J Mater Sci (2007) 42:723–727
DOI 10.1007/s10853-006-1182-5

LETTER

Preparation of CO_2-selective separation membranes with highly chemical and thermal stability prepared from inorganic-organic nanohybrids containing branched polyethers

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Received: 28 June 2006 / Accepted: 25 October 2006 / Published online: 4 January 2007

Global warming is becoming an urgent environmental problem. Among CO_2 separation processes such as cooling and condensation, solvent scrubbing, adsorption and membrane, membrane separation process is utilized for the flue gas emitting from electric power generation plant; iron works plant and cement plant etc. Another important field is removal of CO_2 of natural gas and coal gas [1, 2]. CO_2 storage needs to have low environmental impact, low cost and conform to national and international laws. The main optioned for storing CO_2 underground which have been examined by the IEA Greenhouse Gas R&D Programme are storage in depleted oil and gas reservoirs, deep saline reservoirs and unminable coal seams [3]. A key technology to attain the membrane separation process is the development of a highly CO_2-selective separation membrane with chemical and thermal stability [4]. Recently, active research has been carried out on inorganic-organic nanohybrids prepared by the sol-gel method, which gives products with good thermal and chemical stability and allows formation of high quality membranes [5–8]. Here, nanohybrid means an organic polymer is dispersed at the molecular level in a SiO_2 matrix composed of siloxane networks. The most common method to obtain the nanohybrid utilizes hydrogen-bonding interactions between polar functional groups of organic polymers and silanol groups of the silica matrix. Chujo et al. reported that the polymers could be successfully produced without formation of hydrogen bonds between the polymer molecules. For example, poly(2-methyl-2-oxazoline), poly(N-vinylpyrrolidone) etc. could be dispersed in a silica matrix at the molecular level [9]. In the case of the branched polyether, the polymer may be dispersed at the molecular level through hydrogen bonding between the silanol groups of the silica matrix and the polyether oxygens as indicated in Fig. 1. The membrane formed with the branched polyether shows high CO_2 selectivity at room temperature (selectivity of CO_2 against N_2 is 50 at 308 K). However, the selectivity readily decreases at above room temperature [10]. In this paper, we report a CO_2-selective inorganic-organic nanohybrid membrane with high chemical and thermal stability prepared from the branched polyether.

The typical preparation process of the sol was as follows. To prepare a 5 wt% branched polyether membrane, the sol composition was branched polyether/tetraethoxysilane (TEOS)/acetonitrile = 1:69:465 (weight ratio). The branched polyether was sourced from Daiso Co. Ltd. The molecular weight of the polymer is 520,000 and its molecular structure is shown in Fig. 1. Here, wt% of branched polyether indicates the weight percent of branched polyether relative to the amount of branched polyether and silica hydrolyzed TEOS. Acetonitrile was employed as solvent. In order to perform the hydrolysis, HNO_3 and H_2O were also added in the following mol ratios: TEOS/HNO_3/H_2O = 1:0.01:2. In a typical synthesis, the homogeneous sol was prepared by stirring a mixture of TEOS,

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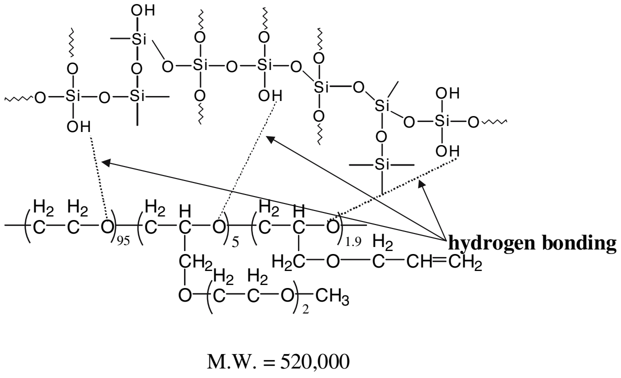


