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Enhanced Oxygen Diffusion through a Porous Membrane Chemically Modified with Cobalt Porphyrin on Its Pore Surface

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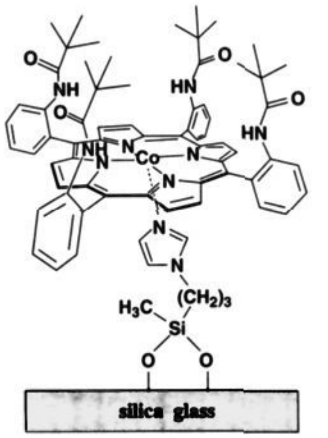
We describe herein the surface diffusion of oxygen through a porous membrane modified with cobalt porphyrin as a chemically specific oxygen carrier on its pore surface, in addition to gas-phase diffusion, to obtain both permselectivity of oxygen *vs* nitrogen and high permeability through the membrane.

Carrier-mediated or facilitated transport is defined as a separation process with a membrane, in which a distinct entity forms an adduct with a specific component, thereby increasing the transport rate of this component relative to other components in the feed stream.[1] This membrane process has been tested for the separation of oxygen and nitrogen from air, which is potentially the most important application because of its enormous market size.[2] Facilitated oxygen transport was first demonstrated using liquid membranes which contained hemoglobin and cobalt–Schiff's base chelates as an oxygen carrier.[3] We have succeeded in facilitated oxygen transport in dry or solvent-free polymer (dense) membranes containing cobalt porphyrins and cobalt–Schiff's base chelates as fixed carriers of oxygen[4] to solve the following problems of liquid membranes: chemical instability of the carrier (irreversible oxidation of cobalt), evaporation loss of the liquid media, temperature limitation of operation, and membrane thickness. However, an upper limit of the permeability coefficient of oxygen (P_{O2}) of 10^2 barrers through the polymer dense membrane remained, despite the oxygen permselectivity attributed to the facilitated transport.

Oxygen permeates in the gas phase by Knudsen diffusion through a porous membrane (pore size ϕ < mean free path of oxygen) with a huge flux of $P_{O2} = 10^4$ barrers. However, the permselectivity (ratio of permeability coefficients) for mixed gases *is inversely proportional to the square root of the molecular weights* of the permeating gases. For oxygen and nitrogen, which have almost the same molecular weight, $P_{O2}/P_{N2} = 0.94$. Surface diffusion of a gaseous permeate has been reported for a porous membrane of which the pore surface has an affinity for the gaseous molecule. However, surface diffusion was observed only for condensable gases such as carbon dioxide and hexane.[5] We describe in this communication for the first time a chemically specific surface diffusion of a noncondensable gaseous molecule, oxygen, in a porous membrane modified on its pore surface with cobalt porphyrin which binds oxygen specifically and reversibly from air.

Chart 1. Cobalt Porphyrin Bonded to the Pore Surface of the Membrane



A Vycor glass membrane (mean pore size $\phi = 4$ nm) was reacted with (3-chloropropyl)dimethoxymethylsilane and imidazole successively, to introduce the imidazolyl group through covalent bonds with silanol on its pore surface.[6] [$\alpha,\alpha,\alpha,\alpha$-Tetrakis(*o*-pivalamidophenyl)porphinato]cobalt (CoP) as an oxygen carrier[7] was fixed on the pore surface in the porous glass through ligation with the imidazolyl group (Chart 1). The five-coordinated structure of deoxy-CoP, which can bind oxygen rapidly, was confirmed by ESR spectroscopy, and the homogeneous introduction of CoP into the membrane was confirmed by X-ray microanalysis.

