GAS SEPARATION BY METAL COMPLEXES: MEMBRANE SEPARATIONS

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Introduction

Gases are separated on a very large scale by cryogenic distillation, membrane or sorption methods. For instance, the production of pure oxygen from air by cryogenic distillation is one of the most important separation processes. However, the membrane method is preferable when O_2-enriched air is required for medical use or effective combustion, and the sorption method is best for removal of O_2 from packaging. The fundamental mechanism of cryogenic distillation is due to a difference in boiling points of the various gases. In the case of the membrane method, a difference in solubility and diffusion of gases is essential for nonporous membranes, while molecular mass or size of gases is a decisive factor for porous membranes where Knudsen diffusion or molecular sieving occurs. The sorption method involves physical sorption and chemisorption, which are characterized by binding energies of about 5–50 kJ mol^{-1} and about 150–500 kJ mol^{-1}.

Unlike most physical sorbents, gas adsorbents containing metal complexes adsorb gas molecules by chemical coordination of the molecules to a central metal atom. Some metal complex adsorbents, because of their strong chemical adsorption, can completely adsorb gas molecules, even at low gas concentrations. The equilibrium between the metal complex (S–M) and the gas (G) is shown in eqn [1]. When this equilibrium shifts to the right, the adsorbent adsorbs gas molecules. When the equilibrium shifts to the left, the adsorbent releases the adsorbed molecules. The equilibrium can be controlled by changing temperature or pressure:

$$\text{S–M} + \text{G} \rightleftharpoons \text{S–M} \cdots \text{G} \qquad [1]$$

Figure 1 shows a schematic illustration of carbon monoxide separation from a carbon monoxide–nitrogen gas mixture by a solid copper complex. Only carbon monoxide can coordinate to copper to form a complex when the adsorbent is exposed to the gas mixture. The adsorbed gas is released when the adsorbent is subjected to high temperature or reduced pressure.

The characteristics of metal complex adsorbents are as follows:

1. Various combination of metal–ligand systems are available for the development of appropriate adsorbents.
2. Even a very dilute gas component in a mixture can be removed due to strong coordinative binding between the central metal and gas molecules.
3. Selective adsorption can be achieved using suitable functional groups of ligands.
4. Such a selective adsorption can possibly be used as a sensor or an indicator by showing colour change of adsorbents.
5. The amount of adsorbed gas molecules per unit mass of the adsorbents is limited because only one or two molecules can coordinate to a central metal atom.
6. The metal complex adsorption system cannot separate gases by their molecular size.
7. In general, the metal complex adsorbent is less stable than other types of adsorbents, such as active carbon and zeolite.

Metal complexes can be used as free-standing adsorbents, but preferably should be spread on to an inert support, such as activated carbon, porous

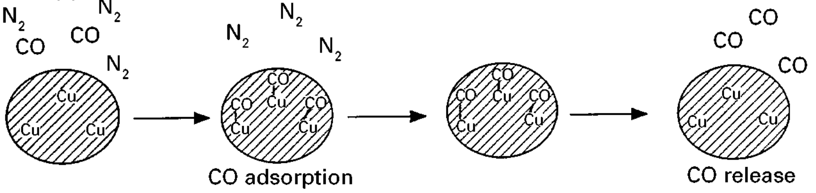

Figure 1 A schematic illustration of the separation of carbon monoxide from a carbon monoxide–nitrogen mixture by a supported copper complex.

carbon fibres, zeolite or porous polymer beads. These supports should have a large surface area to increase the adsorption capacity. Also the adsorbent support should be mechanically strong so as not to break up in use.

Polymeric supports have several advantages. Firstly, polymers can be processed into many shapes, such as thin membranes, hollow fibres or porous beads. Secondly, the wide variety of available polymers means that the structure and surface chemistry of the polymer are easily changed. Thirdly, the metal complex can be easily inserted into a hydrophobic domain, which cannot be achieved with inorganic materials. This offers some protection to water-sensitive metal complexes. Finally, composite materials can be easily formed.