Fig. 1 Molecular structure of branched polyether and its state in silica matrix

H_2O, HNO_3 and acetonitrile for 1 h at room temperature. The branched polyether was added to the sol with continuous stirring for 4 h, which finally afforded a homogeneous sol. To prepare a clear gel, the sol was kept at 423 K for 2 h in a sealed Teflon container. Figure 2 shows the pore size distribution of the gel after calcination for 10 h under atmospheric pressure at 873 K; the distribution was obtained from the measured N_2 adsorption isotherm based on the BJH method [11]. This figure suggests a pore diameter of 2 nm. This pore was consistent with the branched polyether being burned off during calcinations regardless of the amount of the branched polyether. Based on the studies of S. Kasaoka et al. [12] and H. Tadokoro et al. [13], the width of the polymer is estimated about 1.1–1.2 nm in helical structure regardless of molecular weight. This result coincides fairly well with the width of the polymer considering the degree of accuracy of pore size distribution based on the BJH method in the range of around 1–2 nm. This means that the branched polyether is well dispersed at the molecular level over the silica matrix.

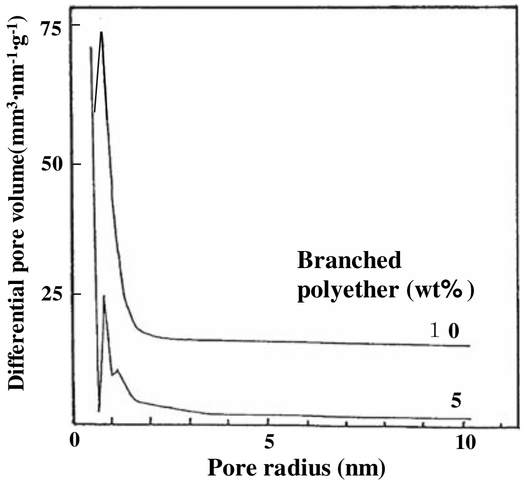


Fig. 2 Pore size distribution after calcination at 873 K for 10 h

A porous alumina tube (NGK Insulator Ltd.) with a mean pore diameter of 0.1 μm, an outer diameter of 10 mm, an inner diameter of 7 mm and a length of about 10 cm was used as a support. In order to prepare the intermediate layer, a commercial silica colloid, Snowtex O (particle size of 10–20 nm, Nissan Chemical Industries, Ltd.), was applied by dip coating of the alumina tube. The tubular support with intermediate layer was dipped with one end closed in the above-described sol, and was withdrawn at a rate of 1 mm s^{-1} and dried at room temperature. The dip coating procedure was performed in a class–1000 clean room at 300 K to avoid dust leading to defects on the membrane. After the dip coating was repeated three times, the membrane was heated to 423 K at a rate of 0.5 K min^{-1}, maintained at the same temperature for 2 h, and then cooled to room temperature at 0.5 K min^{-1}. These coating and heating procedures were repeated twice in a similar manner. Figure 3 shows an SEM (JEOL, JSM–5310) image of a cross-section of the membrane. From the SEM observation, the thickness of the coated membrane is about 1 (μm. One end of the alumina tube was sealed and the other end was connected to a Pyrex glass tube with epoxy resin as the membrane employed here. The photo of the membrane was shown in Fig. 4.

Single gas permeation through these hybrid membranes at different temperatures was measured using CO_2, N_2 by a procedure described elsewhere [14]. Prior to measurement, the membrane was dried at 323 K for 1 h under a reduced pressure of 1 kPa. Figure 5 shows the selectivity of CO_2 against N_2 for membranes formed with different amounts of branched polyether. Here, the selectivity was calculated by the permeance ratio of pure gases, PCO_2/PN_2. Among these