The deeply red-colored membrane reversibly gave the visible absorption spectrum attributed to deoxy-CoP under a nitrogen atmosphere and that attributed to oxy-CoP ($Co/O_2 = 1/1$ adduct) on exposure to air.[8]

$$CoP + O_2 \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} CoP\text{-}O_2 \qquad K = k_{on}/k_{off} \tag{1}$$

The oxygen-binding equilibrium constant of the fixed CoP (K) was determined in eq 1 on the basis of Langmuir's oxygen-binding isotherm ($K = 0.18$ cmHg^{-1}, as the oxygen-binding affinity $p_{1/2}$ (oxygen partial pressure at which half of the CoP binds with oxygen) = 5.6 cmHg, both at 25 °C). The enthalpy and entropy changes ($\Delta H = -13$ kcal/mol, $\Delta S = -37$ eu) for oxygen binding agreed with those of the CoP ligated with imidazole in toluene.[9]

IR absorption of the membrane piece also supported the oxygen adduct formation of CoP: $\nu_{O2} = 1150$ cm^{-1} assigned to the cobalt-bound dioxygen ($\nu_{O2} = 1550$ cm^{-1} for gaseous dioxygen). The amount of oxygen taken up by the membrane was measured with a sorption apparatus;[10] the sorption isotherm obeyed that of

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(1) (a) Matson, S. L.; Herrick, C. S.; Ward, W. J. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 370. (b) Way, J. D.; Noble, R. D. Facilitated Transport. In *Membrane Handbook*; Winston, S. W., Sirkar, K. K., Eds.; van Nostrand Reinhold Pub.: New York, 1993; Chapter 44, pp 833–866.

(2) Anonymous. *Chem. Eng. News* **1990**, *68* (25), 34.

(3) (a) Schlander, P. F. *Science* **1959**, *131*, 585. (b) Johnson, B. M.; Baker, R. W.; Matson, S. L.; Smith, K. L.; Roteman, I. C.; Tuttle, M. E.; Lonsdale, H. L. *J. Membr. Sci.* **1987**, *31*, 31. (c) Nishide, H.; Tsuchida, E. Polymer Complex Membranes for Gas Separation. In *Polymers for Gas Separation*; Toshima, N., Ed.; VCH Pub.: New York, 1991; Chapter 6, pp 182–219.

(4) (a) Nishide, H.; Ohyanagi, M.; Okada, O.; Tsuchida, E. *Macromolecules* **1986**, *19*, 444; **1987**, *20*, 417. (b) Nishide, H.; Kawakami, H.; Kurimura, Y.; Tsuchida, E. *J. Am. Chem. Soc.* **1989**, *111*, 7175. (c) Nishide, H.; Kawakami, H.; Suzuki, T.; Azechi, Y.; Tsuchida, E. *Macromolecules* **1990**, *23*, 3714. (d) Nishide, H.; Kawakami, H.; Suzuki, T.; Azechi, Y.; Soejima, Y.; Tsuchida, E. *Ibid.* **1991**, *24*, 6306.

(5) (a) Kammermeyer, K. *Ind. Eng. Chem.* **1958**, *50*, 697. (b) Sladek, K. J.; Gilliland, E. R.; Baddour, R. F. *Ind. End. Chem. Fundam.* **1974**, *13*, 100. (c) Lee, C. S.; O'Connell, J. P. *AIChE J.* **1986**, *27*, 96. (d) Sirkar, S.; Rao, M. B. *Ibid.* **1990**, *36*, 1249. (e) Kapoor, A.; Yang, R. T. *Chem. Eng. Sci.* **1991**, *45*, 3261.

(6) A hollowed Vycor glass membrane No. 7930 (Corning Inc.) was kept in fuming nitric acid for 1 day. After washing with water to pH 7, the glass was heated stepwise from 80 to 120 °C for 1 day. The activated glass was soaked in a toluene solution of (3-chloropropyl)dimethoxymethylsilane (3 molar equiv of the silanol groups on the glass surface) and a large excess of imidazole successively and was then refluxed for 24 h. After washing sufficiently with triethylamine and toluene, the imidazolyl group chemically bound to the pore surface was analyzed using elemental analysis and ESCA, and ca. 0.5 molar equiv of the silanol group was converted to the imidazolyl group as shown in Chart 1.

(7) (a) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265. (b) Tsuchida, E.; Nishide, H. *Top. Curr. Chem.* **1986**, *132*, 63.

(8) λ_{max}(deoxy) = 528 nm, λ_{max}(oxy) = 548 nm, and isosbestic points at 483 and 538 nm, for the deoxy–oxy alternation.

