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Preparation of a membrane with aligned nanopores using an organic–inorganic hybrid technique

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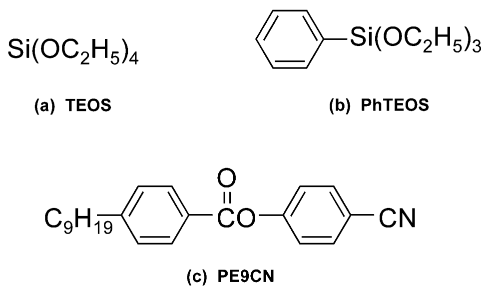
High performance membranes having aligned nanopores were prepared by an organic–inorganic hybrid process using an electric field to align the liquid crystal molecules therein.

Microporous and mesoporous materials have received a great deal of attention for their potential application as molecular sieve membranes, high performance catalysts and catalytic supports. Similarly, many attempts have been made to synthesize mesoporous silica films with controlled pore alignment on substrates.[1–4] However, as the orientations of the resulting mesopores are parallel to the substrate surfaces, such microstructures are not suitable for applications such as gas separation membranes. Other efforts using unidirectional freezing[5] and eutectic decomposition[6] have resulted in porous materials with one-dimensional through channels perpendicular to the substrates. Membranes prepared by unidirectional freezing have large pore diameters (from less than one to several tens of micrometers) suitable for use as membranes for catalytic supports or dust filters, but not for use as molecular sieve membranes. Films prepared by eutectic decomposition, on the other hand, have mesopores (about 4 nm in diameter), and could thus be used for catalysts or membrane reactors. They cannot, however, be used as gas separation membranes because hematite aggregations formed during the oxidation process produce pinholes in the mesoporous silica film on the porous substrates. Furthermore, pore diameters of 4 nm are still too large to provide a molecular sieving effect.

Here, we report the preparation of membranes with aligned nanopores using an organic–inorganic hybrid process capable of producing membranes with high permeance and high selectivity. The proposed novel method combines an organic–inorganic hybrid material of silica and liquid crystal molecules and enables alignment of liquid crystal molecules in the silica matrix by application of an electric field and subsequent removal of the liquid crystal molecules by calcination.

Tetraethoxysilane (TEOS) and phenyltriethoxysilane (PhTEOS) were used as silica sources and *p*-cyanophenyl-*p*-(nonyl)benzoate (PE9CN) was used as liquid crystal molecules for the creation of aligned pores (Scheme 1). The concentration of PE9CN in the PhTEOS was 20 wt.% (0.8 wt.% of total sol weight) and this PE9CN amount corresponded to 12 wt.% of the hybrid formed by theoretical hydrolysis and condensation. SiO_2–$C_6H_5SiO_{3/2}$–PE9CN hybrid membranes were prepared using following molar sol–gel composition: TEOS: PhTEOS:PE9CN:C_2H_5OH-:H_2O:HNO_3 = 0.8:0.2:0.03:20:4:0.01. In a typical synthesis, the homogeneous sol was prepared by stirring a mixture of TEOS, PhTEOS, H_2O, HNO_3 and C_2H_5OH for several hours at room temperature. The PE9CN was then introduced and the resulting sol was vigorously stirred for several hours to obtain a homogeneous mixture.



(a) TEOS (b) PhTEOS (c) PE9CN

Scheme 1

Porous alumina tubes (NGK Insulators, Ltd.; mean pore diameter, 0.1 μm; o.d., 10 mm; i.d., 7 mm; length, ~ 10 cm) were used as the supports. An intermediate layer was coated on the support using the same procedure described by Kuraoka *et al.*[7] The intermediate layer-coated tubes were used as supports for the preparation of membranes. The supports with one end closed were dipped in the sols and withdrawn at a rate of 1 mm s^{-1}, then dried at room temperature. The dip coating procedure was performed in a class 1000 clean room (at 295 K and 50% R.H.) to prevent contamination by dust, which would cause pinholes in the membranes. After repeating the dip-coating step twice, the membranes were heated at 333 K in an electric field (electric field strength: 50,000 V m^{-1}, applied voltage: 200 V, electrode gap: 4 mm) for 3 hours using the apparatus shown in Fig. 1, then cooled to room temperature. After heating and application of the electric field, the membranes were calcined at 873 K for 2 hours in air at heating and cooling rates of 2 K min^{-1}. These coating and heating procedures were repeated twice in the same manner. All membranes were prepared using the same procedure with the exception of the membranes not exposed to the electric field.