Polymer-supported metal complexes or polymer–metal complexes are quite often more stable, more effective, and more easily handled than metal complexes without support for the following reasons:

1. *Diluting effect*: polymers can immobilize the metal complex separately so that aggregation of the metal complex is difficult.
2. *Concentrating effect*: metal complexes fixed in a polymeric support give a reaction field with a higher concentration of active centres than in a solution of the corresponding metal complex.
3. *Field effect*: polymeric supports form a specific reaction field to promote the reaction or to inhibit undesirable side reactions.
4. *Steric effect*: polymeric supports sterically control the approach of molecules to the metal complex.

The polymer–metal complexes can be used for gas separation in the form of adsorbents and membranes. In both cases, the coordination of gas molecules to the metal complex is much stronger than physical adsorption or solubilization into polymers, resulting in higher selectivity for gas separation than metal complexes supported on inorganic materials where the inorganic support itself may adsorb a considerable amount of gas molecules.

The following are industrially important applications of metal complexes for gas separation. However, most have been investigated on just a small laboratory scale. Only the separation of oxygen from air has been the subject of practical research for industrial application on a large scale.

Separation of Carbon Monoxide

Carbon monoxide, one of the most important starting materials for synthesizing organic chemicals, is usually obtained as a gas mixture containing methane, ethane, nitrogen, carbon dioxide and water vapour, by steam reforming of hydrocarbons, partial oxidation processes or gasification of coal. Thus, separation of carbon monoxide from gas mixtures is a significant target for investigation. Although the cryogenic separation process is widely used for carbon dioxide separation, it is difficult to separate carbon monoxide from gas mixtures containing N_2 because their boiling points are close (CO = −191.5°C, N_2 = −195.8°C). For this reason adsorption of carbon monoxide onto metal complexes is still of use. One process is adsorption of carbon monoxide by a copper liquor process using copper(I) ammonium solution, but dry systems have also been proposed. Some adsorbents investigated are listed in **Table 1**.

Introduction of copper(II) ion into Y-type zeolite by cation exchange, followed by reduction under 150 mmHg (1 mmHg ≈ 133.3 Pa) of carbon monoxide at 400°C, gives a Y-type zeolite-supported Cu(I) adsorbent which adsorbs 1.65 mmol of carbon monoxide per g-adsorbent at 25°C, 99 mmHg. The amount of CO adsorbed is almost equal to the moles of attached Cu(I) ion, suggesting that a 1 : 1 Cu(I)–carbon monoxide complex is formed. A similar adsorbent can be made by replacing Y-type zeolite by ZSM-5. The disadvantages of the Cu(I) zeolite-type adsorbents are as follows:

1. Cu(I) is oxidized to Cu(II) by oxygen in the presence of water vapour or ammonia, losing the ability to adsorb carbon monoxide.

Table 1 Adsorption and release of CO by various adsorbents containing Cu

Adsorbent	*Capacity of adsorption (cm^3 g adsorbent^{-1})*	*Adsorption conditions*	*Release conditions*
Cu/Y-type zeolite	30–40	100 Torr, < 100°C	> 300°C, vacuum
Cu/ZSM-5	16	200 Torr, < 50°C	> 300°C, vacuum
Cu(I)/active carbon	24	0.9 atm, 20°C	120°C, 1 atm or 20°C, vacuum
Cu(I)/PS-NH_2	20	0.9 atm, 20°C	80°C, vacuum
$AlCuCl_4$/active carbon	28	0.9 atm, 20°C	180°C, vacuum
$AlCuCl_4$/PS	70	1.0 atm, 20°C	90°C, vacuum

2. Release of carbon monoxide requires a temperature of 300–400°C under vacuum because of the strong carbon monoxide coordination of Cu(I). These severe conditions are unsuitable for good carbon monoxide recovery.

