atm}^{-1}$ with Henry's law being obeyed.

Although dichloromethane had been eliminated as a process solvent due to its low boiling point, other chlorinated solvents with higher boiling points were investigated. Both 1,2,3-trichloropropane and 1,1,2-trichloroethane were examined as solvents for $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. The highest concentration of the complex in trichloropropane was 0.017 M. However, concentrations as high as 0.15 M were obtained in trichloroethane. Although the vapor pressure of trichloroethane is higher than that of trichloropropane, cost favors the trichloroethane. Current bulk prices (1984) are \$0.42/lb for 1,1,2-trichloroethane and >\$1.00/lb for 1,2,3-trichloropropane. Based upon these studies 1,1,2-trichloroethane was chosen as the solvent for $\text{Pd}_2(\text{dpm})_2\text{X}_2$, where X = Cl or Br.

Solubilities of these complexes were quite high in the chlorinated solvents. For instance, $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ has a solubility of 0.15 M in TCE and 0.027 M in trichloropropane (TCP). These solubilities are significantly higher than that of CO in the solvents: $5.7 \times 10^{-3} \text{ M atm}^{-1}$ in TCE and $4.4 \times 10^{-3} \text{ M atm}^{-1}$ in TCP. The CO adducts of these complexes were also very soluble in TCE and TCP. Concentrated solutions of the complexes showed no signs of decomposition after three weeks at room temperature. Some decomposition (visible spectral change) was noted after 6 hours at 100°C, but both complexes were stable

for more than 6 hours at 55°C. Further, $\text{Pd}_2(\text{dpm})_2\text{Br}_2$ exhibited some signs of decomposition (visible spectral change) at 80°C after 6 hours; $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ appeared to be more stable at this temperature.

All of the synthesis gas components dissolved in TCE to varying degrees. Approximate solubilities for CO , N_2 , and CO_2 were measured by gas uptake at room temperature. Experimental data were combined with a literature correlation⁽¹⁸⁾ to provide the information in Table 4.

Several solvents were screened for the study of H_2 separation with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. There were 1,2,4-trimethylbenzene, butylcarbitol acetate, cellosolve acetate, and benzene. The solubility parameter of each was similar to tetrahydrofuran, an excellent but volatile solvent for the ruthenium complex. The three nonvolatile solvents did not have the solvating capability of tetrahydrofuran for the complex (0.016 M). The best of these three solvents was cellosolve acetate with a ruthenium complex solubility of $4.4 \times 10^{-3} \text{ M}$. However, benzene was found to be a better solvent for the ruthenium complex than even tetrahydrofuran. The solubility at 25°C was 0.021 M . Solubilities of the major synthesis gas components in benzene are listed in Table 5.⁽¹⁸⁾

TABLE 4. Approximate Solubilities of Synthesis Gas Components in 1,1,2-Trichloroethane at Atmospheric Pressure

Temperature (°C)	Solubility ($\text{M} \times 10^3$)				
	H_2	CO	CH_4	CO_2	N_2
25	2.1	5.2	16	72	3.4
50		6.1	14	50	4.3
75		6.8	14	40	5.0

TABLE 5. Approximate Solubilities of Synthesis Gas Components in Benzene at Atmospheric Pressure

Temperature (°C)	Solubility ($\text{M} \times 10^3$)				
	H_2	CO	CH_4	CO_2	N_2
25	2.9	7.5	23	110	5.0
50	3.5	8.1	22	81	5.7
75	4.2	8.7	22	63	6.4

Solutions of the complex in benzene were subjected to 19 hours at 55°C under N₂ and CO atmospheres. No decomposition of the complex was observed.

KINETICS AND EQUILIBRIUM OF GAS BINDING

The reversible reactions with CO of the complexes Pd₂(dpm)₂X₂, where X = NCO, Cl, Br, or I, have been well characterized.⁽¹⁰⁾ Figure 5 was derived from laboratory data of these complexes. The bromine-containing complex was selected for laboratory experimentation because its range of reversibility corresponded with CO concentration in typical coal gas under mild conditions of temperature and pressure. With 0.03 moles of Pd₂(dpm)₂Br₂ dissolved per liter, a solution saturated at 0.2 atm of CO and 25°C could flash to 0.4 atm at 80°C while releasing 0.011 moles/liter (see Figure 6). Without the complex, only 10⁻³ moles/liter of CO would be dissolved in TCE under the same conditions; the CO pressure would actually decrease with increasing temperature.

FIGURE 5. Palladium Complex Equilibrium, CO Pressure at Half Saturation

FIGURE 6. Equilibrium of 0.03 M $\text{Pd}_2(\text{dpm})_2\text{Br}_2$ in TCE

Initial work⁽¹⁾ with ruthenium complexes established kinetic coefficients k_1 and k_2/k_{-1} for reactions 9 and 10 as well as for

analogous reactions with CO and O_2 . The rate of the forward reaction was found to decrease in the order $\text{H}_2 > \text{CO} > \text{O}_2$.

Overall equilibrium data were obtained only for hydrogen. After some difficulty in developing a reliable technique, the data of Figure 7 were obtained by sealing a dissolved sample under a hydrogen atmosphere and measuring uv absorbance of hydrogen-free ruthenium complex as a function of temperature. The variation with temperature was small but reproducible. Figure 8 shows that relatively high concentrations of the substituting ligand (PPh_3) are required to reverse the reaction under moderate hydrogen pressures.

FIGURE 7. $Ru(CO)_2(PPh_3)_3$ Equilibrium with H_2 , Temperature Dependence

FIGURE 8. $Ru(CO)_2(PPh_3)_3$ Equilibrium with H_2 , 0.02 M Solution in Benzene at $25^\circ C$

BENCH SCALE OPERATION

Palladium Complex

This section presents results of bench-scale experiments with both palladium and ruthenium-containing complexes. Separation of CO/N₂ and CO/H₂/CO₂/CH₄/N₂ mixtures were examined using 1,1,2-trichloroethane (TCE) both with and without dissolved Pd₂(dpm)₂Br₂. The information presented here compares results obtained with and without complex and relates system performance to physical equilibrium solubility between the gas streams and the circulating solvent. The binary data with and without complex were compared with the mathematical model to determine overall mass transfer coefficients.

An extensive matrix of experimental conditions was tested with the CO/N₂ binary in order to establish a good basis for characterizing mass transfer. CO/N₂ mixtures were fed to the absorber and pure N₂ was fed to the stripper. Table 6 summarizes the experimental data. In most experiments only a small portion of the CO feed was absorbed as would happen in a short segment of a full scale absorber. In #18F a low feed rate was used and more than half of the CO absorbed. The most sensitive dependent variable for characterizing system performance is stripper product CO concentration.

Figure 9 shows the effect of absorber feed concentration with other independent variables held constant. Also shown are the stripper product concentrations that would have been expected in the absence of dissolved complex if the solvent leaving the absorber was saturated with feed gas and that leaving the stripper was free of CO and saturated with N₂ (physical equilibrium). The difference between the lines represents CO that could only have been transferred by the complex and is seen to be relatively constant over a broad range of absorber feed concentrations.

Figure 10 shows the effect of varying stripper gas feed rate while holding all other independent variables constant at two different levels (see Table 6, absorber feed CO is the major difference). The amount of pure CO contained in the stripper product is plotted in Figure 11 for the same experiments indicating that for each set of the other independent variables there is a stripper feed rate that gives a mild optimum efficiency.