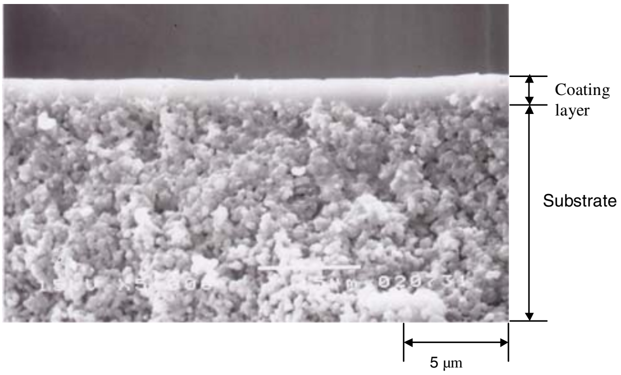


Fig. 3 SEM image of a cross-section of the membrane

Fig. 4 Photograph of membrane

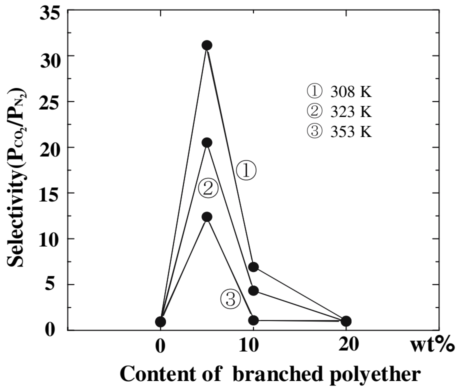


Fig. 5 Selectivity of CO_2 against N_2 vs. content of branched polyether in silica matrix

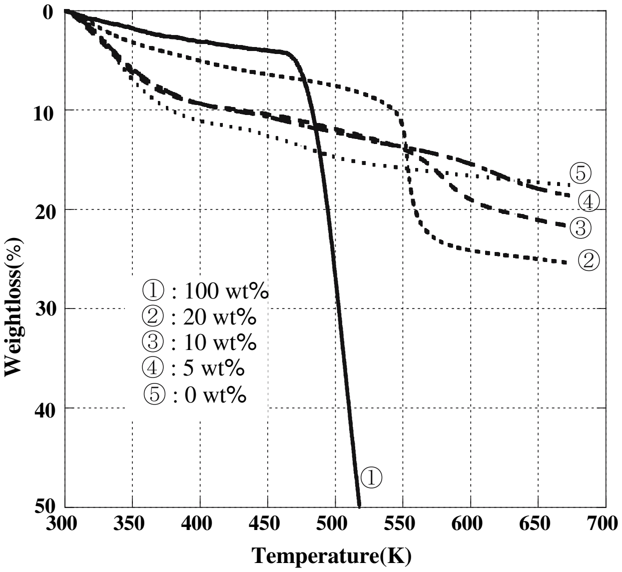


Fig. 6 Thermogravimetric analysis for various contents of branched polyether in silica matrix

membranes, the membrane with 5 wt% branched polyether gives the highest selectivity. This membrane showed $PCO_2/PN_2 = 21$ at 323 K and maintained selectivity at higher temperatures; i.e. $PCO_2/PN_2 = 12$ at 353 K. However, the membrane with 20 wt% branched polyether gave a very small value. Table 1 lists the amount of adsorbed CO_2 observed at temperatures of 308, 323 and 353 K at 0.1 MPa of CO_2 atmosphere measured using a high-precision gas adsorption apparatus (BEL JAPAN INC. BELSORP-mini). As indicated in Table 1, the larger the content of branched polyether, the smaller the amount of CO_2 adsorbed. This is consistent with the CO_2 selectivity with the exception of the 5 wt% branched polyether. The reason for this exception is not obvious. It may be a consequence of the very hydrophilic surface of the silica matrix, whereby water molecules bind tightly to the silica surface and CO_2 molecules, in turn, adsorb to these water molecules. This is supported by the TG curve obtained for the membrane without branched polyether as shown in Fig. 6.

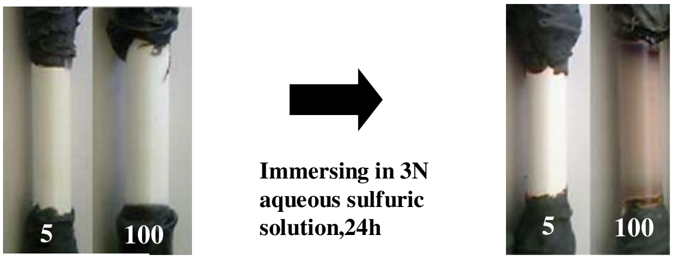
Micro defects on the membrane influenced the selectivity greatly. For the membrane without

Table 1 Amount of adsorbed CO_2 for various contents of branched polyether in silica matrix

