

Reactive polymer membranes containing cuprous complexes in olefin/paraffin separation

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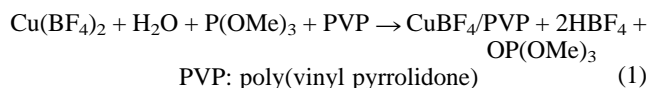
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The reduction of $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ in 1 wt% poly(vinyl pyrrolidone)–methanol solution with trimethyl phosphite produced a solution containing cuprous complexes; the membrane prepared from this solution showed a maximum selectivity of 10 for propylene over propane at room temperature.

Separation of olefin/paraffin mixtures is one of the most important processes in the petrochemical industry.¹ Currently, the separation is often carried out by highly energy-intensive low temperature distillation. Among a number of alternative separation processes, separation by a facilitated transport membrane with Cu^+ or Ag^+ has attracted much interest because of its low energy consumption, compact unit and simple operation.² The basis for the separation is the reversible formation of a π -bonded complex between metal ions, like Cu^+ or Ag^+ , and the olefin.^{3,4} Many studies have been reported on the facilitated transport of olefins by using supported liquid membranes,⁵ ion-exchange membranes⁶ or dense polymer membranes⁷ containing silver ions as carriers. Cuprous ions have also been applied as carriers for facilitated transportation in liquid membranes, but only for transportation of carbon monoxide and not for olefins.⁸ Recently, Lin *et al.* reported the use of CuCl coated γ -alumina membranes in the separation of ethylene/ethane mixtures, but obtained a maximum selectivity of only 1.4 for ethylene over ethane.⁹ To the best of our knowledge, reactive solid polymer membranes containing cuprous ions have never been reported, probably due to the low solubility and the instability of cuprous complexes in water or organic solvents.¹⁰

We report here, for the first time, the direct synthesis of reactive solid polymer membranes containing cuprous complexes and the application of such membranes to the separation of olefin/paraffin mixtures. The addition of trimethyl phosphite to a methanol solution of a cupric salt and an appropriate polymer produced a solution containing cuprous species, which was subsequently coated onto a porous asymmetric membrane. Trimethyl phosphite is known to reduce $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ as in eqn. (1).¹¹ The copper ions were found to exist only in the $\text{Cu}(\text{I})$ state, as identified by iodometry.¹²



The membranes were prepared as follows: $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ (3 mmol, 1 g) and $\text{P}(\text{OMe})_3$ (6 mmol, 1.5 mL) were added to 1 wt% poly(vinyl pyrrolidone) (0.5 mmol, 0.05 g) solution in methanol. The resulting solution was applied to a 5 cm × 5 cm asymmetric porous polysulfone membrane. The membrane was dried for 12 h in air and then vacuum-dried for 12 h at room temperature. Membranes consisted of a thin nanoporous cuprous-poly(vinyl pyrrolidone) top layer and an asymmetric coarse-pore polysulfone support. The thickness of the active layer was 2–3 μm , determined by scanning electron microscopy (not shown).

Separation measurements were performed with the coated membrane placed in a stainless steel separation module with the olefin/paraffin (50/50) gas mixture as described elsewhere.¹³ The flow rates of the mixed gas and the sweep gas (helium) were controlled using mass flow controllers. The total feed pressure of mixed gas was set at 20 psig by back pressure regulators. Average fluxes of ethylene/ethane and of propylene/propane through the membranes were 2×10^{-5} and 1×10^{-5} $\text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$, respectively at room temperature. The permeated gas was analyzed by gas chromatography.¹⁴

Fig. 1 and 2 show the effects of molar ratios of $\text{P}(\text{OMe})_3/\text{Cu}(\text{II})$ and $\text{Cu}(\text{II})/\text{PVP}$ on the separation of olefin/paraffin mixtures. The selectivity for olefin over paraffin increased with increasing molar ratio of $\text{P}(\text{OMe})_3/\text{Cu}(\text{II})$ up to 2 and then

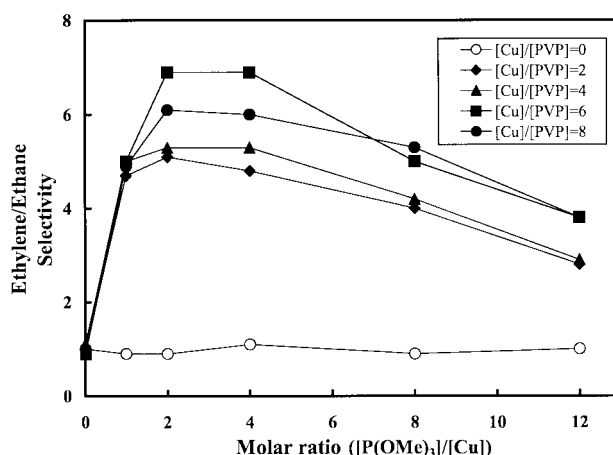


Fig. 1 Effects of molar ratios of $[\text{P}(\text{OMe})_3]/[\text{Cu}]$ and $[\text{Cu}]/[\text{PVP}]$ on the permeation selectivity of ethylene over ethane at 25 °C.