TABLE 6. Bench Scale Experiments Separating CO/N₂ Mixtures with Pd₂(dpm)₂Br₂ in 1,1,2-Trichloroethane

Exp #	TA °C	TS °C	Liquid Circulation ml/min	Absorber Gas Feed sccm	Stripper Gas Flow sccm	mole fraction CO		
						Absorber Feed	Absorber Outlet	Stripper Outlet
11A**	22.0	22.0	218.0	846.0	321.0	0.1186	NA	0.0055
11B**	22.0	22.0	218.0	846.0	98.0	0.1186	NA	0.0215
11C**	22.0	22.0	145.0	846.0	98.0	0.1186	NA	0.0197
12A	23.5	54.5	86.5	846.0	98.0	0.1176	0.1112	0.0514
12B	25.8	48.9	145.0	846.0	98.0	0.1161	0.1107	0.053
12C	27.5	53.5	145.0	846.0	45.0	0.1196	0.114	0.1352
13A	23.6	52.0	145.0	846.0	319.0	0.119	0.1114	0.0162
13B	25.0	52.4	218.0	846.0	319.0	0.1161	0.1071	0.0158
13C	25.1	52.5	203.0	1118.0	754.0	0.1317	0.1245	0.0085
13D	25.5	53.2	203.0	1118.0	98.0	0.1317	0.1276	0.0691
13F	26.1	53.9	203.0	424.0	45.0	0.1156	0.1039	0.1284
13G	26.6	53.3	215.0	217.0	45.0	0.1007	0.0865	0.1004
13H	26.6	53.4	215.0	217.0	20.0	0.1007	0.0917	0.1547
13I	24.8	56.0	86.5	217.0	20.0	0.1007	0.0921	0.1941
14A	23.2	52.4	145.0	418.0	97.0	0.0334	0.0288	0.0148
14B	23.5	53.2	145.0	418.0	45.0	0.0334	0.0294	0.0422
14C	23.7	53.2	145.0	418.0	20.0	0.0392	NA	0.0688
14D	23.9	53.9	145.0	891.0	97.0	0.0392	0.0349	0.0258
14E	23.3	54.7	86.5	891.0	97.0	0.0324	0.0252	0.0347
14A'	23.3	53.7	145.0	218.0	20.0	0.1069	0.0884	0.1353
14B'	23.3	54.2	86.5	218.0	20.0	0.1219	0.1069	0.1534
14C'	24.3	54.5	145.0	418.0	97.0	0.047	0.0415	0.0274
14D'	24.5	55.0	145.0	418.0	45.0	0.047	0.0419	0.0578
15A	24.5	55.5	86.5	192.0	97.0	0.2275	0.1953	0.0943
15B	24.8	55.8	86.5	192.0	28.0	0.2318	0.2017	0.2557
15C	25.0	56.0	86.5	192.0	5.0*	0.2335	0.2208	0.5199
15D	24.9	56.0	86.5	204.0	28.0	0.505	0.4679	0.3909

TABLE 6. (contd)

Exp #	TA °C	TS °C	Liquid Circulation ml/min	Absorber Gas Feed sccm	Stripper Gas Flow sccm	mole fraction CO		
						Absorber Feed	Absorber Outlet	Stripper Outlet
15E	24.7	56.1	86.5	204.0	33.0*	0.5078	0.4941	0.7344
15F	26.9	53.6	55.0	204.0	7.0*	0.5094	0.5011	0.7428
18A	24.5	53.3	145.0	310.0	318.4	0.9813	0.964	0.0779
18B	25.1	54.0	145.0	317.0	318.4	0.4979	0.4679	0.0521
18C	25.6	52.5	145.0	303.0	318.4	0.1764	0.1533	0.0267
18D	27.0	57.6	188.5	1188.0	935.0	0.5132	0.502	0.0238
18E	26.2	54.3	145.0	135.0	318.4	0.5148	0.4099	0.0579
18F	26.2	54.4	145.0	51.0	318.4	0.5353	0.2465	0.0506
19A	26.8	72.5	145.0	99.0	319.2	0.2499	0.153	0.0338
19B	27.1	75.6	145.0	99.0	97.2	0.2705	0.1654	0.1358
19C	27.2	73.8	145.0	99.0	28.0	0.2671	0.1739	0.3086
19D	27.3	73.1	145.0	99.0	9.3*	0.258	0.2019	0.6484
19E	27.5	72.2	145.0	99.0	15.0*	0.5041	0.3423	0.7521
19F	27.7	72.3	145.0	286.5	319.2	0.5162	0.4715	0.0703
19G	26.3	73.4	86.5	286.5	319.2	0.5167	0.4803	0.0572

* Measured at exit with no strip feed. All other stripper flows are metered N₂ feed rates.

** Exp #11 was completed with TCE solvent only. All subsequent experiments were completed with a single charge of Pd₂(dpm)₂Br₂ at 0.03 moles/liter.

FIGURE 9. Effect of Feed CO Concentration

FIGURE 10. Effect of Stripper Gas Feed Rate

FIGURE 11. Effect of Stripper Gas Rate

Figure 12 and 13 show only the enhancement due to the complex relative to physical equilibrium. In each figure three pairs of experiments are presented where absorber feed rate or liquid circulation rate were varied while other independent variables remained the same. Enhancement was greater at higher gas rates and lower liquid rates.

Experimental data were compared with the mathematical model. Figures 14 and 15 show some early results indicating that the mass transfer coefficient is in the same order of magnitude with and without complex. Enhancement apparently occurs primarily through the addition of chemical equilibrium to the physical equilibrium capacity of the solution. Figures 16 and 17 show that a mass transfer coefficient (k_1a) of 0.06/s correlates the range of stripper temperatures and the CO feed concentrations tested. The mass transfer model and equilibrium data, confirmed by experiment, can be used to design full scale equipment for process evaluation.

Two series of experiments explored the action of the $\text{Pd}_2(\text{dpm})_2\text{Br}_2$ solution in 1,1,2-trichloroethane on a five component gas mixture. Results are listed

FIGURE 12. Effect of Absorber Feed Rate

FIGURE 13. Effect of Liquid Circulation Rate

FIGURE 14. Correlation of Stripper Gas Rate Effect with Model

FIGURE 15. Correlation of Liquid Rate Effect with Model

FIGURE 16. Correlation of Stripper Temperature Effect

FIGURE 17. Correlation of Absorber Feed CO Concentration Effect

in Table 7 along with a third series (#20) performed after the solution had been flushed from the system with clean solvent. The mixed gas feed contained H_2 , CO, CO_2 and CH_4 in the approximate ratio 1.7:1:1.2:0.5 diluted with varying amounts of N_2 as shown. Comparing stripper product concentrations with absorber feed and product concentrations we see an increase in the CO/ H_2 and CO/ CH_4 ratios in the experiments with complex present. Without complex the stripper product CO/ H_2 ratio is still somewhat enhanced relative to the absorber but not the CO/ CH_4 ratio. The CO/ CO_2 ratio on the other hand is the same or smaller in the stripper product than it is in the absorber even with complex present. Without complex there is a strong selectivity for CO_2 over CO.

The mixed gas data can be explained in terms of combined physical solubility and chemical complexation effects. Detailed analysis would be too complex for the scope of this study but some interesting process applications can be projected. CO_2 is an order of magnitude more soluble in the 1,1,2-trichloroethane solvent than CO or N_2 (see Table 4) which are in turn more soluble than H_2 . Methane is intermediate between CO_2 and CO. When $Pd_2(dpm)_2Br_2$ is added, the resulting solution is selective for all of the non-hydrogen components of an oxygen-blown coal gas. Although the applications involving separation of CO from air blown coal gas remain possible, the high physical solubilities of CO_2 and CH_4 raise the possibility of one step purification for hydrogen-rich streams from oxygen blown coal gasifiers as well. Both types of application will be discussed under Subtask B.4.

After two months of gas separation experiments, spectroscopy indicated that 25-30% of the complex was not $Pd_2(dpm)_2Br_2$ and, thus, unavailable for reversible CO uptake. Due to the presence of a metallic mirror on the interior of some solution storage vessels, reduction-oxidation reactions which form $Pd(dpm)Br_2$ are suspected. Treatment with sodium borohydride and hydrogen chloride may be one route to regenerate the active dimer.⁽¹⁹⁾ Some exposure to oxygen occurred during storage of the dissolved complex which may have contributed to or initiated the redox reactions. This should be avoidable in commercial operations. A further cause of this decomposition is suspected to be due to dehydrochlorination of TCE. Hydrogen chloride exposure to the palladium complex may also cause loss of the active dimer.

