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A novel inorganic–organic hybrid membrane for oxygen/nitrogen separation containing a cobalt(II) Schiff base complex as oxygen carrier using poly(*N*-vinylpyrrolidone) as mediator

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A novel oxygen selective inorganic–organic hybrid membrane containing (*N,N′*-disalicylideneethylenediaminato)cobalt(II) (salcomine) as an oxygen carrier was prepared *via* the sol–gel method using poly(*N*-vinylpyrrolidone) (PVP) as the mediation agent.

Oxygen selective membranes are important in various fields such as medicine, oxygen-enriching combustion systems, and fuel cell systems. Much attention for oxygen-enriching organic polymer membranes has been focused on the synthesis of polymers where the solubility of oxygen is greater than that of nitrogen.[1] However, no permselective membrane has been successfully prepared so far using this approach. Recently, the method of oxygen carrier addition to improve the oxygen selectivity of an organic polymer gas separation membrane operating at around room temperature has attracted tremendous attention. Some efforts have been made to facilitate transport using transition-metal complexes such as cobalt porphyrin complexes[2] and cobalt Schiff base complexes.[3] In all earlier investigations it was claimed that high O_2 selectivity could only be achieved at lower operating pressures and temperatures.

A large variety of inorganic–organic hybrids prepared by the sol–gel method has been reported.[4–8] Among these, the most common method utilizes hydrogen bonding interactions between polar functional groups of organic polymers and silanol groups of silica gels. Examples include organic polymers such as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone) incorporated homogeneously into silica gels at the molecular level.[5,6,8]

Here, we report the preparation of a SiO_2–(*N,N′*-disalicylideneethylenediaminato)cobalt(II) (salcomine) hybrid membrane using poly (*N*-vinylpyrrolidone) (PVP) as a mediation agent, that is capable of selective separation of oxygen. Salcomine is a well known oxygen carrier complex. Unfortunately, there is no interaction between salcomine and silica, which makes it difficult to integrate it at a molecular level. To solve this problem, we proposed to use PVP as a mediation agent which contains amide carbonyl groups in its structure. Hydrogen bonding interactions between amide carbonyl and silanol groups of silica along with coordinate bonding interactions between nitrogen atoms of amide carbonyl groups and Co(II) in the salcomine can help to disperse organic and inorganic components at a molecular level. Based on this concept, we have prepared novel inorganic–organic hybrid membranes containing oxygen carrier complexes, using the sol–gel technique.

Tetraethoxysilane (TEOS) was used as the silica source and the PVP had a molecular weight of *ca.* 630 000; the concentration of PVP in the TEOS was *ca.* 11 wt%. A selective SiO_2–PVP–salcomine hybrid membrane was prepared using the following molar sol–gel composition: TEOS : EtOH : H_2O : HNO_3 : salcomine = 1 : 20 : 2 : 0.01 : 0.01. In a typical synthesis, the homogeneous sol was prepared by stirring a mixture of TEOS, H_2O, HNO_3 and EtOH for several hours at room temperature. PVP was added to the sol with continuous stirring. Finally, after stirring for 3 h, salcomine was introduced into the sol and resulting sol was vigorously stirred for several hours to obtain a homogeneous sol.

Porous alumina tubes (NGK Insulator, Ltd.; mean pore diameter, 0.1 μm; o.d, 10 mm; i.d, 7 mm; length, *ca.*10 cm) were used as supports. Tubular supports with one end closed were dipped in the sols, withdrawn at a rate of 1 mm s^{-1}, and then dried at room temperature. The dip coating procedure was performed in a class 1000 clean room (295 K and 50% relative humidity) to avoid dust which leads to pinholes on membranes. After the dip-coating was repeated twice, the membranes were heated to 423 K at the rate of 0.5 K min^{-1}, maintained at the same temperature for 2 h, then cooled to room temperature at 0.5 K min^{-1}. These coating and heating procedures were repeated twice in a similar manner. Hybrid membranes without salcomine were also prepared by the same procedure.

The structures of the hybrid membranes were determined using FTIR (FTIR-8700, Shimadzu). FTIR spectra of both SiO_2–PVP–salcomine and SiO_2–PVP hybrids showed a typical band at *ca.* 960 cm^{-1} associated with the stretching mode of Si–OH,[9] along with the characteristic bands related to the Si–O–Si bond (*ca.* 1220, 1080, 800 and 460 cm^{-1}),[9] which confirm the presence of Si–O–Si networks in the hybrids. Other characteristic bands originating from PVP were also observed (Fig. 1). The band at *ca.* 1650 cm^{-1} is due to the stretching band of amide carbonyl groups. Compared to that of PVP, these bands were shifted to lower wavenumbers indicating the existence of hydrogen bonding between amide carbonyl and silanol groups in the hybrids.[5] This provides evidence that in hybrids the inorganic segments (silica) and organic ones (PVP) are very well dispersed at the molecular level in accord with the previous reports.[5,6,8] The spectra of SiO_2–PVP and SiO_2–PVP–salcomine hybrids were quite similar since the amount of salcomine incorporated was very low (1 mol% relative to TEOS). However, PVP aids to dissolve salcomine homogeneously in

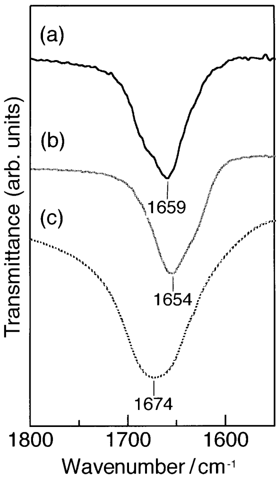

Fig. 1 IR spectra of (a) SiO_2–PVP–salcomine hybrid, (b) SiO_2–PVP hybrid and (c) PVP.

