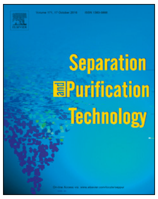
Separation and Purification Technology 210 (2019) 29–37

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Mixed matrix membranes incorporated with three-dimensionally ordered mesopore imprinted (3DOm-i) zeolite

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ABSTRACT

MFI and LTA zeolites were synthesized inside three-dimensionally ordered mesoporous (3DOm) carbon. After the removal of the carbon, a highly crystalline 3DOm-imprinted zeolite with tunable and ordered mesopores was obtained. The nominal mesopore size can be finely controlled from 5 to 15 nm by changing the cage size of the 3DOm carbon. Under different synthesis conditions, the crystal size of the 3DOm-imprinted (3DOm-i) MFI was tuned from approximately 100 nm to several micrometers. The 3DOm-i zeolite was mesoporous and exhibited a spherical shape with a rough external surface. With the synthesis of 3DOm-i zeolites, mixed matrix membranes (MMMs) were prepared by incorporating them into a commercial polyimide matrix (i.e., Matrimid® 5218). Both MFI- and LTA-containing MMMs exhibited good adhesion between the zeolites and polymer because of their imprinted mesopore structure and rough external surface. Also, both MMMs exhibited a substantial increase in permeability to all the gas penetrants used in this work (except for NF_3), resulting in an excellent N_2/NF_3 separation efficiency.

1. Introduction

Recently, it has been shown that the incorporation of porous functional materials including zeolite, metal organic frameworks (MOFs), silica, and carbon molecular sieves into a polymer matrix is useful for enhancing the separation performance of polymeric membranes in terms of gas permeance and selectivity [1–4]. MOFs are frequently selected as a dispersed media for the fabrication of mixed matrix membranes (MMMs) because they can be tailored in terms of their microstructure design and high affinity towards polymer matrices. However, relatively few attempts to fabricate MMM-dispersing zeolites have been made because of their poor compatibility with polymers, although zeolites possess well-defined microporous configurations with a rigid pore structure. MMMs containing zeolite often exhibit undesirable polymer/zeolite interfaces such as their “sieve-in-cage” morphology and polymer chain rigidification, leading to a significant decrease in the gas separation performance [5].

To overcome these issues, three strategies have been proposed: tuning of the polymer matrix, the development of novel MMM fabrication routes, and the tailoring of the zeolite morphology. Primarily, low-molecular-weight polymers (LMWPs) with polar atoms and a planar structure, such as 2-hydroxy-5-methylaniline (HMA) [6] and p-nitroaniline (pNA) [7], have been added to the polymer matrix to improve compatibility. The LMWPs induce enhanced contact between the polymer matrix and the zeolite, but antiplasticization causing an increase in the stiffness originates from the reduced rates of segmental motion of the polymer chain that occurs at the same time. MMMs prepared using this approach exhibited increased gas selectivity with a slight reduction in their gas permeance. Block copolymers and polymer blending of both rigid and flexible polymers were also used in the

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Abbreviations: APTES, aminopropyltriethoxysilane; APTMSP, aminopropyltrimethoxysilane; 3Dom, three-dimensionally ordered mesoporous; FFT, fast-Fourier-transform; HMA, 2-hydroxy-5-methylaniline; HZS, hollow silicalite-1 sphere; LMWP, low-molecular-weight polymer; MMM, mixed matrix membrane; MOF, metal organic framework; NMP, N-methyl-2-pyrrolidone; pNA, p-nitroaniline; SAC, steam-assisted crystallization; SAXD, small-angle X-ray diffraction; SAXS, small-angle X-ray scattering; SDA, structure directing agent; TEOS, tetraethyl orthosilicate; XRD, X-ray diffraction

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https://doi.org/10.1016/j.seppur.2018.07.082
Received 3 May 2018; Received in revised form 28 July 2018; Accepted 28 July 2018

preparation of MMMs [8–10]. The flexible segments improved contact with the zeolite whereas the glassy polymer portion served to discriminate between the gas molecules. The resultant MMMs exhibited improved gas permeance with moderate gas selectivity.

To prepare the MMM, a priming method whereby zeolite was initially mixed with 10–20% of the total amount of the polymer was used to improve the compatibility between the zeolite and the polymer [11,12]. Most studies involving MMMs now include a priming step to enhance the filler/polymer interface contact and to attain uniform dispersion of the fillers in the polymer matrix. Although the priming treatment improved certain gas separation performance attributes of MMMs containing zeolite, defects commonly occur in the interfaces and have not been thoroughly resolved. As an alternative process, the annealing of MMMs above the glass transition temperature of the polymer matrix was also explored, together with different heating and quenching protocols [13,14]. However, these approaches were less effective for preventing defects such as “sieve-in-a-cage.”

Zeolite crystals have also been tailored to improve the interfacial contact with the polymer matrix by chemical and morphological alteration. Zeolite crystals were chemically modified by silanation on their external surface using silane coupling agents such as aminopropyltriethoxysilane (APTES) and aminopropyltrimethoxysilane (APTMSP) [8,15–17]. Previous studies of MMMs using silane-modified zeolites demonstrated successful elimination of interfacial voids and exhibited improved gas separation performance. However, partial blockages of the zeolite pores by silane coupling agents were observed in most reports; therefore, further studies addressing the control of the number of coupling points on the zeolite surface are currently being undertaken.