TABLE 7. Experiments Using Mixed Gas Feed

Exp #	TA °C	TS °C	Liquid Circulation ml/m	Absorber Gas Feed sccm	Stripper Gas Flow sccm	Absorber Feed, Vol %					Absorber Exit, Vol %					Stripper Product, Vol %				
						H ₂	CO	CO ₂	CH ₄	N ₂	H ₂	CO	CO ₂	CH ₄	N ₂	H ₂	CO	CO ₂	CH ₄	N ₂
16A	23.8	54.0	145.0	870	903	39.0	22.8	27.0	10.3	0.9	41.5	23.4	22.8	10.6	1.6	0.3	1.0	5.1	0.4	93.2
16B	23.7	56.0	86.5	870	903	39.0	22.8	27.0	10.3	0.9	41.5	23.4	23.2	10.7	1.3	--	0.9	4.7	0.3	94.1
16C	23.8	56.9	86.5	870	45	39.0	22.8	27.0	10.3	0.9	--	32.1	39.6	14.7	1.2	2.6	12.1	33.7	3.4	47.9
16D	24.1	55.9	86.5	160	45	39.4	23.0	26.9	10.3	0.3	44.8	21.9	19.5	10.6	3.0	2.9	13.2	30.8	3.9	47.3
16E	25.2	54.8	145.0	160	45	39.4	23.0	26.9	10.3	0.3	43.6	21.7	21.1	10.2	3.2	4.6	13.2	29.1	4.4	48.7
16F	25.1	55.7	86.5	870	319	39.4	23.0	26.9	10.3	0.3	41.6	23.2	23.6	10.5	1.0	0.3	2.3	11.0	0.7	85.7
16G	26.8	54.2	39.2	870	45	39.4	23.0	26.9	10.3	0.3	40.6	22.9	25.5	10.4	0.6	1.4	9.2	28.2	2.2	56.1
16H	25.4	55.2	86.5	835	319	20.6	11.5	13.6	5.2	49.1	21.0	11.3	11.8	5.1	50.8	--	1.2	5.3	0.3	93.2
17A	24.3	55.8	86.5	870	11.9*	39.3	22.5	26.5	10.2	1.6	40.2	22.5	26.3	10.2	0.8	11.3	38.0	41.0	8.0	1.7
17B	24.6	56.5	86.5	160	11.7*	39.3	22.5	26.5	10.2	1.5	41.4	21.6	25.7	10.3	0.9	11.0	37.8	41.0	8.1	2.1
17C	25.6	54.2	47.6	870	9.1*	39.3	22.5	26.5	10.2	1.5	40.1	22.5	26.7	10.2	0.3	9.3	40.1	40.8	8.0	1.8
17D	25.3	54.8	86.5	865	6.2*	20.3	11.3	13.9	5.1	49.4	20.4	11.1	13.7	5.1	49.7	6.3	25.5	20.7	4.4	43.0
17E	25.6	55.5	86.5	865	50	18.8	11.5	14.7	5.2	49.8	19.9	11.1	13.35	15.1	50.6	1.8	9.8	18.4	2.8	67.4
17F	25.8	55.8	86.5	775	50	7.9	4.3	5.3	1.9	80.6	--	5.1	7.0	2.2	85.6	0.6	5.5	7.7	1.1	85.1
17G	25.7	55.7	86.5	800	50	2.9	1.6	1.9	0.1	95.0	2.3	1.4	1.8	0.7	93.8	0.2	2.3	3.4	0.4	93.9
20C	26.9	55.2	86.5	880	97	39.9	22.6	26.6	10.2	0.1	41.3	23.4	23.6	10.3	1.4	1.1	2.5	18.1	2.5	65.8
20D	26.7	55.4	86.5	842	97	20.9	11.5	13.6	5.1	48.9	-----na-----					1.1	1.7	15.9	1.5	79.7
20E	27.1	55.4	86.5	842	28	20.7	11.6	13.6	5.2	49.0	-----na-----					3.3	5.0	21.0	3.8	66.9
20F	26.7	55.2	86.5	842	<1*	20.8	11.5	13.6	5.2	48.9	20.6	11.5	13.4	5.1	49.4	----- no gas flow -----				
20A ¹	26.7	56.1	86.5	1060	2*	36.0	21.0	25.0	10.0	8.0	35.7	21.3	24.7	9.6	8.7	18.2	18.4	39.1	9.6	14.6

* Measured at exit with no strip feed. All other stripper flows are metered N₂ feed rates.

Ruthenium Complex

Initial experiments with gas mixtures containing H_2 , CO , CO_2 , CH_4 , and N_2 showed that $Ru(CO)_2(PPh_3)_3$ reacted almost irreversibly with CO to form $Ru(CO)_3(PPh_3)_2$ with no measurable formation of $Ru(H)_2(CO)_2(PPh_3)_2$ even under a 2:1 atmosphere of hydrogen and carbon monoxide. Although the forward reaction with CO had been found to be an order of magnitude slower than the reaction with hydrogen, apparently CO release is extremely slow resulting in complete conversion to the tris carbonyl. Subsequent experiments were performed with hydrogen and nitrogen mixtures.

Based on the equilibrium data of Figure 8, a triphenylphosphine concentration of 1.0 M was selected to provide adequate reversibility. Since temperature has little effect on the equilibrium, absorption and stripping were both performed at ambient temperature. Helium was used as the stripping gas in anticipation of demonstrating selectivity for H_2 by comparing stripper product gas samples with control experiments performed with benzene alone.

Results are listed in Table 8. As shown by Figure 18, no significant enhancement in selectivity for hydrogen was measured under a variety of conditions. Figure 19 shows the only significant difference between the control experiments and those with the complex: a reduced total gas transfer from the absorber to the stripper. The latter result would occur due to a reduction in the solubility of both hydrogen and nitrogen when 1.0 M triphenylphosphine is added to benzene.

In retrospect, failure to measure enhanced hydrogen uptake in the bench-scale tests can be explained by solution kinetic limitations. The rate of reaction of dissolved hydrogen must be at least as fast as physical absorption in order to demonstrate enhancement. Experimental design, performed when only preliminary data on the hydrogen-complex equilibrium were available, indicated that solution kinetics would be somewhat faster than mass transfer. The more accurate data of Figure 7 indicated that higher than expected concentrations of triphenylphosphine would be required. Repeating the mass transfer-solution kinetic calculations with the new data showed that reaction should be significantly slower than mass transfer. Higher concentrations of triphenylphosphine reduced the concentration of the rate-limiting intermediate $Ru(CO)_2(PPh_3)_2$.

TABLE 8. Results of Gas Separations Performed with 0.021 M $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and 1.0 M PPh_3 Dissolved in Benzene

Exp #*	Solution Circulation (mL/min)	Absorber Gas Feed (sccm)	Stripper He Feed (sccm)	Absorber Feed Comp.		Stripper Exit (Bal. He)		H_2/N_2
				Nitrogen (mole %)	Hydrogen (mole %)	Nitrogen (mole %)	Hydrogen (mole %)	
1C	215	120	110	0	100	0.47	9.08	NA
1	215	120	110	0	100	0.46	4.56	NA
2C	70	940	905	0	100	0.48	0.36	NA
2	70	940	905	0	100	0.36	0.11	NA
3C	215	880	905	52.16	49.56	1.16	0.36	0.31
3	215	880	905	50.24	49.26	0.81	0.13	0.16
4C	215	880	110	50.32	47.72	5.05	3.77	0.75
4	215	880	110	52.77	49.15	3.2	2.25	0.70
5C	215	119	110	44.91	53.3	4.99	4.34	0.87
5	215	119	110	46.37	53.78	2.83	2.58	0.91
6.1C	215	125	110	72.75	17.76	9.24	1.17	0.13
6.2C	215	125	110	83.36	14.69	8.67	0.82	0.09
6.1	215	125	110	82.19	17.08	8.76	1.73	0.20
6.2	215	125	110	81.52	16.49	5.01	0.19	0.04
6.3	215	125	110	79.12	19.94	3.7	0.54	0.15
6.4	215	125	110	77.74	18.48	4.1	0.57	0.14
7C	170	119	110	45.23	56.75	4.8	4.32	0.90
8C	70	119	110	45.13	56.53	2.97	1.92	0.65
9C	215	220	110	87.01	10.53	8.69	0.45	0.05
9	215	220	110	87.39	11.53	4.32	0.16	0.04
10C	120	430	63	91.29	5.2	12.48	0.13	0.01
10	120	430	63	90.91	5.66	6.27	0.05	0.01
11C	120	220	63	88.18	8.08	12.4	0.64	0.05
11.1	120	220	63	85.38	10.8	7.09	0.29	0.04
11.2	120	220	63	87.3	8.99	6.25	0.14	0.02

* Note that experiments marked with C were controls run with benzene alone.

