

Alkene/alkane permselectivities of a carbon molecular sieve membrane

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A carbon molecular sieve membrane, whose pore dimension is slightly changed upon mild activation, exhibits excellent permselectivities for alkene/alkane gas pairs.

Separation of light alkenes/alkanes has been recognized to be a key technology in the petrochemical industry. Propene/propane is a representative example, since propene is an important petrochemical feedstock and useful in the production of many chemicals. Several methods including distillation, adsorption, absorption and membrane separation have been employed for separation of propene from propane.¹ Among them, membrane separation is expected to be superior to other methods, since it is an energy saving process. Up to now, membrane separation of propene from propane has been investigated mainly by using polymeric membranes.²⁻⁴ However, the drawbacks are the relatively lower permselectivity and lack of thermal and chemical stabilities of the polymeric membranes. These have led to further trials to develop thermally and chemically stable inorganic membranes which exhibit a better separation performance for propene/propane.^{5,6} One of the candidates is a carbon molecular sieve (CMS) membrane obtained by pyrolysis of a polymeric precursor. The CMS membrane has been extensively studied and shown to have high gas permselectivities, *i.e.* a molecular sieving effect.⁷⁻¹¹ In our previous papers,^{12,13} CMS membranes prepared by pyrolysis of both flat and capillary Kapton polyimides had been reported to exhibit the highest gas permselectivities for inorganic gas pairs. Here, we report the excellent propene/propane permselectivity of a CMS membrane whose pore dimension has been slightly expanded.

The original CMS membrane was fabricated by pyrolysis of a Kapton polyimide film (Toray - Du pont Inc.) between graphite blocks at 1273 K for 2 h at a heating rate of 10 K min⁻¹ at 10⁻⁵ Torr.¹² The membrane thus obtained was revealed by chemical analysis and IR spectroscopy to consist of almost only carbon. The membrane is essentially X-ray amorphous and was considered to have a turbostratic structure,¹⁴ in which layer-planes of graphite-like structures are dispersed in a non-crystalline material. Because the original membrane has pores of only *ca.* 3.7 Å which are too small for permeation of hydrocarbons such as propene, the membrane was further calcined under mild activation in order to slightly enlarge the pore dimension. The original membrane was heated to 673 K at a heating rate of 10 K min⁻¹ under flowing Ar (>99.99%, 100 ml min⁻¹), and then He (>99.995%, 100 ml min⁻¹) containing water vapour (*ca.* 20 mmHg). After 10 min the He was replaced by Ar and the sample allowed to cool to room temperature.

Pore size distributions were obtained from analysis of adsorption isotherms at 298 K of probe gas molecules with different kinetic diameters σ ¹⁵ (CO₂, C₂H₆, n-C₄H₁₀, i-C₄H₁₀) by application of the Dubinin-Astakhov equation [eqn. (1)],¹⁶

$$W = W_0 \exp[-A/E]^n, \quad A = RT \ln(P_s/P) \quad (1)$$

where W is the pore volume, A is the adsorption potential, P_s is the saturated vapour pressure, P is the equilibrium vapour pressure, E is the characteristic energy of adsorption, and W_0 is the limiting micropore volume whose pore size is assumed to be larger than the kinetic diameter of each adsorbate. The samples were degassed at 573 K for 2 h under vacuum prior to each

adsorption measurement. The adsorption isotherms obtained for both the CMS membranes before and after the mild activation step revealed that the former adsorbed only the smallest CO₂ molecule ($\sigma = 3.3$ Å), whereas the latter adsorbed even the larger C₂H₆ molecule ($\sigma = 3.9$ Å). The results suggest that the mild activation step is effective for the gradual increase of pore dimensions. It was clear from the obtained pore size distributions that the average pore size increased from *ca.* 3.7 to 3.9 Å due to the mild activation step. Fig. 1 demonstrates that larger pores of 4.0–4.3 Å which were not present in the original membrane appear to exist in the modified one.