(9) The hollow glass was filled with a dichloromethane solution containing CoP, and a vacuum applied from the exterior resulted in evaporation of dichloromethane and introduction of CoP. Homogeneous introduction of CoP into the membrane was recognized by the homogeneous red coloring on the broken pieces of the membrane and by the homogeneous Co distribution in the membrane as determined by X-ray microanalysis. The five-coordinated CoP structure was confirmed by ESR spectroscopy: $g_{\parallel} = 2.08$, $g_{\perp} = 2.00$.

(10) Nishide, H.; Kawakami, H.; Toda, S.; Tsuchida, E.; Kamiya, Y. *Macromolecules* **1991**, *24*, 5851.

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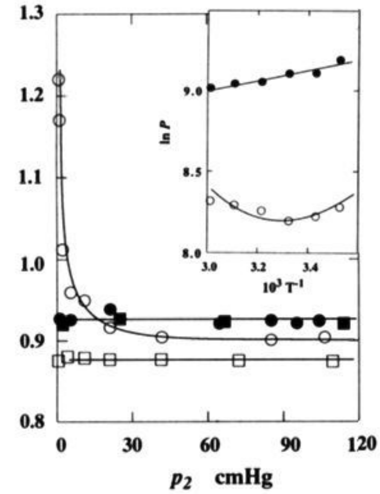


Figure 1. Effect of upstream gas pressure and temperature on the permeability coefficients for the CoP membrane (oxygen (○); nitrogen (●)) and the inactive Co^{III}P control membrane (oxygen (□); nitrogen (■)) at 25 °C.

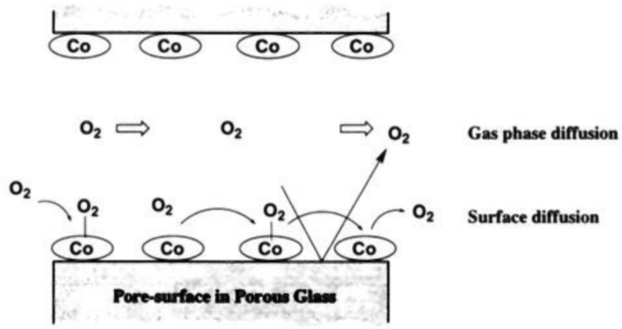
Langmuir, and the saturated amount of oxygen sorption was 0.80 cm^3 (STP) g^{-1}, which almost corresponded to the introduced amount of CoP and was enhanced at lower temperature. These results indicated that the CoP fixed in the membrane acts as a chemically specific and Langmuir-type oxygen-binding site.

Photodissociation and recombination of bound oxygen from and to the CoP fixed on the pore surface were observed by laser flash photolysis.[11] The reaction was surprisingly rapid, and the oxygen-binding rate constants ($k_{on} = 2.8 \times 10^6$ M^{-1} s^{-1}, $k_{off} = 3.4 \times 10^3$ s^{-1}) estimated assuming pseudo-first-order kinetics were comparable with those of the corresponding CoP–imidazole in toluene solution. The oxygen-binding kinetics directly in response to the atmospheric oxygen pressure suggest that CoP is located on the inside surface of the micropores. CoP is kinetically active to bind oxygen even after fixation in the membrane and acts as an effective carrier for the passage of oxygen.

The pore structure of the membrane modified with CoP was studied by BET nitrogen adsorption measurement:[12] pore volume ϵ = 23%, tortuosity τ = 8.2 cm/cm, specific surface area 123 m^2/g, mean pore size 2.6 ± 1 nm (62%). These data also support the incorporation of CoP on the inside of the micropores of the membrane. The average pore size was still 2.6 nm to allow gas-phase diffusion of oxygen and nitrogen.

Gas-phase diffusion through the CoP-modified membrane was confirmed by using a control membrane, *i.e.*, the same membrane modified with inactive Co^{III}P. As shown in Figure 1, the permeability coefficients[13] for the control membrane were independent of upstream pressure with $P_{O2} = 8.8 \times 10^3$ barrers and $P_{N2} = 9.4 \times 10^3$ barrers at 25 °C and $P_{O2}/P_{N2} = 0.93$ (theoretical 0.93): Gas-phase or Knudsen diffusion is predominant for the membrane.

