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Permselectivity improvement in membranes for CO_2/N_2 separation

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ABSTRACT

In this work, small-pore zeolites of different topology (CHA, LTA5, Rho), all with Si/Al ratio of 5, have been added to highly permeable poly(1-trimethylsilyl-1-propyne) (PTMSP) to increase its selectivity and thermal and mechanical stability. Membranes were characterized by TGA, XRD, SEM and CO_2 and N_2 single gas permeation measurements at different temperatures. TGA reveal that the thermal resistance of the mixed matrix membranes (MMM) is as good as that of pure PTMSP polymer membranes. XRD and SEM results reflect that there is good interaction between the fillers and the membrane matrix, at 5 and 10 wt.% zeolite loadings, while at 20 wt.% a dual layer structure is formed, when Rho zeolite is the filler, because the particle size of Rho is higher than those of LTA5 or CHA, and voids appear that limit the permselectivity performance. In single gas permeation of N_2 and CO_2, the influence of temperature, zeolite loading and type is analyzed. The selectivity of pure PTMSP is considerably enhanced with the addition of the zeolites and the increase of temperature, and the MMM loaded with 5 wt.% zeolite surpassed the Robeson's upper bound for CO_2/N_2 separation, without decreasing the permeability too much. Upon increasing temperature from 298 to 333 K, the permselectivity is enhanced even further without loss of permeability. The 5 wt.% loaded membranes were tested in CO_2/N_2 mixed gas separation experiments at 333 K and 12.5 wt.% CO_2 in the feed, and the permselectivity of LTA5- and Rho-PTMSP membranes was further enhanced, compared with the single gas permeation experiments.

1. Introduction

The atmospheric concentration of greenhouse gases (GHGs) has increased significantly over the last century [1]. Carbon dioxide is the main component of these gases, and its accumulation in the environment is leading to severe global warming issues, which makes necessary finding a feasible separation technology for the removal of CO_2 from flue gases. Membrane technology appears to be an attractive option in terms of energy saving, modularity, ease of scaling up and control [2], such as those energy intensive based on wet scrubbing using aqueous amine solutions [3]. In a typical coal-fired power plant the flue gas is about 323 K, nearly at atmospheric pressure, and has a CO_2 content as low as 10–15% and partial pressure of 10–15 kPa [4]. Therefore, membranes with high CO_2 permeability and moderate selectivity over other gases are required in order to allow working in a wider range of operating conditions in post-combustion [5]. Besides, membranes should present good thermal and mechanical properties and be robust enough for long term operation [6]. In particular, the impact of membrane material in CO_2 removal is as important as the process conditions [7].

Polymeric membranes appear, currently, to be the most advanced option for membrane-based post-combustion carbon capture in terms of CO_2/N_2 permselectivity [8]. However, the lack of thermal stability or inadequate performance in terms of permselectivity limit their use in industrial separations. In fact, there is a well-known trade-off between selectivity and permeability for a specific pair of gases separation [9]. One of the ways of improving the performance of polymer membranes is based on the concept of mixed-matrix membranes (MMM), which combine the molecular sieving effect and other characteristics of the dispersed fillers with the processing feasibility of polymeric materials to achieve a new material with enhanced mechanical and functional properties [10]. Components selection is a key feature in the development of new MMM. A good adhesion between polymer and sieve is a factor of paramount importance in order to achieve a defect-free MMM with synergistic properties, and this limits the choice of candidate materials [11].

Since polymer selection determines the minimum separation performance, poly (1-trimethylsilyl-1-propyne) (PTMSP), which is the organic polymer with the highest permeability reported, being

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located at the right of the Robeson's upper bound [9], is selected as continuous matrix in this work. The CO_2 permeability of PTMSP reported in literature covers a range between 16,000 and 38,000 Barrer at 298 K [12,13], probably because the different stages of aging affecting PTMSP performance [14]. The high permeability of PTMSP is based on high solubility and high diffusivity and is probably related to its very low density (0.75 g cm^{-3}) and its extremely high free volume (0.29) [15,16], accounting for the presence of microvoids [12], compared with the rest of dense glassy polyimides [17]. The glassy structure of PTMSP explains the low chain mobility with a glass transition temperature greater than 523 K [15], which makes it a promising material for high temperature membrane separations, but leads to loss of permselectivity with time due to physical aging phenomena upon permeation and CO_2 plasticization. The addition of properly selected inorganic fillers is supposed to enhance membrane selectivity when no defects are present [18–20].