After drying at 373 K in a vacuum oven for 1 hour, single gas permeations of He, N_2, and CO_2 through the membranes were measured at 298, 373 and 473 K using the same procedure as that described by Kuraoka *et al.* [7] One end of the tubular membrane was sealed and the other end was connected to a Pyrex glass tube with epoxy resin. The membrane modules were supported in a gas flow cell. Pressure differences of the gases through the membranes were kept constant and permeance was measured using a mass flow meter. Table 1 lists the permeances of He, N_2 and CO_2 through the membranes prepared with and without exposure to the electric field and shows the selectivity factors α = PHe/PN_2 and PCO_2/PN_2, where PHe, PN_2 and PCO_2 are the permeances of He, N_2 and CO_2, respectively. Permeances of He and CO_2 through the membranes exposed to the electric field were as much as three or more times higher than those through the membranes not exposed to the electric field. On the other hand, permeances of N_2 through the

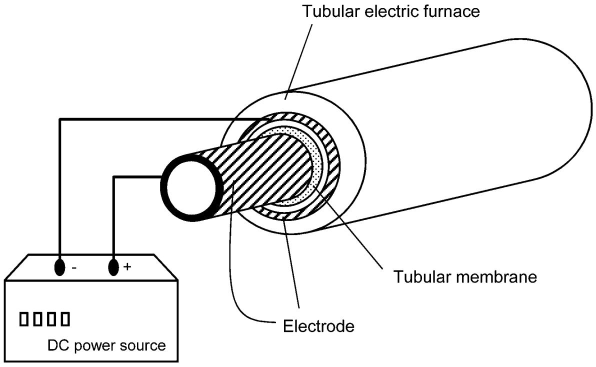


Fig. 1 Schematic diagram of apparatus for applying electric field.

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membranes exposed to the electric field were lower than through those without exposure to the electric field. Accordingly, selectivity factors of He and CO_2 in relation to N_2 through the membranes exposed to the electric field were high and 10 times larger than the theoretical Knudsen values. These high selectivities were evidence of molecular sieve membranes having micropores. High permeance through the membranes is due to alignments of the liquid crystal molecules in the hybrid material exposed to the electric field. These aligned liquid crystals produced pores as result of calcination, thus the permeance of membranes exposed to the electric field became high due to a shortening of permeation channels in the membrane. To confirm the alignment of the liquid crystal molecules in the hybrid, the order parameter[8] of the liquid crystal molecules in the hybrid was determined by polarized FT-IR spectroscopy[8] using a hybrid material formed in an electric field on Si flat substrate. Figs. 2 and 3 show schematic diagrams of the measurement configuration for polarized FT-IR and polarized FT-IR spectra of –CN bonds in the hybrid exposed to the electric field (tilt angle $\phi = 30$ degrees), respectively. The sample was tilted to align with angle ϕ to evaluate the order parameter toward the perpendicular of substrate surface. The order parameter calculated from the result was about 0.24. And the order parameter of the hybrid exposed no electric field was -0.02 in the same measurement. Order parameter $S = 1$ means the molecules are completely aligned to the normal of the substrate surface, $S = -1$ means the molecules are completely aligned to the parallel of the substrate surface and $S = 0$ means the molecules exist at random. Therefore, this result means that liquid crystal molecules in the hybrid exposed to the electric field were in some degree aligned along the normal of the substrate surface. This alignment of the liquid crystal molecules caused high permeance through the membranes exposed to the electric field.

Table 1 Permeances and selectivity factors through membranes with and without electric field exposure

		10^{-10} Permeance/ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$			Selectivity factor	
Membrane	T/K	N_2	He	CO_2	He/ N_2[a]	CO_2/ N_2[b]
Membrane with electric field	298	1.1	300	17	265	15
	373	1.6	810	15	506	9
	473	4.2	1800	47	428	11
Membrane without electric field	298	9.1	100	6.0	11	0.7
	373	8.2	220	6.1	27	0.8
	473	8.3	510	13	61	1.6

[a] Theoretical selectivity factor based on Knudsen flow is 2.6. [b] Theoretical selectivity factor based on Knudsen flow is 0.8.

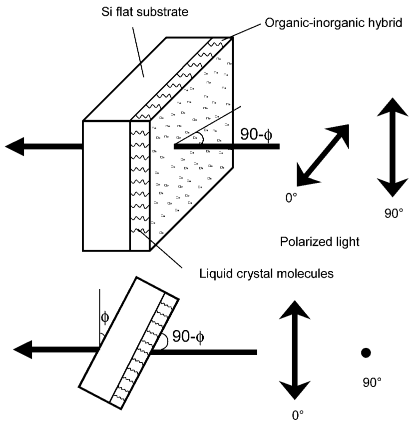

Fig. 2 Schematic diagram of measurement configuration for polarized FT-IR spectroscopy.

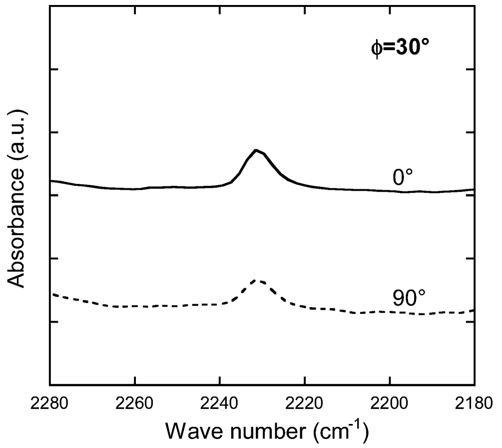

Fig. 3 Polarized FT-IR spectra of –CN bonds in the hybrid material.

In conclusion, high performance membranes having aligned nanopores were prepared by an organic–inorganic hybrid process using an electric field to align the liquid crystal molecules therein. Analytical results indicate that the liquid crystal molecules in the hybrid were aligned by the application of an electric field and that the pores in the membrane were introduced by the subsequent removal of the aligned liquid crystal molecules.

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