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Boehmite-phenolic resin carbon molecular sieve membranes—Permeation and adsorption studies

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A B S T R A C T

Composite carbon molecular sieve membranes (c-CMSM) were prepared in a single dipping–drying–carbonization step from phenolic resin solutions (12.5–15 wt.%) loaded with boehmite nanoparticles (0.5–1.2 wt.%). A carbon matrix with well-dispersed Al_2O_3 nanowires was formed from the decomposition of the resin and dehydroxylation of boehmite. The effect of the carbon/Al_2O_3 ratio on the porous structure of the c-CMSM was accessed based on the pore size distribution and gas permeation toward N_2, O_2, CO_2, He, H_2, C_3H_6 and C_3H_8. c-CMSM with higher carbon/Al_2O_3 ratios had a more open porous structure, exhibiting higher permeabilities and lower permselectivities. c-CMSM performance was above the upper bound curves for polymeric membranes for several gas pairs, particularly for C_3H_6/C_3H_8 (permeability toward C_3H_6 of 420 barrer and permselectivity of 18.1 for a c-CMSM with carbon/Al_2O_3 ratio of 4.4).

Unsupported films were also prepared (carbon/Al_2O_3 ratio 7.3) and crushed into small flakes. Equilibrium isotherms of H_2, N_2, O_2, CO_2, C_3H_8 and C_3H_6 at 293 K were determined on these flakes to obtain the kinetic and adsorption selectivities toward gas pairs of interest; obtained adsorption and diffusion coefficients accurately predicted the permeabilities of all studied gases except CO_2 (experimental and predicted permeabilities of 1148 and 154 barrer, respectively).

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1. Introduction

Membrane technologies are a cheap and clean technology for gas separation. In particular, polymer membranes have been used extensively for gas separation in the last few decades. Two key parameters characterize the separation performance of membranes: the permeability and the selectivity. The permeability characterizes the ability of the membrane to be permeated by a solute while the selectivity characterizes the ability of this membrane to discriminate the permeation transport of a species compared to the mixture (Mulder, 2000). It was recognized that these are trade-off parameters since an increase in the permeation of a given species generally origins

a decrease in the selectivity and vice versa (Robeson, 2008; Rungta et al., 2012). Robeson (1991, 2008) reported the separation upper bound limit of polymer membranes for several binary gas mixtures of interest. The upper bound relationship for membrane gas separations correlates the log of the selectivity versus the log of the permeability of the more permeable gas for achieving the desired result of a high selectivity combined with a high permeability. Microporous membranes are capable of overcoming this upper limit since they show much higher permeabilities for equivalent selectivities. CMSM are a class of inorganic porous membranes that display the aforementioned good selectivity/permeability relationship (Campo et al., 2010a; Centeno and Fuertes, 1999, 2001; Centeno

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Nomenclature

Variables

A	structural model constant $(\mathrm{mol\,m^2\,kg^{-1}\,s^{-1}\,Pa^{-1}})$
b	adsorption affinity coefficient $(\mathrm{Pa^{-1}})$
D	diffusivity $(\mathrm{m^{-2}\,s^{-1}})$
D_0	diffusivity at zero loading $(\mathrm{m^{-2}\,s^{-1}})$
Err	fitting error
F	fractional uptake (at a given time)
F_c	chemisorption fractional uptake
H	Heaviside function
J	permeating flux $(\mathrm{mol\,m^{-2}\,s^{-1}})$
k	LDF mass transfer coefficient $(\mathrm{s^{-1}})$
L	membrane permeability $(\mathrm{mol\,m\,m^{-2}\,s^{-1}\,Pa^{-1}})$
MSC	model selection criteria
m_t	mass at instant t (kg)
m_0	initial mass (kg)
m_∞	equilibrium mass (kg)
n	SIPS equation parameter
n_p	number of parameters
n_v	number of experimental values
p	partial pressure (Pa)
P	total pressure (Pa)
q	surface concentration $(\mathrm{mol\,kg^{-1}})$
q^{exp}	experimental surface concentration $(\mathrm{mol\,kg^{-1}})$
q_{avg}^{exp}	average of experimental surface concentration $(\mathrm{mol\,kg^{-1}})$
q^{max}	maximum surface concentration $(\mathrm{mol\,kg^{-1}})$
q^{model}	surface concentration given by model $(\mathrm{mol\,kg^{-1}})$
r_c	chemisorption uptake rate $(\mathrm{s^{-1}})$
$\Re$	gas constant $(\mathrm{Pa\,m^3\,mol^{-1}\,K^{-1}})$
S	permselectivity
S_d	activation entropy of diffusion $(\mathrm{J\,mol^{-1}\,K^{-1}})$
t	time (s)
t_c	chemisorption time (s)
u	Toth equation parameter
T	absolute temperature (K)
z	spatial coordinate (m)