FIGURE 18. Mole Ratio of H₂/N₂ in Stripper Product

FIGURE 19. Percentage H₂ and N₂ in Stripper Product

Future work with the ruthenium complex will focus on substituting a modified ligand for at least one of the PPh_3 groups. The ligand will be selected to reduce the strength of the Ru-CO bond while providing a basic site for ion-exchange. If successful, reduced Ru-H bond strength would also likely result and lower concentrations of triphenylphosphine, or its equivalent, would be required. The net effect should be higher concentrations of the active intermediate and improved kinetics.

SYSTEM ECONOMICS

The information discussed within this section concerns potential system applications and projected economics for gas separation using $\text{Pd}_2(\text{dpm})_2\text{X}_2$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$.

Potential System Applications

$\text{Pd}_2(\text{dpm})_2\text{X}_2$ has two unique properties of commercial interest. It can selectively remove CO from mixtures with hydrogen and nitrogen and it can react with hydrogen sulfide yielding hydrogen gas (discussed under Task C). The CO reaction is reversible and was well characterized in bench-scale experiments. Insufficient data are available on reversibility to include the sulfur reaction in conceptual designs, but its potential utility in combination cleanup-separation schemes is obvious.

The properties of the palladium complex indicate potential advantages over existing technology both for hydrogen production from oxygen-blown coal gas and for production of byproduct CO for chemical use from an oxygen or air blown gasification facility. While fixed bed, selective adsorption technology (i.e., pressure swing adsorption) can produce high purity hydrogen from feeds with as little as 60% hydrogen, hydrogen recovery decreases for feeds containing less than 85% hydrogen.⁽²⁰⁾ Dry membrane technology (for example, the Prism® system) can achieve good recovery with staging, but hydrogen is produced in the low pressure stream requiring recompression. Separation of CO from nitrogen can be accomplished with a copper complex (i.e., COSORB®) but only in a water-sensitive system requiring feeds with moisture reduced to the ppm level.

Figure 20 shows a block flow diagram for hydrogen production from oxygen blown coal gas using a $\text{Pd}_2(\text{dpm})_2\text{X}_2$ -based separator. Only a relatively robust, high temperature, shift catalyst is required. Unconverted CO is recycled by the complex and CO_2 , not removed in the acid gas unit, is recycled by physical solubility. Figure 21 shows an air-blown gasification facility producing fuel gas and high purity CO for chemical production. Carbon monoxide is an important feedstock for intermediate chemicals used in plastics manufacture.

$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ reacts with CO, as does the palladium complex; however, it also reacts reversibly with hydrogen gas. These reactions raise the possibility of selectively separating CO and hydrogen from low-BTU, air-blown, coal gasifier product to yield medium-BTU fuel or chemical synthesis gas. Although bench-scale tests showed that the dissolved complex reacted with CO to the

FIGURE 20. Process for Recovery of Hydrogen from Coal Gas

FIGURE 21. Process for Recovery of Carbon Monoxide from Coal Gas

exclusion of hydrogen, addition of a charged ligand to hold the complex in an ion exchange membrane may give appropriate reversibility for both reactions.

No commercial technology is currently available for one step separation of CO and H₂ from nitrogen bearing streams. As a result, expensive air separation units are usually specified for producing synthesis gas from coal. Availability of a simple, CO-H₂ selective separator would eliminate the need for oxygen plants wherever air-blown gasification would be more economical.

Projected Economics

Selectivity can be enhanced using dissolved complexes in absorber-stripper systems as demonstrated with palladium in bench-scale experiments, or in membrane systems. In both design options, the amount of the relatively expensive complex required for a given separation capacity is crucial to system economics. Estimates and projected costs are presented for hydrogen production from oxygen-blown coal gas, carbon monoxide production from air-blown coal gas and synthesis gas production from oxygen enriched air-blown coal gas. These are compared with the costs of existing technologies.

Using the mathematical model developed for bench-scale design, palladium inventories per unit capacity were estimated for an absorber and stripper producing hydrogen in the "Separation System" block of Figure 20. Calculations were based on 0.03 molar Pd₂(dpm)₂Br₂ in 1,1,2-trichloroethane solvent. It was assumed that a higher ratio of effective surface area to geometrical surface can be achieved in a scaled up system than was the case in the bench-scale experiments. A mass transfer coefficient of 0.06/sec and a 10 vol.% liquid hold-up were used based on literature correlations for one inch packing rings operated at a liquid/gas weight ratio of 200. At the 85°C stripping temperature selected, a steam-solvent vapor mixture could be used at atmospheric pressure. The flowsheet of Table 9 was developed based on 95% efficient separation of CO and CO₂ from H₂ and N₂ and an even split of methane between the product streams. A 100 psig absorption pressure was selected and the model used to calculate the required packing heights for 95% recovery of CO from an inert gas entering with 11% CO at 100 lbs/ft²/h. Absorption required 6 meters of packing and stripping 9 meters (Figure 22). At the selected pressures, the assumed efficiencies for hydrogen yield and removal of carbon dioxide by solubility

TABLE 9. Gas Separation Flowsheet for Hydrogen from Coal Gas

Component	Raw Gas Feed (%) [*]	Steam Feed (%) [*]	Shift Inlet (%) [*]	Shift Exit (%) [*]	Acid Gas Removed (%) [*]	CO-Rich Recycle (%) ^{**}	H ₂ -Rich Product (%) ^{**}
CH ₄	0.3	--	0.4	0.4	0.7	0.8	0.4
H ₂	29.8	--	21.7	47.9	81.2	10.5	97.1
CO	41.0	--	32.7	6.5	11.1	27.2	0.7
CO ₂	10.2	--	10.0	36.2	6.1	15.0	0.4
H ₂ O	16.9	20.0	34.5	8.3	0.1	46.4	0.4
H ₂ S	1.1	--	0.2	0.2	0.03	0.0	0.0
N ₂	0.7	--	0.5	0.5	0.8	0.1	1.0
moles	100.0	20.0	154.6	154.6	91.1	35.4	72.4

* Projected gasifier pressure, 40.8 atm.

** H₂-rich product leaves at the absorber design pressure of 7.8 atm while the CO-rich recycle is leaves the stripper at 1 atm.

should be easily achieved. Since the stripper product is compressed and recycled, the overall yield of hydrogen based on input CO and hydrogen is 100%. In practice some minor losses would occur in the carbon dioxide removal system.

For the calculated palladium complex requirement, the impact of replacement cost on cost of hydrogen separation is significant. Cost of Pd₂(dpm)₂Br₂ was estimated at \$650/lb based on a 25% mark-up for palladium and 100% for the organic starting materials over market values. The calculated initial investment in palladium complex is therefore 60¢ per 1000 standard cubic feet (MSCF) of annual hydrogen capacity. If we assume 75% of the palladium value can be recovered in reprocessing, replacing degraded complex should cost \$200/lb. Figure 23 shows the effect of replacement time on total separation cost assuming a capital investment of \$1.60/MSCF of annual capacity charged at 30% per year. Direct comparison with existing technology is difficult because a second, expensive low temperature shift step is generally added to proposed flowsheets followed by selective adsorption for final purification. Selective adsorption alone, starting with a 90% hydrogen feed, adds in the range of 30 to 50¢/MSCF.⁽²¹⁾ The current price for purified H₂ is about \$12.50/MSCF.⁽²²⁾

FIGURE 22. Computer Model Design for CO-H₂ Separation

FIGURE 23. Effect of Complex Life on the Separation Cost for Hydrogen

A system to separate CO from air-blown coal gas (Figure 21) was designed with similar assumptions to those outlined above. Both the absorber and stripper required 5.5 meters of packing when the complex $\text{Pd}_2(\text{dpm})_2\text{I}_2$ was used. The initial investment in complex would be 4.6¢ per annual pound of CO capacity based on the flowsheet of Table 10. Figure 24 shows the effect of replacement

TABLE 10. Gas Separation Flowsheet for CO from Coal Gas

Component	Raw Gas Feed (%)*	Acid Gas Removed (%)*	H ₂ -Rich Fuel Gas (%)*	CO-Rich Product (%)**
CH ₄	1.2	1.8	1.2	3.6
H ₂	15.7	22.9	28.6	4.7
CO	16.3	23.8	7.8	73.0
CO ₂	6.9	0.5	0.1	2.0
H ₂ O	24.6	0.4	0.4	2.2
H ₂ S	0.6	0.04	0.0	0.0
N ₂	34.7	50.6	61.9	14.5
moles	100.0	68.5	52.1	16.7

* The gas pressures were projected at 8.2 atm.