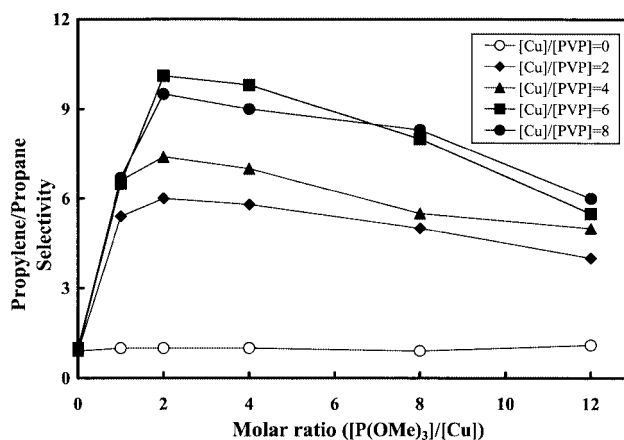


Fig. 2 Effects of molar ratios of $[\text{P}(\text{OMe})_3]/[\text{Cu}]$ and $[\text{Cu}]/[\text{PVP}]$ on the permeation selectivity of propylene over propane at 25 °C.

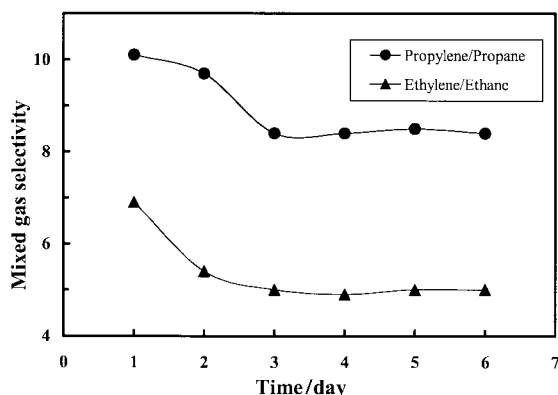


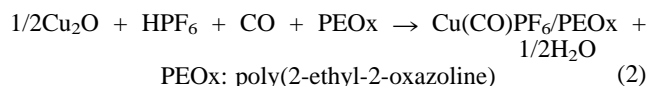
Fig. 3 Change of mixed gas selectivities with time.

gradually decreased with further increase in the molar ratio. It is likely that coordination of trimethyl phosphite is taking place to a certain extent, which could reduce the complexation ability of cuprous ion towards olefin. As expected, the membranes did not show any selectivity for olefin over paraffin at $P(\text{OMe})_3/\text{Cu}(\text{I}) = 0$, confirming that only $\text{Cu}(\text{I})$ is responsible for the selectivity. The copper ions present in the membrane prepared in the absence of $P(\text{OMe})_3$ exist only as $\text{Cu}(\text{II})$, for which complexation with olefin is impossible. The higher permeability ratio of propylene/propane in comparison with that of ethylene/ethane can be ascribed to the difference in diffusion rates of the mixed gases. The molar ratio of $\text{Cu}(\text{II})/\text{PVP}$ was also varied in the range from 0 to 8. As shown in Fig. 1 and 2, the selectivity increased with increasing molar ratio of $\text{Cu}(\text{II})/\text{PVP}$ up to 6. No appreciable selectivity at $\text{Cu}(\text{II})/\text{PVP} = 0$ demonstrates that the PVP-only membrane is not effective for the olefin/paraffin separation and the separation is not taking place by simple diffusion and desorption across the PVP only membrane. Membranes with the molar composition of $P(\text{OMe})_3:\text{Cu}(\text{II}):\text{PVP} = 2:1:6$ were subjected to a seven day permeation test as shown in Fig. 3. The selectivity decreased from 8 to 5 for ethylene/ethane and from 10 to 7 for propylene/propane during the first two days of the experiments and remained constant thereafter, demonstrating that the membranes were stable for at least a week. It is assumed that trimethyl phosphite present in the membranes may play a role in preventing $\text{Cu}(\text{I})$ from being oxidized to $\text{Cu}(\text{II})$ by trace amounts of oxygen or water in the feed gas.

Other cuprous membranes were also prepared using $\text{Cu}(\text{ClO}_4)_2$ and $\text{Cu}(\text{SO}_3\text{CF}_3)_2$, and tested for the separation of olefin/paraffin mixtures. The selectivities were lower by a factor of approximately 2 than the selectivities from the $\text{Cu}(\text{BF}_4)_2$ membranes. This can be attributed to the fact that ClO_4^- and CF_3SO_3^- are more strongly binding anions than BF_4^- and consequently the reversible complexation of olefins is

somewhat inhibited. In fact, the membranes containing CuCl showed much lower ethylene/ethane permeation selectivity, possibly due to the competitive complexation of ethylene and Cl^- .⁹

In a separate experiment, a polymer membrane containing $\text{Cu}(\text{CO})\text{PF}_6$ was prepared according to eqn. (2).



The membrane thus obtained was very unstable and showed no selectivity for the separation of propylene/propane mixtures. However, interestingly, when small amounts of trimethyl phosphite were added to the polymer solution of eqn. (2), the resulting membrane showed a maximum separation factor of 5 for the propylene/propane mixture. This result implies that trimethyl phosphite is functioning as a stabilizer for cuprous ion.

Investigations on the interactions between polymers and copper salts are in progress to improve the properties of cuprous ion-containing membranes.

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