Zeolites were the first molecular sieves used as fillers in polymer matrices for gas separation because of their crystalline character with well-defined pore structures and shape selectivity properties [21]. Zeolite 4A nanoparticles have been widely reported in the literature to increase the permselectivity performance of glassy polyimides such as Matrimid [22], P84 [23], polyvinyl acetate [24], polycarbonate [25], or poly ether sulfone (PES) [26], and rather constant selectivity. However, adhesion with the commercially available polymers mentioned above is still a major challenge and many efforts have been made regarding preparation methods such as priming [26], zeolite modification by organic linkers [27] or zeolite preheat treatment [28]. Besides, zeolite 4A with a Si/Al ratio of 1 is very sensitive to the presence of moisture, which is a main component in flue gas, constituting a problem because the adsorbed water may not be easily released at the membrane separation temperatures [28]. The effect of Si/Al ratio on LTA fillers in PTMSP for CO_2/N_2 separation was studied in a previous work, using zeolites with Si/Al ratio 1 (Zeolite A) and ∞ (ITQ-29) [29]. The membranes prepared with low Si/Al ratio showed the highest CO_2 permeability and selectivity, surpassing Robeson's upper bound even at 333 K, due to better adhesion between zeolite A and the polymer matrix, obtaining a dual layer structure that approached the membrane performance to that of a pure zeolite A membrane at 20 wt.% zeolite A loading. Pure silica ITQ-29 did not dispersed or adhered too well with the rigid structure of the super glassy PTMSP polymer [30]. The ideal CO_2 adsorbent is a material with an intermediate CO_2 affinity, high adsorption capacity, combined with good selectivity and easy regeneration. This applies also for an effective filler for CO_2 selective MMM. Kosinov et al. [31] have just presented promising CHA (SSZ-13) purely inorganic hollow fiber CO_2 selective membranes but they did not manage a Si/Al ratio as high as 5 into a defect-free zeolite layer. In the particular case of PTMSP, as far as we know, only Woo et al. [20] and Fer nández-Barquín et al. [29] employed porous zeolites to modify the gas separation performance of the PTMSP. As far as we know, no works have yet been reported employing CHA or Rho zeolites into a MMM using PTMSP.

This is the reason why, in this work, we study the effect of small-pore zeolites with Si/Al ratio of 5 and different structures (CHA, LTA5 and Rho), as well as good CO_2 adsorbing capacity, on the PTMSP matrix for MMM performance in CO_2/N_2 separation. MMM were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), and pure gas permeation of N_2 and CO_2, in the temperature range of 298–333 K, taking into account the mechanical and thermal stability. The most promising membranes were also measured in dry 12.5% CO_2/87.5% N_2 mixture separation at 333 K, to evaluate gas separation performance.

2. Experimental

2.1. Preparation of MMM

MMM were prepared following the procedure described in our previous work [29]. Poly(trimethylsilyl propyne) (PTMSP) was purchased from ABCR GmbH (Germany) with a purity of 95%, dried at 70 °C for several hours before being dissolved in toluene. The difference is that in this work, the zeolite fillers employed have different topologies, CHA, LTA and Rho.

Zeolites were synthesized at the Instituto de Tecnología Química in Valencia, according to procedures reported in literature [36,40,41], with a Si/Al molar ratio of 5 and the properties that are summarized in Table 1.

The gases used in the experiments were carbon dioxide (99.97%), oxygen (>99.999%) and nitrogen (>99.999%) provided by Air Liquide (Spain).

The membrane thickness was measured by means of a digital micrometer (Mitutoyo digimatic micrometer, IP 65) with an accuracy of 0.001 mm. The average thickness of the membranes is 72.75 ± 5.46 μm, not being influenced by the type of zeolite, and not far from the nominal thickness of 100 μm expected. As all the membranes have similar thicknesses, the permeability values are not affected by this parameter. The density of same membranes was also determined after the permeation tests, to study gravimetrically the integrity or possible physical aging of the membrane. The nominal filler loading used were 5, 10 and 20 wt.% referred to PTMSP polymer concentration.

2.2. Characterization

Thermogravimetric analysis have been performed to determine the thermal degradation of the MMM using a DTG-60H thermobalance (Shimadzu, Japan) in air atmosphere at a heating rate of 10 K min^{-1} up to 973 K. The sample temperature was measured with an accuracy of ±0.1 K and the TG sensitivity was about 1 μg.

The cross-sectional areas and the morphology of selected membranes of each composition were observed by scanning electron microscopy, using a Jeol JSM 5410 equipment, located at the Universidad Politécnica de Valencia. Membrane samples were fractured in liquid nitrogen, to obtain a clean cross section that is coated with gold to reduce the charging effects on the polymer surface.

The X-ray diffraction of zeolite crystals and MMM was measured at the Servicio de Difracción de Rayos X y Análisis por Fluorescencia del Servicio General de Apoyo a la Investigación de la Universidad de Zaragoza. Data were collected at room temperature using a Rigaku/D/max 2500 diffractometer, provided with rotating anode, at 40 kV and 80 mA Cu Kα radiation with λ = 1.5418 Å and graphite monochromator.

Single gas permeability of N_2 and CO_2 was determined within the temperature range 298–333 K in a constant volume system experimental setup shown in Fig. 1. The membrane module consists of two stainless steel pieces with a cavity where the membrane is placed on a 316LSS macroporous disk support of 20 μm

Table 1
Properties of the zeolites employed in this work.

Zeolite	Particle size (μm)[a]	Density (g/cm^3)	Pore volume (cm^3/g)	Pore size (Å)	Si/Al	Reference
CHA	1.0	1.508	0.33	3.8	5	[31,35,36]
LTA5	0.5	1.498	0.27	4	5	[32,39,40]
Rho	1.5	1.442	0.26	3.6	5	[33,34,37,41]

[a] Observed by SEM, except Rho, which forms agglomerates with PTMSP as binder, so the particle size is taken from [33].