** The CO-rich product was assumed as 1.4 atm.

FIGURE 24. Effect of Complex Life on the Separation Cost for Carbon Monoxide

time on total separation cost assuming a capital investment of 9¢ per annual pound of CO capacity charged at 30% per year. Separation costs between 4-6¢/lb have been published⁽²³⁾ for the commercially available COSORB® process producing 150 million pounds per year of CO from similar feed gases. Complex life greater than one year would apparently be required to be competitive.

Cost and lifetime of the palladium complexes are the greatest source of uncertainty in the above evaluations. The burden of complex cost could be significantly reduced for both the hydrogen and CO applications if the complex could be used in a membrane system. Design of such a system would be speculative at this point, but we estimate that the contribution of palladium complex cost to initial investment as well as sensitivity to replacement time could be reduced by an order of magnitude. Flowsheets would be similar to those shown in Figures 20 and 21 and Tables 9 and 10 except that more dilute strip gas streams would be required to compensate for isothermal operation. The order of magnitude reduction in palladium inventory was estimated based on laboratory kinetics, literature values for diffusivity and recent publications on facilitated transport.⁽²⁴⁾

Figure 25 illustrates a possible application of the ruthenium complex in a facilitated ion exchange membrane (IEM). The feed gas used for the example represents the product of a Texaco gasifier blown with oxygen-enriched (45%) air. Below 1000 tons/day coal capacity, enriched air would likely be more economical than oxygen gasification with a process such as the proposed IEM available to recover CO and H₂ from the nitrogen-containing product.

Economic comparison is difficult at this early stage because performance assumptions must be made and because no competitive technology is commercially available for the same separation. The figure shows COSORB® and pressure swing adsorption (PSA) technologies in series separating CO and hydrogen from the same feed gas. It was assumed that the PSA system could accomplish 70% recovery of hydrogen which is probably high for this application in which a significant amount of purge would be required to clear adsorbed N₂ from the PSA beds. The capital cost of the IEM unit was estimated by using a 50% premium over a vendor quote for a conventional membrane system designed for the same permeate rate, assuming a facilitation factor of 15 and adding the cost of ruthenium at \$90/troy ounce (Ru amounted to only 1% of the capital cost). In mid-1985 dollars the estimated investment to process 4800 moles/hr of stream A is \$8.2 MM. Published cost information on the COSORB® and PSA units adjusted to the same basis gives \$14 MM and \$1.7 MM, respectively.^(21,23) These estimates indicate that conventional technology would cost twice as much for the same separation with a lower recovery than the IEM.

The IEM unit is shown in a system that would consume about 500 tons/day of coal and produce either 27 MM standard cubic feet per day of synthesis gas for chemical production (producing n-butanol, isocyanates or 2-ethyl hexanol requires synthesis gas in this range of capacity) or a similar quantity of hydrogen (to power fuel cells for about a 50 MW capacity). Other possible applications would include splitting a CO + H₂ stream from a larger air or oxygen-blown gasifier-based power plant for coproduction of chemicals. The assumptions regarding performance of the IEM are equivalent to a membrane cost of \$2.70/ft² and a CO+H₂ flux of 9 SCF/ft²/day. Figure 26 shows the effect of the flux assumption on the membrane capital cost charged at 30%/year. These costs should be compared with capital cost savings from gasifying 500 tons of coal per day with air rather than oxygen.

CO+H₂ Recovery: 98%

Stream	A	B	C
H ₂ , %	24	1	37
CO, %	38	2	51
CO ₂ , %	8	22	8
N ₂ , %	30	75	4
P, psia	115	110	15

Ru-Facilitated IEM

Pressure Swing Adsorption

CO+H₂ Recovery: 86%

Stream	A	B	C1	C2
H ₂ , %	24	15	<1	99
CO, %	38	4	98	<1
CO ₂ , %	8	15	2	<1
N ₂ , %	30	66	<1	<1
P, psia	115	15	100	100

Conventional Technology

FIGURE 25. Ruthenium-Facilitated IEM System Application, Small Scale Synthesis Gas or Fuel Cell Hydrogen

FIGURE 26. Membrane Separation Cost for H₂ and CO from Air Blown Coal Gas

EXAMINATION OF REVERSIBLE H₂S BINDING

A solution of Pd₂(dpm)₂Cl₂ in dichloromethane when exposed to H₂S produced H₂ gas and Pd₂(dpm)(μ-S)Cl₂. Thus, hydrogen was split from the H₂S molecule and sulfur was incorporated between the two palladium atoms. The reaction is shown below:

Quantitative measurement using a standardized gas chromatographic procedure indicated that 97% of the theoretical amount of hydrogen was detected. Both ¹H-NMR and ³¹P-NMR confirmed the structure of Pd₂(dpm)₂(μ-S)Cl₂ as similar to that previously reported.⁽¹⁸⁾ The reaction of Pd₂(dpm)₂Br₂ with H₂S was considerably slower than that of Pd₂(dpm)₂Cl₂, while Pd₂(dpm)₂I₂ did not seem to react at all with H₂S. This indicates some specificity for H₂S within the Pd₂(dpm)₂X₂ series.

When $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$ was exposed to 3.5 atm of CO it appeared that the CO was inserted into the bridged A-frame between the sulfur and palladium atoms. Preliminary analysis suggests a $\text{PdC}(\text{O})\text{S Pd}$ structure.

Several attempts were made to regenerate $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ from $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$ by oxidizing the sulfur to SO_2 . Initial oxidation attempts with H_2O_2 , pyridinium chlorochromate, pyridinium dichromate, and m-chloroperbenzoic acid produced mixtures of $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO}_2)\text{Cl}_2$, $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO})\text{Cl}_2$, and $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. The appearance of $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO})\text{Cl}_2$ is quite interesting since this complex has not been reported previously and few $\mu\text{-SO}$ complexes are known. A two step oxidation of $\mu\text{-S}$ to $\mu\text{-SO}_2$ is implied. The ^{31}P -NMR spectrum of $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO})\text{Cl}_2$ shows an $\text{AA}'\text{BB}'$ pattern with chemical shifts of $\delta_{\text{A}} = \delta_{\text{A}'} = 0.67$ ppm and $\delta_{\text{B}} = \delta_{\text{B}'} = 19.09$ ppm. The coupling constants are $J_{\text{AA}'} = 89.93$ Hz, $J_{\text{AB}} = J_{\text{A}'\text{B}'} = 359.32$ Hz, $J_{\text{AB}'} = J_{\text{A}'\text{B}} = 321$ Hz and $J_{\text{BB}'} = 24.79$ Hz. Computer generated spectra confirmed the assignments of chemical shifts and coupling constants. Collection of diffraction data of a single crystal of $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO})\text{Cl}_2$ has been completed.

The SO_2 adduct was formed in high yields when the oxidation was performed at -20°C with two equivalents of oxidant. Alternatively, oxidation of $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$ with a slight excess of m-chloroperbenzoic acid at -20°C followed by addition of hydrazine to eliminate excess oxidant gave the desired $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO}_2)\text{Cl}_2$ in 76% yield.

The violet $\text{Pd}_2(\text{dpm})_2(\mu\text{-SO}_2)\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes lose SO_2 when N_2 is bubbled through the solution. The rate of SO_2 loss decreases in the qualitative order $\text{I} > \text{Br} > \text{Cl}$ as judged by color change in samples of similar concentrations.