Content of branched polyether	Amount of adsorbed CO2 [mol/g] × 10^{-5}		
	Temperature		
	308 K	353 K	423 K
0 wt%	54	51	38
5 wt%	69	46	36
10 wt%	22	17	13
20 wt%	1.6	2.5	2.0

Table 2 Permeance of CO_2 through membranes formed with 0–20 wt% branched polyether in the gas permeation temperature region from 323 to 353 K

Content of branced polyether	Temp. (K)	Permeance (mol/m^2 s Pa) P_{CO_2}
0 wt%	323	1.4×10^{-8}
	338	1.4×10^{-8}
	353	1.1×10^{-8}
5 wt%	323	8.4×10^{-9}
	338	3.9×10^{-9}
	353	5.1×10^{-9}
10 wt%	323	1.0×10^{-9}
	338	5.3×10^{-9}
	353	7.5×10^{-9}
20 wt%	323	3.3×10^{-9}
	338	4.3×10^{-9}
	353	4.5×10^{-9}



Immersing \ Membrane	5 wt% Branched polyether		100 wt% Branched polyether	
	Permeance mol/m^2·s·Pa	Selectivity P_{CO_2}/P_{N_2}	Permeance mol/m^2·s·Pa	Selectivity P_{CO_2}/P_{N_2}
before	$P_{CO_2} = 8.4 \times 10^{-9}$	31.1	$P_{CO_2} = 3.7 \times 10^{-10}$	26.0
after	$P_{CO_2} = 8.4 \times 10^{-9}$	30.5	$P_{CO_2} = 1.9 \times 10^{-7}$	0.79

Fig. 7 Comparison of chemical stability between membranes formed with 5 wt% branched polyether and membrane formed with 100 wt% branched polyether

branched polyether, the adsorbed CO_2 value is very large; however, the selectivity is very low. In this case micro defects might exist on the membrane surface, which may be the cause of the low selectivity. As the membrane formed with the branched polyether has good film-forming ability, it may be possible to obtain defect-free membranes. Table 2 lists values for permeance of CO_2 through the membranes formed with 0~20 wt% branched polyether at the gas permeation temperature region from 323 to 353 K. The permeance of the membrane formed without branched polyether is one order larger than those of other membranes formed with branched polyether. Permeance of He of the membranes with 0 wt%, 5 wt% and 10 wt% branched polyether was 3.8×10^{-8}, 2.0×10^{-9} and 3.1×10^{-9} (mol/(m^2 s Pa)), respectively at 323 K. As He is nonadsorbable gas, permeance characteristics of He trough the membranes reflect on the physical structure of the membrane. Permeance of He of the membrane with 0 wt% branched polyether is 19 times and 12 times larger than that of the membranes with 5 wt% and 10 wt% branched polyether. These results support the evidences of micro defects on the membranes.

Chemical stability of the membrane formed with 5 wt% branched polyether and a membrane composed of only branched polyether was investigated by immersing the branched polyether membrane in 3 N aqueous sulfuric acid for 16 h at room temperature. As indicated in Fig. 7, in the case of the membrane formed with 5 wt% branched polyether, the CO_2 selectivity before and after immersion was almost the same. On the other hand, in the case of the membrane composed of only branched polyether, there was no CO_2 selectivity observed after immersion. Further, the color of the membrane formed with 5 wt% branched polyether hardly changes in contrast to the color of the membrane composed of only branched polyether, which changes distinctly. The membrane formed with 5 wt% branched polyether clearly has excellent chemical stability.

Thermal stability was evaluated by thermogravimetric analysis (Thermo Plus TG8120, Rigaku) and the results are shown in Fig. 6. It is clear that the thermal stability is remarkably improved by nanohybridization with a silica matrix.

In conclusion, a CO_2-selective membrane with high thermal and chemical stability could be obtained by dispersing a branched polyether at the molecular level in a silica matrix. This membrane has the potential for actual use in both CO_2 selectivity and permeance applications [1, 2, 15].

Acknowledgements The authors would like to thank Mr. Takaaki Sakai and Mr. Masato Tabuchi of *Daiso Co. Ltd.* for preparation of the branched polyether.

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