Although active carbon is capable of adsorbing gases, it cannot be used as a selective carbon monoxide adsorbent because of the general physical adsorption involved. However, activated carbon, having a very large surface area, can be used as a support. An adsorbent can be made holding 14.1 mmol of CuCl (94%), with a surface area of 744 $m^2\,g^{-1}$, about 70% of that of the activated carbon (1044 $m^2\,g^{-1}$) used. The activated carbon-supported CuCl adsorbs 88% carbon monoxide per Cu(I) (24 cm^3 STP per g-adsorbent) under a $CO–N_2$ (9 : 1) mixture at 20°C. The adsorbent totally releases the adsorbed carbon monoxide at 120°C under 1 atm or 20°C under 0.4 mmHg, and can be used repeatedly. The high capacity of carbon monoxide adsorption results from the highly dispersed $CuCl_2^-$ on active carbon prepared from CuCl in hydrochloric acid solution. Carbon-supported CuCl prepared in ethanol or water does not show high carbon monoxide adsorption. Carbon-supported CuCl prepared from CuCl in 20% ammonia solution exhibits 83% carbon monoxide adsorption to the Cu(I) content under the same conditions mentioned above. A similar carbon monoxide adsorbent, prepared from $CuCl_2$ instead of CuCl, adsorbs 67% carbon monoxide to the $CuCl_2$ added. The active site is however found to be Cu(I) by X-ray photoelectron spectroscopy (XPS), presumably because the Cu(II) is reduced by the activated carbon during the preparation.

Macroreticular (MR) polystyrene (PS) resin with primary and secondary amino groups can be used as a support for CuCl. The polymeric adsorbent adsorbs 15.9% carbon monoxide per Cu(I) (21 cm^3 STP per g-adsorbent) under the same conditions described above. The adsorbent partially releases carbon monoxide in 10 min at 80°C under 1 atm, and repeatedly adsorbs 9.1% carbon monoxide per Cu(I). The other ion exchange resins show poor capacity of carbon monoxide adsorption (**Table 2**), showing that the coordination of the amino groups to Cu(I) is essential. The adsorbent does not adsorb methane, hydrogen or nitrogen, but does adsorb some carbon dioxide (3.7 cm^3 per g-adsorbent). The capacity is however much smaller than that of carbon monoxide (21 cm^3) because most of the amino groups of the resin coordinate to CuCl, and few free amino groups remain.

Table 2 Capacity of CO adsorption for various ion exchange resin-supported CuCl[a]

Ion exchange resin	*Functional group*	*Adsorbed CO*[b]
Anion exchange resin	$–NH_2$, –NH–	15.9
Weak cation exchange resin	–COOH	1.2
Strong cation exchange resin	$–SO_3H$	0.8
Polystyrene resin	None	2.2

[a] The adsorbents were prepared from 10.0 g of resin and 9.9 g (100 mmol) of CuCl in 80 cm^3 acetonitrile.

[b] Adsorbed CO under 1 atm of $CO–N_2$ (9 : 1) mixture at 20°C.

Polystyrene-supported CuCl shows very poor capacity for carbon monoxide adsorption (**Table 2**). Copper(I) chloride is known to make a double salt with aluminium chloride, and the double salt forms a π-complex with aromatic hydrocarbons such as toluene, giving a stable carbon monoxide absorbent even in the presence of oxygen or carbon dioxide:

$$AlCuCl_4(\text{toluene}) + CO \underset{\Delta}{\rightleftharpoons} AlCuCl_4(CO) + \text{toluene}$$

This absorbent ($AlCuCl_4$ toluene solution, so-called COSORB solution) is very unstable in water, however, decreasing irreversibly the capacity of carbon monoxide absorption. Therefore, the water content of gas mixtures must be reduced to less than 1 p.p.m. prior to using this solution. Addition of linear PS to an $AlCuCl_4$–toluene solution dramatically increases the stability to water, presumably because PS coordinates $AlCuCl_4$, forming a hydrophobic domain around the water-sensitive $AlCuCl_4$ molecule, thereby protecting it from water.

MR cross-linked PS resin (Bio-Beads SM-2, divinylbenzene content: 20%, surface area: 300 $m^2\,g^{-1}$) is an excellent support for $AlCuCl_4$, providing a water-resistant solid carbon monoxide adsorbent. The adsorbent adsorbs an equimolar amount of carbon monoxide in 10 min under 1 atm of carbon monoxide at 20°C, and partially releases the carbon monoxide under 7 mmHg at 20°C. After 10 min desorption of CO, the adsorbent still adsorbs 54% carbon monoxide per Cu(I) the second time, and this is a reversible capacity for carbon monoxide adsorption under the conditions mentioned above. The capacity of reversible carbon monoxide adsorption increases by applying higher vacuum or higher temperatures during the desorption part of the cycle. The water-resistivity of the adsorbent strongly depends on the solvent used for preparation. Carbon disulfide gives a water-resistant adsorbent, while toluene gives a water-sensitive material. The water-resistant adsorbent has a uniform distribution of $AlCuCl_4$ in PS resin, whereas the water-sensitive adsorbent possesses a lot of crystalline deposits, consisting mainly of CuCl, in the beads and much salt, mainly $AlCl_3$, on the surface.