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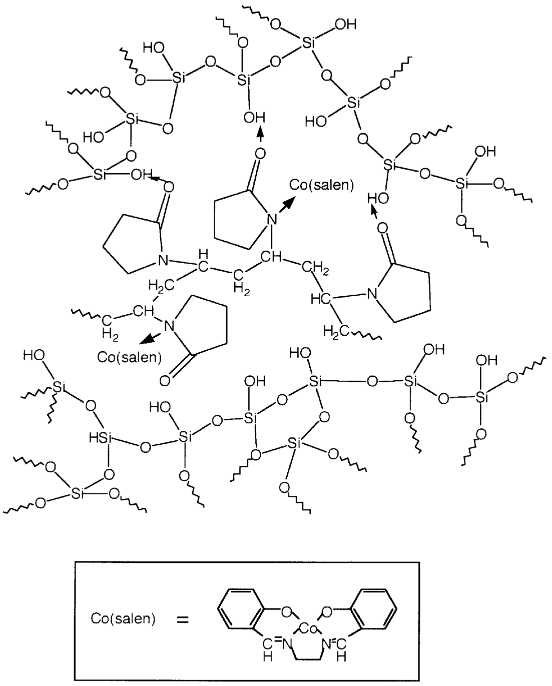

Fig. 2 Schematic representation of the structure of the SiO_2–PVP–salacomine hybrid membrane.

Table 1 Permeances and selectivity factors of O_2 and N_2 through the SiO_2–PVP–salcomine and SiO_2–PVP hybrid membranes at 298, 373 and 423 K

Membrane	T/K	10^{-10} Permeance/ mol m^{-2} s^{-1} Pa^{-1} O_2	N_2	Selectivity factor P_{O_2}/P_{N_2}[a]
SiO_2–PVP–salcomine	298	1.2	0.84	1.4
	373	4.0	0.87	4.6
	423	5.0	0.84	6.1
SiO_2–PVP	298	1.5	1.5	1.0
	373	1.2	1.1	1.0
	423	0.77	0.77	0.99

[a] Theoretical selectivity factor based on Knudsen flow is 0.94.

the sol. A possible schematic structure of the membrane is proposed in Fig. 2. As shown, silica and PVP were dispersed at a molecular level due to strong hydrogen bonding between amide carbonyl and silanol groups. Also, PVP and salcomines were well dispersed at a molecular level as nitrogen atoms of amide carbonyl groups were coordinated with Co(II) in the salcomines.[2,3] Therefore, high dispersion of salcomines in the SiO_2–PVP hybrid at the molecular level and a well dispersed inorganic–organic structure of the SiO_2–PVP–salcomine hybrid is evident.

Single gas permeation through these hybrid membranes at different temperatures was measured using O_2 and N_2 using the procedure described elsewhere[10] after drying at 373 K in a vacuum oven for 1 h. Table 1 lists the permeances of O_2 and N_2 through the SiO_2–PVP–salcomine and SiO_2–PVP hybrid membranes and shows the selectivity factor $\alpha = P_{O_2}/P_{N_2}$, where P_{O_2} and P_{N_2} are the permeances of O_2 and N_2, respectively. SiO_2–PVP–salcomine hybrid membrane showed oxygen selectivity even at high temperatures. Although the initial selectivity at 298 K was not that high (P_{O_2}/P_{N_2} = 1.4), the selectivity was found to increase with increasing temperature. At 423 K, the O_2/N_2 selectivity factor was 6.1, and the permeance of O_2 was 5.0×10^{-10} (mol m^{-2} s^{-1} Pa^{-1}). This selectivity factor is greater than the theoretical Knudsen value (P_{O_2}/P_{N_2} = 0.94) which can be ascribed to the strength of the Co(II)–oxygen complex bonds, which are strong at higher partial pressures of oxygen; therefore, salcomine effectively only releases oxygen at temperatures > 373 K, that is strongly trapped by salcomine at low temperature and thus lowers the mobility of oxygen. The absence of oxygen selectivity for the SiO_2–PVP hybrid membrane (without salcomine) confirms that oxygen selectivity is strongly related to the presence of salcomine.

In conclusion, SiO_2–(*N*,*N′*-disalicylideneethylenediaminato)cobalt(II) (salcomine) hybrid membranes for oxygen separation were prepared by the sol–gel method using poly(*N*-vinylpyrrolidone) (PVP) as a mediation agent. Results indicates that the proposed structure of the membrane consisted of well dispersed inorganic (SiO_2) and organic (PVP, salcomine) segments at a molecular level. This membrane can be classified as a high O_2 selectivity membrane even at high oxygen partial pressure and relatively high temperature.

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