Chart 2. Oxygen Transport through the CoP-Modified Porous Membrane



P_{O2} and P_{N2} for the CoP-modified porous membrane are also shown in Figure 1. P_{N2} is larger than P_{O2} at the higher region of upstream nitrogen pressure $p_2(N_2)$ and is independent of $p_2(N_2)$, because nitrogen permeates through the membrane according to gas-phase diffusion and the fixed carrier CoP does not bind with nitrogen. On the other hand, P_{O2} is small with $P_{O2}/P_{N2} = 0.94$ at the high $p_2(O_2)$ region because of the saturation of CoP with oxygen but steeply increases with a decrease in $p_2(O_2)$: (P_{O2}/P_{N2}) reaches 1.4 at $p_2(O_2) = 0.7$ cmHg. These indicate that the CoP fixed on the pore surface interacts specifically with oxygen and augments the diffusion of oxygen in the membrane ascribed to chemically specific surface diffusion (Chart 2).

In contrast to the temperature dependence of P_{N2}, P_{O2} has a minimum at ca. 35 °C, as shown in Figure 1. This means that the surface diffusion of oxygen involves a chemical reaction with CoP in addition to its gas-phase diffusion.

Total gas flux could be considered to be the sum of the surface diffusion and the gas-phase diffusion, as given in eq 2,

$$P_{O2} = P_S + P_g = \frac{1}{\tau}D_S\frac{C_SK}{(1 + Kp_2)^2} + \frac{\epsilon}{\tau}D_g\frac{1}{RT} \qquad (2)$$

where D_S and D_g are diffusion constants for the surface and gas-phase diffusion, respectively. C_S is the concentration of active CoP in the membrane with the oxygen-binding equilibrium constant K (given in eq 1). p_2 is the upstream gas pressure.

The permeability coefficient of the surface diffusion (P_S) was obtained by subtracting the permeability coefficient of the gas-phase diffusion (P_g) measured for an ideal gas (here helium) from the total gas diffusion.

Substituting the C_S, K, ϵ, τ, and p_2 values in eq 2 yields the gas-phase diffusion constant of oxygen, $D_g(O_2) = 2.5 \times 10^{-3}$ cm^2 s^{-1} at 25 °C, and that of nitrogen, $D_g(N_2) = 2.7 \times 10^{-3}$: their ratio, 0.94, also supports gas-phase diffusion. The surface diffusion constant, $D_S(O_2) = 2.9 \times 10^{-5}$, was 100 times smaller than $D_g(O_2)$. The activation energy of $D_g(N_2)$ was 0, which is also consistent with that of gas-phase diffusion for nitrogen. On the other hand, the activation energy of $D_S(O_2)$ for oxygen was 11 kcal/mol, which corresponds to the chemically specific surface diffusion and is comparable with the activation energy of the oxygen-binding reaction (10 kcal/mol).

In eq 2, C_S and K also contribute to P_{O2} in addition to $D_S(O_2)$. The enormously large C_S of 0.7 cm^3/cm^3 is caused by the large surface area of the porous membrane and enhances P_S by overcoming the small D_S. The requisites for establishing a much higher P_{O2} are a higher C_S, a moderate K, and a higher D_S. The third is connected with a larger k_{on} and k_{off} in the oxygen-binding reaction of the carrier CoP.

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(11) A laser flash (575 nm) was applied perpendicularly to the light path of a rapid and sensitive spectrophotometer (Unisoku FR-2000), and the membrane was placed at the junction of the laser flash and the light path at a 45° angle to both. The rapid UV absorption change was recorded with the spectrophotometer using a kinetic data processer to cancel the noise caused by scattered light.

(12) The pore volume of the membrane was estimated by subtracting the specific volume of the membrane itself from that measured by Hg. The specific surface area was determined by BET nitrogen adsorption (Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.). Pore size distribution was determined from the pressure at equilibrium at each supplied pressure of nitrogen (Cranston, R. W.; Inkley, F. A. *Adv. Catal.* **1957**, *9*, 143). Tortuosity was estimated by assuming gas-phase diffusion in tubes (Satterfield, C. N. In *Mass transfer in Heterogeneous Catalysis*; MIT Press: Cambridge, MA, 1970; pp 41–72).

(13) The permeability coefficients were obtained by a cross-flow permeation method with helium as the sweep gas.