Gel-type PS (divinylbenzene content: 1%)-supported $AlCuCl_4$ adsorbs carbon monoxide much more slowly than the MR-type adsorbent, and it takes about a day to attain equilibrium. In consequence, the MR-type resin, which possesses macropores even in a dry state, is essential for the preparation of solid gas adsorbents.

Separation of Nitrogen Monoxide (NO)

Nitrogen oxides and sulfur oxides are major air pollutants. Unlike sulfur oxides which have been decreasing in the atmosphere, nitrogen oxides, particularly nitrogen monoxide (NO) in combustion and exhaust gases, still cause difficulties. For removal of nitrogen monoxide, in general, catalytic processes using ammonia, carbon monoxide or hydrocarbons as a reducing agent are applied.

Another possibility of removing nitrogen monoxide from gas mixtures might be the use of metal complex adsorbents at lower temperatures. The nitrogen monoxide adsorbents are expected to adsorb nitrogen monoxide completely, even at very low concentrations of nitrogen monoxide, and to be stable to water vapour, SO_2, dust, etc., which are often contained in combustion and exhaust gases.

Natural jarosite, $KFe_3(SO_4)_2(OH)_6$, possesses a layer structure in the crystal. Jarosite synthesized from $Fe(SO_4)_2$ and K_2SO_4 (3 : 1) adsorbs 5.3×10^{-4} mmol of nitrogen monoxide per g-adsorbent (surface area: 7.3 $m^2\,g^{-1}$). The other synthetic jarosites, $MFe_3(SO_4)_2(OH)_6$ (M = Na, Rb), show no difference in nitrogen monoxide adsorption.

α-FeOOH crystals can be prepared from $Fe_2(SO_4)_3$ and Na_2CO_3 by heat treatment. Powdery crystal α-FeOOH, whose surface area is 60 $m^2\,g^{-1}$, adsorbs 0.4 mmol of nitrogen monoxide per g-adsorbent at 30°C under 600 mmHg of nitrogen monoxide partial pressure, whereas α-FeOOH supported on activated carbon fibre (surface area: 870 $m^2\,g^{-1}$) adsorbs 4.67 mmol of nitrogen monoxide under the same condition (a 12 times higher capacity than that without activated carbon fibre as a support). This adsorbent adsorbs 0.043 mmol per g-adsorbent even under 300 p.p.m. of nitrogen monoxide at 100°C, but little more than 10% of the nitrogen monoxide adsorbed can be released under vacuum due to its strong adsorption.

Active carbon-supported $FeCl_2$ completely adsorbs nitrogen monoxide in 25 min from a 6 dm^3 NO–N_2 mixture (NO: 1000 p.p.m.) when the gas mixture is circulated at 1.6 $dm^3\,min^{-1}$. The adsorbent releases 28% adsorbed nitrogen monoxide in 15 min at 120°C. The apparent equilibrium constant of the adsorbent is around 1500 atm^{-1}.

Iron(II) ethylenediaminetetraacetic acid (EDTA) solution is a well-known nitrogen monoxide absorbent, adsorbing 0.5 mol of nitrogen monoxide per mole of Fe from NO–N_2 mixtures (NO: 1000 p.p.m.) at 55°C. However, the absorbent is easily oxidized by oxygen due to the unstable Fe(II) ion. To overcome this problem, a chelate resin, cross-linked PS with iminodiacetic acid moieties, has been used as a polymeric support. The Fe(II) supported on chelate resin adsorbs almost all the nitrogen monoxide in 15–20 min from a 6 dm^3 of NO–N_2 mixture (NO: 1000 p.p.m.) when the gas mixture is circulated at 1.6 $dm^3\,min^{-1}$. The adsorbent releases all the adsorbed nitrogen monoxide under 3 mmHg at 100°C, and can be reused repeatedly. The capacity of nitrogen monoxide adsorption for the chelate resin-supported Fe(II) is dependent on the washing solvent. This is because the porosity or the surface area increases (**Table 3**) when the water-swollen resin-supported Fe(II) is dried after washing with water-miscible organic solvents. Coexistence of a high valent cation such as Fe(III) further increases the surface area to achieve more effective nitrogen monoxide adsorption.