The physical morphology of zeolites was also tailored for MMM production. Grignard treatment to increase the surface roughness of zeolites was proposed by Koros et al. [18]. $Mg(OH_2)$ whiskers grown on the zeolite surface during the Grignard treatment promote interfacial contact of the roughened zeolite with the polymer matrix, resulting in significant changes in the gas permeation relative to the neat polymer. MMMs containing mesoporous zeolite were also studied and exhibited considerable improvement in their gas permeance and selectivity, relative to conventional zeolite [19]. Although mesopores in the zeolite do not contribute to gas separation, they allow for the facile diffusion of the penetrant. Furthermore, polymer chains penetrated the mesopore during MMM preparation, leading to enhanced interfacial contact between the zeolite and polymer. Zornoza et al. reported on the fabrication of an MMM containing hollow silicalite-1 spheres (HZSs), prepared by the seeded growth of zeolite particles attached to a mesoporous silica sphere [20]. The morphology of the HZSs, with a dispersible spherical shape, large particle size, and surface roughness, provided good dispersion in the polymer matrix and increased zeolite/polymer interfacial contact. The MMMs exhibited improved gas separation performance toward H_2/CH_4, CO_2/N_2, and O_2/N_2. For the MMM with the tailored zeolite, morphological tuning was shown to be a facile approach to attaining high-performance materials because it is straightforward and applicable to various zeolite/polymer pairs. Furthermore, problems such as chain rigidification and pore blockage were prevented. Among the many possible zeolite morphologies, mesoporous features with roughened external surfaces and spherical crystal shapes are the most useful ones for attaining good dispersion owing to the good interfacial contact and easy dispersion into the polymer solution.

Recently, silicalite-1 zeolite with ordered mesoporosity in three-dimensionally ordered mesoporous (3DOm) carbon was produced using highly ordered colloidal crystals of silica nanoparticles [21,22]. The attractiveness of this approach arises from the ordered pore topology of the 3DOm carbon, which enables rapid mass transport during confined growth and imparts a structured three-dimensional mesoporosity on the crystalline materials after its removal. Therefore, it provides a favorable environment for zeolite growth in confined spaces, allowing the easy crystallization of zeolites with different frameworks such as BEA, FAU, LTA, and LTL in the template. The overall morphology of the three-dimensionally ordered mesopore imprinted zeolite (3DOm-i) is characterized by near-spherical shapes with external surface roughness, and mesopore structure from the core to the outer surface that forms because of the close-packed arrangement of the spherical nanocrystals. The configuration of the 3DOm-i zeolite involving the spherical shapes, mesopore structure, and external surface roughness can be utilized as a dispersal media for yielding high-performance MMMs.

To explore this possibility, an MMM was fabricated by mixing 3DOm-i zeolites with polyimide. First, the replication process of the 3DOm-i MFI inside 3DOm carbon was investigated, and the fidelity of the replication process was confirmed. Next, 3DOm-i zeolite was crystallized in various cage sizes of 3DOm carbon, and its mesopore size distribution and corresponding crystal shape and size were characterized. Finally, MMMs containing 3DOm-i MFI and LTA were fabricated by blending 3DOm-i zeolites with polyimide (Matrimid®). We selected these two distinct zeolites because MFI has a non-polar framework, with 10 member rings (φ ≈ 0.55 nm), whereas the LTA zeolite is defined by an 8-member ring (φ ≈ 0.40 nm) with a high polar framework. They were blended with a polyimide matrix exhibiting a high intrinsic gas permselectivity. The gas separation performance of the resultant MMMs toward various gas pairs was determined and the potential of 3DOm-i zeolite as a dispersal media for MMM is discussed.

2. Experimental

2.1. Synthesis of size-tunable silica nanoparticles and 3DOm carbon

Silica nanoparticle sols were synthesized, as described previously, by the hydrolysis of tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) in aqueous solutions of the basic amino acid lysine (Sigma-Aldrich) [23]. Lysine was dissolved in deionized water, followed by the addition of TEOS. Thereafter, the solutions were brought to the desired temperatures (60 °C for the 10-nm and 90 °C for the 20-nm silica particles). The molar composition of the synthetic solution was 60 SiO_2:1.2 lysine:9500 water:240 ethanol. Particle growth was achieved under continuous magnetic stirring at 500 rpm for 48 h. The 30- and 40-nm silica particles were synthesized using a seeded growth technique, in which the 20-nm particles were used as seeds. Subsequent repeated additions of TEOS, followed by growth at 90 °C for 24 h under vigorous stirring, was performed 1 and 3 times to increase the particle size to 30 and 40 nm, respectively. The final molar compositions were 150 SiO_2:1.2 lysine:9500 water:600 ethanol for the 30-nm particles and 490 SiO_2:1.2 lysine:9500 water:2940 ethanol for the 40-nm particles.

The 3DOm carbons were fabricated according to the method reported by Yokoi et al. [24]. We further modified this method to make 3DOm carbons with larger cages [23]. Colloidal crystal templates were formed by evaporating water from the lysine–silica nanoparticle sols in an oven at 70 °C for 24 h. After calcination of the product in a furnace at 550 °C for 12 h, furfuryl alcohol (Aldrich) and oxalic acid (Aldrich) were forced into the space between the packed silica nanoparticles for subsequent replication. The resulting product was heated to 90 °C for 1 day to attain the polymerization of the furfuryl alcohol, and then placed under flowing N_2, first at 200 °C for 3 h to cure the polymer, and then at 900 °C for another 3 h to carbonize the polymer. The template silica nanoparticles were dissolved in 6 M KOH solution (Aldrich) at 180 °C for 3 days to yield a mesoporous carbon replica, which was then thoroughly washed with deionized water until the pH was nearly neutral.

2.2. Crystallization of the 3DOm-i zeolite in 3DOm carbon

Steam-assisted crystallization (SAC) was used for the confined synthesis of 3DOm-i MFI in the 3DOm carbon template. In a typical synthesis, 3DOm carbons were impregnated to incipient wetness with a clear solution of tetrapropylammonium hydroxide (40%, TPAOH, Alfa