The reaction of H_2S with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ was also examined. The product was a mixture of the oxidative adduct, $\text{Ru}(\text{SH})(\text{H})(\text{CO})_2(\text{PPh}_3)_2$, and the sulfur coordinate, $\text{Ru}(\text{H}_2\text{S})(\text{CO})_2(\text{PPh}_3)_2$ (45%) at 25°C in tetrahydrofuran (thf). The ratio of products remained the same even after 18 hours. However, when the reaction was performed at 60°C the sulfur coordinated complex was the only product at 98% yield. Refluxing the oxidative adduct in thf under N_2 did not convert it to the sulfur coordinate. However, refluxing the oxidative adduct under an H_2 atmosphere in the presence of triphenylphosphine yielded the sulfur

coordinate in 58% yield. There was no evidence of the oxidative adduct after 0.5 hour. Combination of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and H_2S in thf at -35°C gave a 95% yield of the oxidative addition product. The ^1H -NMR spectra of the two hydrogen sulfide products are quite distinct: oxidative adduct, $\delta_{\text{SH}} = -3.52$ (doublet of triplets) and sulfur coordinate, $\delta_{\text{SH}_2} = -2.59$ (triplet).

When the hydrogen adduct, $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ was exposed to H_2S while in refluxing thf, the product was the sulfur coordinate. At room temperature the dihydride formed a 1:1 mixture of sulfur coordinate and oxidative adduct when exposed to H_2S . The carbon monoxide adduct, $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, when exposed to H_2S in refluxing thf was not as readily converted to the sulfur coordinated complex. Approximately 10% of the H_2S exchanged complex was observed after 3 hours. Of considerable interest was the recovery of 96% $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ after exposing $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ in thf to H_2S and triphenylphosphine followed by refluxing under nitrogen. This suggests that H_2S can be reversibly removed under specific conditions.

The analog, $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$, where py = pyridyl, reacted with H_2S in a similar manner. At 25°C , the product contained 86% of the oxidative adduct and 14% of the sulfur coordinate after one hour. The yield of this mixture was 91%.

The $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ complex was also exposed to H_2S while in dichloromethane solution. The isolated crystalline product was examined with ^1H -NMR and appeared to contain two types of hydride bonds (Ir-H). This suggests that both cis and trans isomers were formed. The iridium complex oxidatively added a hydride and a mercaptan (SH) group to the metal.

GLOSSARY

The abbreviations for ligands and complexes used in this report are shown below with their chemical nomenclature.

PPh_3	triphenylphosphine
dpm	bis(diphenylphosphino)methane
Ph_2Ppy	diphenylpyridylphosphine
Ppy_3	tripyridylphosphine
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$	dicarbonyltris(triphenylphosphine)ruthenium
$\text{Pd}_2(\text{dpm})_2\text{Cl}_2$	dichlorobis[μ -bis(diphenylphosphino)methane]- dipalladium(Pd-Pd)
$\text{Co}(\text{N}_2)(\text{PPh}_3)_3$	(dinitrogen)tris(triphenylphosphine)cobalt
$[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$	bis(cyclopentadienyltricarbonylchromium)
$(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$	cyclopentadienylhydridotricarbonylchromium

Section 1

The association for the purpose of the law is to be determined by the facts and circumstances. The association is not to be determined by the mere fact that the parties are related by blood or marriage. The association is to be determined by the facts and circumstances, and the law is to be applied accordingly.

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CONCLUSIONS

The separation of gases, especially hydrogen and carbon monoxide, using coordination complexes was previously explored in a micro-batch manner⁽¹⁾. The results of that work were used to operate a continuous bench-scale apparatus consisting of absorber and stripper columns. Separation of CO/N₂ and CO/H₂/CO₂/CH₄/N₂ mixtures were examined using 1,1,2-trichloroethane (TCE) both with and without dissolved Pd₂(dpm)₂Br₂.

The separation of the binary gas mixture (CO/N₂) was enhanced by the presence of the complex, particularly at higher gas rates and lower liquid rates. The quinary gas mixture produced rather interesting results within the system. With the complex an increase in the CO/H₂ and CO/CH₄ ratios was noted by comparing stripper product concentrations with those of the absorber feed and product streams. Without complex the CO/H₂ ratio was still somewhat enhanced, but the CO/CH₄ ratio was not. The complex reduced the strong selectivity for CO₂ over CO due to the physical solubility of CO₂ in TCE. These results are due to the combined physical solubility and chemical coordination effects. For instance, CO₂ is an order of magnitude more soluble in TCE than CO or N₂, which are in turn more soluble than H₂. Methane solubility is intermediate between that of CO₂ and CO. The presence of the palladium complex allows a "selectivity" for all the gases except hydrogen. Thus, a one-step, hydrogen separation can be achieved from gas mixtures with compositions similar to that of oxygen-blown coal gas.

The projected economics for hydrogen separation by this process are critically dependent on the lifetime of the palladium complex in solution. The laboratory experience with trichloroethane as the solvent suggested that the complex longevity was less than needed for commercial application. However, previous experience with dichloromethane as a solvent for the complex was very favorable. Thus, solvent choice has a considerable effect on the lifetime of the complex.

Results from the mixed gas experiments with the ruthenium complex indicated that CO release was extremely slow, even with mixtures having twice as much H₂ than CO. With binary (H₂/N₂) mixtures, no significant enhancement for

hydrogen was noted under a variety of conditions. Refined solution kinetics showed that the H_2 uptake should be slower than mass transfer through benzene. Modification of the ligands should improve these kinetic limitations.

An alternative complex, $[(C_5H_5)Cr(CO)_3]_2$, was found to have excellent promise as a reversible H_2 carrier.

The dissolved palladium complex was found to strip hydrogen gas from H_2S . The sulfur from H_2S was incorporated within the complex, but could be removed (as SO_2) with a variety of mild oxidants. There was a definite specificity for H_2S within the $Pd_2(dpm)_2X_2$ series since the chloro-complex reacted relatively fast while the iodo-complex appeared inert to H_2S . The potential utility of this reaction in a combination cleanup-separation scheme is evident.

FUTURE DIRECTIONS

The properties and the preliminary economics of the palladium complex indicate potential advantages over existing technology both for hydrogen production from oxygen-blown coal gas and for production of byproduct CO for chemical use from an oxygen or air blown gasification facility. While fixed bed, pressure swing adsorption can produce high purity hydrogen from feeds with as little as 60% hydrogen, hydrogen recovery decreases for feeds containing less than 85% hydrogen.⁽²⁰⁾ Thus, no commercial technology is currently available for one step separation of CO and H₂ from nitrogen bearing streams. As a result, expensive air separation units are usually specified for producing synthesis gas from coal. Availability of a simple, CO-H₂ selective separator would eliminate the need for oxygen plants wherever air-blown gasification would be more economical.

Further improvement of the system discussed in this report could be achieved by utilizing the complex as a carrier within a facilitated transport membrane. The advantage of facilitated transport combined with coordination complexes depends upon the increase in selectivity due to the complexes. Further, this can be combined with the selectivity of specific solvents (immobilized liquid membranes). Such a system was examined at PNL. A membrane cell was kindly loaned to us by J. D. Way and R. D. Noble of the National Bureau of Standards Center for Chemical Engineering. Celgard® 2500, a polypropylene film, was the membrane material and TCE was the liquid used to complete the immobilized liquid system. The TCE was removed from the membrane with time indicating the need for a less volatile liquid. The palladium complex was dissolved in TCE and applied to the membrane surface. Unfortunately, <0.1g of complex was retained within 200 cm² of membrane. The gas compositions (N₂-CO) were not noticeably different with the addition of the dissolved complex. Thus, it is apparent that attachment of a complexing agent to an ion exchange membrane (IEM) is necessary to achieve higher concentrations of the complex. This would also eliminate the stringent requirements for the immobilized solvent; i.e., that it be an excellent solvent for the complex and also relatively nonvolatile. Attachment of the complex in this manner could also be quite helpful for the ruthenium complex since it would reduce the basicity of the

metal center. This, in turn, would reduce the tenacity of the metal for both H_2 and CO which should improve reversibility of the initial gas binding.