Table 3 Effects of the washing solvent on the ability for NO adsorption and the surface area for chelate resin-supported Fe(II)

Solvent	*Adsorption rate*[a] *(10^{-2} mmol min^{-1})*	*Adsorbed NO*[b]	*Surface area*[c] *($m^2\,g^{-1}$)*
Chloroform	0.36	0.789	2.3
Water	0.30	> 0.425	3.2
Acetone	1.04	0.933	17.2
2-Propanol			31.7
Ethanol	1.54	0.997	31.1
Methanol	1.54	0.997	43.1

[a] Amount of adsorbed NO in 15 min.
[b] Equilibrium NO adsorbed against NO introduced.
[c] Measured by a Brunauer–Emmett–Teller (BET) method.

Separation of Ethylene (C_2H_4)

Ethylene is one of the most important raw materials in the petrochemical industry and is also an accelerator for ripening fruit. Ethylene is produced on a large scale by the thermal cracking of naphtha and natural gas, and obtained in mixtures with methane, ethane, propane, propylene, hydrogen, carbon dioxide, nitrogen and water. In this case, a large quantity of gas mixture has to be treated to obtain pure ethylene. On the other hand, a small amount of ethylene must be thoroughly removed from fruit packaging so that fruit does not ripen too quickly.

In industry ethylene is purified mostly by large scale distillation, and sometimes by using membrane separation. For removal of ethylene from fruit packaging, no good adsorbent has yet been developed. The solid metal complex adsorbent mentioned here may provide a new material for both purposes.

Y-type zeolite-supported Cu(I) adsorbs 3.10 mmol of ethylene per g-adsorbent (1.9 mmol of ethylene per mole of Cu(I)) under 250 mmHg of ethylene at 25°C and releases 73% of the adsorbed gas in 60 min. Y-type zeolite-supported Ag(I) adsorbs 3.28 mmol of ethylene per g-adsorbent and releases 54% of the gas under the same conditions.

MR-type PS resin with primary and secondary amino groups, which is used as a support for CuCl as described above for carbon monoxide adsorption, also works as an ethylene adsorbent. An adsorbent prepared from 10 g of resin and 15.0 g (152 mmol) of CuCl in water–acetonitrile (1 : 1) reversibly adsorbs 15 mmol of ethylene and 1.9 mmol of ethane, while the resin itself (10 g) adsorbs 5.0 mmol of ethylene and 6.5 mmol of ethane at 20°C under 1 atm. The coverage of CuCl over the surface of the resin is supposed to restrict physical adsorption and increases chemisorption or coordination.

MR-type PS-supported $AlCuCl_4$ adsorbs ethylene very rapidly, and the equilibrium ratio of the adsorbed ethylene to the CuCl added is 1.40 mol-C_2H_4/mol-Cu (89 cm^3 STP of ethylene per g-adsorbent). The adsorbent releases a part of the adsorbed gas under 8 mmHg at 20°C for 10 min, and adsorbs 0.29 of mol-ethylene per mol-Cu in the second and later passes. When an ethylene-adsorbed adsorbent is cycled at 90°C under 1 atm and at 142°C under 8 mmHg to release ethylene, the adsorbent removes 0.47 and 0.87 of mol-ethylene per mol-Cu, respectively, in the second adsorption cycle. Although the PS-supported $AlCuCl_4$ adsorbs both ethylene and carbon monoxide, the coordination of ethylene to Cu(I) is stronger than that of carbon monoxide. Thus, the equilibrium molar ratio of adsorbed ethylene–carbon monoxide is 5 : 1 when the adsorbent is exposed to a 1 : 1 ethylene–carbon monoxide mixture.