Permeabilities of selected single gases were measured at 308–373 K with a high-vacuum time-lag method. The permeabilities of inorganic gases for the original CMS membrane were of the order of kinetic gas diameters¹⁵ except for H₂ (Fig. 2). The permselectivities measured at 308 K for the

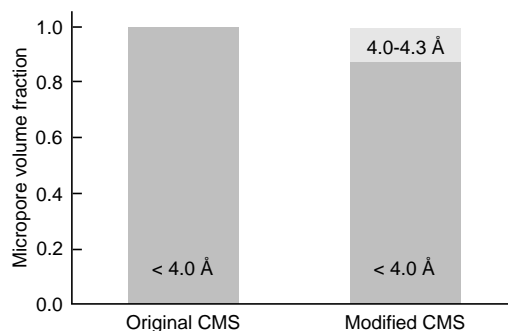


Fig. 1 Change in micropore volume fraction of each pore size for the original and modified carbon molecular sieve (CMS) membranes

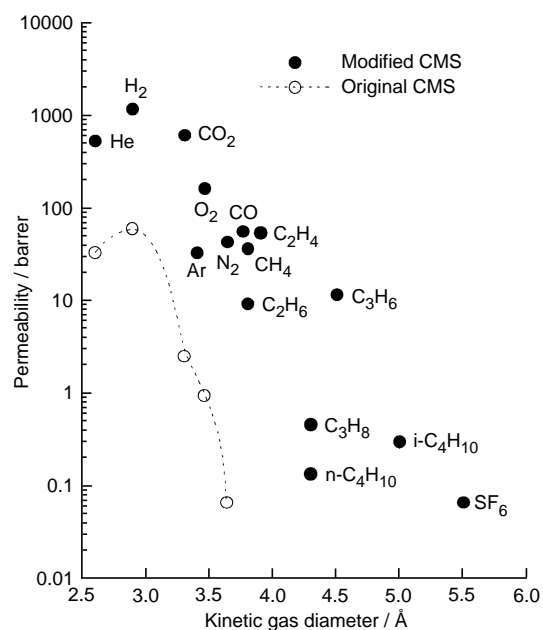


Fig. 2 Permeabilities of selected gases for the original and modified CMS membranes measured at 373 K. Permeabilities are given in barrer, where 1 barrer = 1 × 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ (cmHg)⁻¹.

membrane exceeded 1000 and 100 for H₂-N₂ and CO₂-N₂, respectively. These extremely high permselectivities, by which the membrane can discriminate between smaller and larger molecules, were a consequence of a pore dimension suitable for separation of such inorganic gas pairs.

The permeabilities for the modified CMS membrane were 10–700 times higher than those for the untreated membrane mainly due to the enlarged pore dimension. It was also shown from further permeation tests that there is an appreciable permeation of larger hydrocarbons. In particular, the permselectivities for light alkene/alkane gas pairs of the same carbon number were high. Permselectivities for propene/propane, for instance, were > 100 at 308 K, much higher than previously reported values for polymeric membranes.^{2–4} A rather high permselectivity of *ca.* 6 was also obtained at 308 K for ethene/ethane. These rather high permselectivities for the alkene/alkane gas pairs may arise from several factors including size effects, diffusivity and/or sorptivity, and the nature of surface functional groups that can be induced by the modification. A detailed study will now be undertaken on the permeation of hydrocarbons in modified CMS membranes to elucidate the factors leading to high permselectivities.

Considering the drawbacks of polymeric membranes (thermal and chemical instabilities *etc.*), the CMS membrane reported here activated under mild conditions is shown to be a promising candidate for alkene/alkane separation; other candidates for alkene/alkane separation are sol-gel derived inorganic membranes.^{5,6} Silica membranes prepared by Asaeda *et al.*⁵ exhibited permselectivities of 26 and 75 at 308 K for propene/propane single gas and gas mixtures, respectively, attributed to

the selective adsorption of propene. However it appears to be difficult to prepare inorganic membranes which exhibit good propene/propane separation by the sol-gel method.⁶

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