An alternative strategy that we consider promising for H_2 separation, and to our knowledge has not been investigated, is the use of catalysts that will reversibly incorporate hydrogen into a substrate(s); i.e., catalyze hydrogenation and dehydrogenation reactions. Such a catalyst/substrate system in an immobilized liquid membrane (ILM) will give facilitated transport of hydrogen where the carrier is now the substrate rather than the transitional metal. We expect that the transition metal concentration in a catalytic facilitated transport system will be approximately two orders of magnitude less than that in a transition metal carrier system. Thus, the utilization of the transition metal complex is much more efficient since the metal merely acts as a shuttle between dissolved H_2 and the actual substrate carrier. The use of catalytic amounts of complex considerably lowers capital outlay without sacrificing selectivity or permeability.

The ultimate driving force for H_2 permeation in this catalytic system is the differential partial pressure of H_2 on either side of the membrane. Hydrogen entering the membrane is used to hydrogenate an unsaturated substrate. The hydrogenated substrate diffuses across the membrane and is dehydrogenated forming hydrogen, which exits the low pressure side. This allows the substrate to diffuse back across the membrane. The effective hydrogen concentration within the membrane (concentration of dissolved H_2 + concentration of hydrogenated substrate) is not limited by the normal solubility of H_2 in the solvent resulting in high H_2 selectivity. Hydrogen permeability is, in part, a function of the kinetics of the overall reaction.

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STATEMENT

The undersigned do hereby certify that the within and foregoing is a true and correct copy of the original as the same appears in the records of the County of [] State of []

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EXPERIMENTAL

All laboratory syntheses were performed under Schlenk (vacuum or inert gas) conditions.

Copper (II) Dimethoxide

Lithium ribbon (0.71 g, 0.102 mole) was placed in a 250 mL flask and 100 mL of methanol was added. A CuCl_2 (6.29 g, 0.047 mole) solution in 50 mL of methanol was added dropwise. The resulting green precipitate turned blue after 4 days of stirring. The blue precipitate was filtered, washed with methanol, and dried under vacuum.

$\text{Na}[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]$

The procedure developed by R. B. King⁽⁸⁾ was used for preparation of this intermediate. Freshly cracked cyclopentadiene (5.9 mL, 72 mmol) was added to Na sand (1.37 g, 60 mmol) in 50 mL of diglyme and stirred overnight. This solution of NaC_5H_5 was added to solid $\text{Cr}(\text{CO})_6$ (8.8 g, 40 mmol) and refluxed 7.5 h. The solution of $\text{Na}(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3$ thus formed was divided in half for the preparation of $[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ and $(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$.

$[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$

To half of the above prepared solution of $\text{Na}(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3$ was added allylbromide (3.0 mL, 35 mmol) and the solution turned green. Methanol (5 mL) and 150 mL of water were added to precipitate the dimer complex which was then filtered and washed with 200 mL of pentane. The dimer was purified by sublimation at 100°C and 0.06 torr.

$(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$

Diglyme was removed from half of the previously prepared solution of $\text{Na}(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3$ and the yellow solid was redissolved in 40 mL of 0.5N NaOH. The solution was washed with 80 mL of ether and the NaOH solution filtered and acidified with 2N acetic acid (ca 35mL) to give a green precipitate.⁽⁹⁾ Sublimation at 50 to 60°C gave a low yield of $(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$.

$\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$

Hydrogen sulfide was bubbled for 20 minutes through a solution of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ (0.6 g, 0.57 mmol) in 40 mL of dichloromethane. The color of the solution instantly changed from orange to brown upon addition of H_2S . Diethyl-ether was added to precipitate the brown product. This solid was recrystallized from a solution of dichloromethane and ether. The yield was 0.6 g, 97% of theoretical. Both ^1H -NMR and ^{31}P -NMR were consistent with the assigned structure.

$\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Br}_2$

A solution of $\text{Pd}_2(\text{dpm})_2\text{Br}_2$ (0.3 g, 0.26 mmol) in 40 mL of dichloromethane was saturated with H_2S and stirred for 15 hours. Ether was added to precipitate the brown product: yield, 0.27 g, (88%). Calcd. for $\text{Pd}_2\text{C}_{50}\text{H}_{44}\text{P}_4\text{Br}_2$: C, 51.13; H, 3.78; S, 2.73. Found: C, 51.16; H, 3.71; S, 2.85.

$\text{Pd}_2(\text{dpm})_2(\mu\text{-SO})\text{Cl}_2$

To 0.31 g, 0.28 mmol, of $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$ in 20 mL of dichloromethane at -20°C was added 0.58 g, 0.28 mmol of m-chloroperbenzoic acid in 10 mL of dichloromethane (also at -20°C). The solution was slowly warmed to 25° and ether was added to precipitate the sulfoxide product; 0.27 g for 86% yield.

Oxidation of $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$

To 0.11 g (0.1 mmol) of $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$ in 50 mL of dichloromethane (containing 1 mL of ethanol) at -20°C was quickly added 56 mg (0.28 mmol) of m-chloroperbenzoic acid in 5 mL of dichloromethane. The solution was stirred at -20° for 15 minutes. Then 2 mg (0.06 mmol) of hydrazine in 1 mL of dichloromethane was added. After 5 minutes at low temperature the solution was refluxed for about 5 minutes. The solution was concentrated to 15 mL by rotary evaporation. Orange crystals were precipitated by ether; 80 mg for 76% yield.

$\text{Pd}_2(\text{dpm})_2(\mu\text{-SO}_2)\text{Cl}_2$

Sulfur dioxide was bubbled for 20 minutes through a solution of 0.4 g, 0.38 mmol, of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ in 20 mL of dichloromethane. The color of the solution changed from red to purple. Ether was added to precipitate the purple crystals. The yield was 0.4 g (98%).

$\text{Pd}_2(\text{dpm})_2(\mu\text{-SO}_2)\text{Br}_2$

Sulfur dioxide was added to 0.2 g, 0.17 mmol, of $\text{Pd}_2(\text{dpm})_2\text{Br}_2$ dissolved in 80 mL of dichloromethane. The color of the solution changed to a brownish purple. Ether was added to precipitate the crystalline product. The yield was 0.18 g (97%). Both ^1H -NMR and ^{31}P -NMR were consistent with the assigned structure.

$\text{Ru}(\text{CO})_2(\text{H}_2\text{S})(\text{PPh}_3)_2$

To 0.28 g (0.30 mmole) $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ dissolved in 40 mL of tetrahydrofuran was added an atmosphere of H_2S . The solution was refluxed for 15 min. The color of the solution changed from yellow to a greenish orange. The volume of the solution was reduced and hexane was added. yellow crystals (0.21 g, 98% yield) of the sulfur-coordinated complex were obtained.

$\text{Ru}(\text{H})(\text{SH})(\text{CO})_2(\text{PPh}_3)_2$

To 0.17 g (0.18 mmole) of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ dissolved in 50 mL of thf at -35°C (CH_3CN -liquid N_2 bath) was added H_2S for 2 hours. The volume of the solution was reduced to 10 mL and hexane (-35°C) was added. Yellow oxidative adduct (0.12 g, 95% yield) was obtained.

$\text{IrH}(\text{SH})(\text{CO})\text{Cl}(\text{PPh}_3)_2$

To 0.3 g, 0.33 mmol, of $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ dissolved in 30 mL of dichloromethane was added H_2S until the solution was saturated with the gas. The color of the solution changed from yellow to light yellow during one hour of stirring. Volume of the solution was reduced under vacuum to 15 mL, and hexane was added to precipitate the white product. Both ^1H -NMR and ^{31}P -NMR were consistent with the structure.

STANDARD OPERATING PROCEDURES FOR GAS SEPARATION BENCH SCALE APPARATUS

EQUIPMENT DESCRIPTION

The bench scale apparatus, Figure 26 consists of an absorber, stripper and associated equipment. Solution containing the dissolved complex circulates between the absorber and stripper absorbing CO , H_2 and/or CO_2 and transferring them to the stripping gas. Valves in flowmeters F2, F3 and F4 control flow of gas from the supply cylinders. The speed of the pump controls and F1 monitors flow of solution. Heaters, controlled by H1, H2 and H3, heat solution and gas entering the stripper. Additional trace heaters maintain external temperature for the stripper and stripper exit gas line. The cooler, controlled by water flow and level, cools solution leaving the stripper. The condenser, controlled by water flow, cools gas leaving the stripper and condenses vaporized solvent. Manometers M1, M2 and M3 monitor liquid feed, stripper and absorber differential pressures, respectively as well as providing relief in case of overpressure. Thermocouples (T1 through T19) monitor temperatures as indicated and supply control points for the heaters. Liquid sample valves are located at S5 through S8 while S1 through S4 allow direct gas sampling by syringe. Table 11 lists equipment specifications.