A similar adsorbent, MR-type PS-supported $AgAlCl_4$, adsorbs an equimolar amount of ethylene per Ag under 1 atm at 20°C and releases almost all the ethylene under 8 mmHg at 20°C. The adsorbent does not adsorb carbon monoxide at all under 1 atm at 20°C, and therefore can be used as a selective ethylene adsorbent. The adsorbent is water-resistant, although $AgAlCl_4$ is water-sensitive, as is $AlCuCl_4$. The stability of the adsorbent is attributable to the location of $AgAlCl_4$ at the hydrophobic sites of the PS resin surrounded by several aromatic rings.

Separation of Oxygen

Oxygen, which can be prepared by separation from air, is one of the most important industrial chemical products and is produced on the largest scale by weight in the world. Thus, separation of oxygen from air is an important process in industry, and is mainly performed by low temperature distillation. It is also important to increase (or decrease) oxygen concentration for medical use and effective combustion (or inhibition of nitrogen monoxide production).

Haemoglobin and nyoglobin are typical examples of metal complexes which can reversibly bind an oxygen molecule in nature. So, the separation of oxygen from air with solid metal complexes has received considerable attention in the search for alternative procedures to low temperature distillation. Cobalt(II) Schiff's base complexes, such as a complex of cobalt(II) with bis(salicylidene)diaminoethane (Co(salen)), were objects of initial research in the 1940s on reversible oxygen absorbents and were later developed for on-board oxygen support systems for the US Air Force. Oxygen binds preferentially to cobalt by exposing the complex to air at room temperature to form cobalt(III) superoxide. Heating (thermal swing adsorption: TSA) or reducing pressure (pressure swing adsorption: PSA) facilitates release of oxygen from the complex. Up to 3000 oxygenation/deoxygenation cycles have been carried out with the same sample. After 3000 cycles the remaining activity was still 50%. Chemical engineering research was carried out using the system involving Co(salen)-type adsorbents. The US Air Force studied the cobalt(II) complex of bis(3-fluorosalicylidene)diaminoethane or fluomine for potential use in providing breathing oxygen for crews of military aircraft. This compound gives the best performance among all oxygen adsorbents so far with its fast and reversible binding of oxygen, as well as good stability, but could not be applied in practice due to the high cost.

Several other transition metals, such as manganese, iron, chromium, nickel, copper, titanium, and so on, have been used to synthesize various kinds of oxygen adsorbents by complexing with various types of ligands. They show reversible oxygen binding and release, but none has achieved commercial success for separation of oxygen from air.

Cobalt(II) Schiff's base complex has been tried, fixed in a polymer matrix. A poly(4-vinylpyridine)-attached cobalt(II) Schiff's base complex can be used for gas chromatography because oxygen comes out later than the other gases, such as nitrogen. Cobalt bis(salicylideneamino)propylamine-attached polystyrene and polyoctylmethacrylatecobalt disalicylidenethylenediamine films have been found to be useful for concentrating oxygen. Membranes of this latter material concentrate 8.3% oxygen in 5 h and 13.1% in 42 h from air. The permeability coefficient and the separation factor (O_2/N_2) under 10 mmHg of feed gas are 10^{-9} and 15, respectively, for this membrane containing 12 wt% of the complex. The experimental results were analysed using the dual-mode sorption model. Although several interesting studies have been reported on facilitated oxygen transport membranes employing the transition metal–oxygen complexes, they have a number of inherent limitations from a practical viewpoint, for example, the lifetime of membranes, the relationship between quality and quantity of the separation, and so on.

Conclusion

Metal complex adsorbents used for carbon monoxide, nitrogen monoxide, ethylene and oxygen separation have been described in this article. Few examples of adsorbents for other gases are known, but theoretically any gas capable of coordinating to metal complexes can be separated in this way. A variety of metal complexes can be synthesized by changing metal and ligand, and therefore supported metal complexes are promising materials for gas separation. However, from a practical viewpoint, there are many limitations, for example, lifetime of the materials and the cost of the separation. Since the greatest advantage of systems using solid metal complexes is complete separation, the adsorbents of solid metal complexes may be used for the purpose of the complete removal of small amount of gaseous molecules from closed systems in the future.

Further Reading

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