Greek symbols

λ	blocking parameter
θ	fractional coverage of the pore surface
δ	membrane thickness (m)
ζ	Elovich equation constant
ξ	Elovich equation constant $(\mathrm{s^{-1}})$
Λ	half of slab thickness (m)
ρ_s	solid density $(\mathrm{mol\,kg^{-3}})$

Subscript

i	species (i)

Superscripts

h	high pressure side of the membrane
l	low pressure side of the membrane

et al., 2004; Hagg et al., 2003; Kim et al., 2004; Kita et al., 1997; Lagorsse et al., 2004).

Although more expensive than polymeric membranes, they have a tunable pore size distribution and are more thermally, chemically and wear resistant. Carbon membranes have a complex pore structure that combines the sieving effects of the smaller pores with preferential adsorption on its larger ones. This bi-modal distribution can lead to high selectivities while maintaining good permeabilities (Saufi and Ismail, 2004). However, carbon membranes also have their own drawbacks, such as brittleness and their fabrication suffers from poor reproducibility (Koros and Mahajan, 2000). Moreover, when exposed to air or to impurities such as large organics and water vapor they are known to exhibit a decrease in performance (Jones and Koros, 1994, 1995; Lagorsse et al., 2008; Menendez and Fuertes, 2001). It was verified that the existence of oxygen-based functional groups on the surface of the carbon membranes could enhance the adsorption of water vapor and then increase the water obstruction effect (Lagorsse et al., 2008), which limits the applicability of this type of membranes. In this context, new approaches concerning the preparation of CMSM have been proposed. Namely, the concept of composite carbon molecular sieve membranes (c-CMSM) – incorporation of nanoparticles in the carbon matrix – has appeared as an alternative to improve the permeation performance, chemical and thermal stability of CMSM (Barsema et al., 2003, 2005; Liu et al., 2006, 2009; Park et al., 2004, 2005; Teixeira et al., 2011, 2012; Xiao et al., 2010; Yin et al., 2010; Yoda et al., 2004; Zeng et al., 2008).

Kim et al. (2002, 2003) prepared c-CMSM from metal-substituted sulfonated polyimides and observed that the permeabilities increased with the ionic radius of the metal ions (Kim et al., 2003). Barsema et al. (2003, 2005) dispersed Ag nanoparticles into P84 and P84/SPEEK precursors and observed that the O_2/N_2 selectivity of the c-CMSM was higher than that of the non-functionalized CMSM. Yoda et al. (2004) reported a 17-fold enhancement of H_2/N_2 selectivity of CMSM after adding Pt and Pd to polyimide precursors. Hollow-fiber CMSM derived from sulfonated poly(phenylene oxide) (SPPO) were prepared by Yoshimune et al. (2006). Metal cations such as Na^+, Mg^{2+}, Al^{3+}, Ag^+, Cu^{2+} and Fe^{3+} were ion-exchanged with the proton of the sulfonic acid group of SPPO and the effects on gas transport properties for the carbonized membranes investigated; Ag-SPPO membranes carbonized at 923 K had the best performance for O_2/N_2 separation. Park et al. (2004, 2005) reported that silica loaded c-CMSM exhibited better performances due to the fast diffusion on silica microporous domains. Novel c-CMSM has also been successfully prepared through the incorporation of nano-sized zeolites into the polymeric precursor, revealing excellent performances (Liu et al., 2006, 2009).

This work proposes the incorporation of low cost nanoparticles (boehmite) in a low cost, high carbon yield polymer (phenolic resin) to prepare a composite carbon membrane in a single dipping–drying–carbonization step. During carbonization, the polymer decomposed forming a carbon matrix with homogeneously distributed Al_2O_3 nanofillers, derived from the dehydration of the boehmite nanoparticles. c-CMSM with three different polymer/boehmite compositions were prepared (keeping the same carbonization conditions) and their separation properties for several gas pairs of interest discussed. The decrease in performance of the c-CMSM due to air exposure (aging) was also studied.

2.   Experimental

2.1.   Materials

The industrial phenolic resin was supplied by Euroresinas-Indústrias Químicas, SA. N-Methyl-2-pyrrolidone was