NORMAL OPERATIONS

Charging Solution

Before charging solution to the system, the levels in M1, M2 and M3 should be checked. The gas blanket between the pump discharge line and M1 should be maintained as required using the purge meter or vent valve. The solution level on the process side of the purge meter (B) should be above the tee by about 1/2 of the M1 reading (A).

Solution can be added to the system at S6, S7 or S8. Approximately 250 ml should be required for steady operation. The exact amount will vary and should be adjusted to maintain an operable level in the base of the stripper. During high-temperature regeneration experiments, solvent vapor loss through the condenser vent may be appreciable. The resulting gradual drop in the stripper

TABLE 11. Equipment Specifications

Flowmeters

<u>#</u>	<u>Tube</u>	<u>Range, sccm</u>
F1	604	20-502 water
F2	602	20-860 N ₂
F3	603	100-2440 N ₂
F4	602	20-860 N ₂

Pump

Magnetically coupled, carbon gear pump
 Capacity: 300 ml/min @ 0 psig
 240 ml/min @ 40 psig (max)
 Suction: 6 ft H₂O dry, 28.5 in Hg when primed
 Maximum Temperature: 135°C

Heaters

<u>#</u>	<u>Power, Watts @ 120 Vac</u>	<u>Max Temp, °C</u>
H1	312	650
H2	312	650
H3	312	650
Trace Heaters	142 each	450

base level should be made-up by adding solvent. In all cases, volumes or weight and complex contents of all additions and removals (including samples) should be carefully recorded.

Initially, solution should be added at S7 and pumped through the system until circulation is established and a steady level obtained in the stripper base. Additional solution will be required when gas flow is started. If pressure at S7 makes addition difficult, S8 may be used.

Heat Up

Before the initial charge of solution, set points for the variable transformers controlling trace heating of the stripper and stripper outlet gas line should be determined. The voltages should be adjusted to maintain T12, T13 and T14 close to the desired operating temperature and the gas line temperature at least 10°C hotter. Stripper temperatures may take several hours to equilibrate. Circulation will cause readings to change but the voltage settings

should not be adjusted because the intent is only to balance heat loss. Temperature control is to be achieved with the gas and liquid heaters (H1, H2 and H3). Cooling water flow should be established through the cooler and condenser before beginning circulation.

After circulation is established, H1 and H2 should be used to raise the temperatures at T8 and T9 until the desired temperature is reached at T16. If conditions require setting T8 or T9 near or above the boiling point of the solvent, care should be taken to reduce the set points as soon as any flow reduction is made. T8 and T9 should never exceed 250°C.

While establishing gas flow and before starting feed of absorbed components to the absorber, H3 should be used to obtain the desired stripping temperature at T11. T10 should not exceed 250°C.

Circulation and Gas Flow

A small nitrogen feed to both the absorber and stripper should be established to prevent backflow of solution. The pump speed should be increased gradually to allow solution to return to the base of the stripper. If solution is building up in the absorber base, the absorber nitrogen flow may need to be increased before full liquid circulation can be achieved. If solution is not building in the absorber but the stripper base level is too low to cover the liquid outlet, solution should be added at S7 or S8.

Gas flow should be established with nitrogen to both columns (F2, F3) and, when temperatures are set, absorber nitrogen (F3) should be reduced to the desired setting and replaced with the desired flow of absorbed gas (F4). While establishing nitrogen flow, additional solution may be required.

Data Collection

The primary data are gas compositions (from GC samples), flowmeter readings, temperatures, manometer readings and liquid sample analytical results. These data, as well as sufficient notes to allow reproduction of the experiment, and any unusual observations should be recorded on data sheets or in a laboratory notebook. Experience with the system will determine the time and number of samples required to establish steady-state operation.

Shut Down

Heaters H1, H2 and H3 should be shut off, gas flows reduced to a nitrogen purge to each column and, after T8 and T9 have dropped below 50°C, liquid circulation stopped. Liquid will accumulate in the base of the stripper. If desired the stripper can be drained with S7 and most of the remaining solution recovered by pumping out the cooler and pump discharge lines. The nitrogen purges and cooling water flows can then be stopped. Gas supply should be shut off at the cylinders. A typical start-up/shut-down check list is included as Table 12.

TABLE 12. Start-Up/Shut-Down Check List

Start Up

Gas Chromatograph On and Standard Run
Data Logger On (low heater set points)
Cooler Water On
Condenser Water On
Manometers Charged
Trace Heaters Set
Solution Charged
N₂ Purge to Columns (F2 and F3, low settings)
Solution Circulating
H1, H2, H3 Heaters Set, Desired Temperatures Reached
F2 and F3 to Full Flow
Additional Solution Charged (if stripper base level low)
Manometer M1 Nitrogen Blanket Set (A=2B)
F4 Flow Set

Shut Down

F4 Stopped
H1, H2, H3 Off, T8 and T9 Below 50°C
F2 and F3 Reduced
Circulation Pump Off
Condenser Water Off
Cooling Water Off

ABNORMAL OPERATIONS

Because flammable and/or toxic gases and liquids are to be used in substantial quantities, the operator should be prepared to handle abnormal conditions. Proper response will minimize equipment damage and loss of materials as well as reducing hazards. Leaks, flooding, overpressure, overheating, utility outages and fire are discussed.

Leaks

The location of the apparatus in a fume hood should minimize exposure of operators but care should be taken to test for leaks regularly. Pressure checks can be performed between experiments using M1 with the condenser and absorber vents closed. Trichloroethane, the first solvent to be tested, has low hazard potential except that it can be absorbed through the skin, potentially carrying metal bearing complexes. Any contact with solution should be avoided.

If leaks are observed during operation, any feed of CO- or H₂-containing gases should be stopped (F4), heaters shut off, the system drained and pump stopped as appropriate. The pump should not be run dry for extended periods. H1 and H2 should be shut-off as soon as any loss of circulation occurs.

Flooding

Flooding will occur when excessive gas and/or liquid flows are used and can occur in either column. An unusually high reading in M2 or M3 would be the first sign of trouble followed by loss of solution circulation and, if uncorrected, transport of solution out through the vents. Reducing gas flows (F4 first) should alleviate the problem but if flow from the absorber to the stripper has been interrupted, H1 and H2 should be shut off until circulation is re-established.

Overpressure

The gas cylinders and the pump are the mechanical sources of pressure in the system. The cylinder regulators should be set to about 5 psig which, together with the hydrostatic relief of M3 should minimize any overpressure from those sources. Overtemperature may also result in overpressure through

boiling of solvent. Early evidence of the problem may be found in manometer readings or gas flows. One of the 30 mm ID connectors may open before any other loss of system integrity. Depending on severity of the problem, flows should be reduced or stopped. In the latter case heaters should be shut off as well.

Overtemperature

Excessive temperatures can result in boiling solvent and/or degradation of complex. Careful monitoring of T11 and T16 should maintain temperatures well below the boiling point of the solvent and T8 through T10 should never exceed 250°C. In the case of overtemperatures, heater settings should be reduced but flow maintained.

Utility Outages

Operation of the apparatus requires electricity, cooling water and ventilation. If any of these are lost, gas flows should be stopped (F4 first), H1, H2 and H3 shut off and the pump stopped. In the case of a power outage, care should be taken to assure that heaters and the pump are switched off or unplugged to avoid problems when power is restored.

Fire

A gas leak or solvent leak (if a flammable solvent is used) may ignite. Gas flows should be stopped at the cylinders and F4 closed if possible. The heaters and pumps should be shut off at the lab circuit breaker and the hood sash lowered if possible. Unless the fire can be quickly and easily extinguished a fire alarm should be sounded.

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