Journal of Membrane Science 499 (2016) 65–79

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Recent developments in zeolite membranes for gas separation

Nikolay Kosinov [a], Jorge Gascon [b], Freek Kapteijn [b], Emiel J.M. Hensen [a,*]

[a] Schuit Institute of Catalysis, Laboratory of Inorganic Materials Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] Catalysis Engineering, ChemE, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form
16 October 2015
Accepted 20 October 2015
Available online 24 October 2015

Keywords:
Zeolite membranes
Gas separation
8MR zeolites
High-silica zeolites

ABSTRACT

The latest advances in the field of zeolitic membranes for gas separation are critically reviewed with special emphasis on new synthetic protocols. After introducing the most relevant aspects to membrane performance, including adsorption trends, permeation mechanisms and support effects, we review recent achievements in membrane synthesis and discuss in detail the effect of zeolite topology and chemical composition on membrane gas separation. We pay special attention to promising 8MR high-silica structures. As the formation of defects during synthesis remains one of the major challenges for large-scale production of such membranes, we review various approaches to either limit defect formation or decrease their adverse effect by post-synthesis modification. Finally, the current challenges for this field of research are summarized and an outlook is offered on approaches to decrease fabrication costs, improve reproducibility and rational design of zeolite membranes.

Contents

1. Introduction

Membrane technology constitutes an increasingly important, convenient and versatile way of separating gas mixtures. Compared with other approaches, membranes reduce energy and other

* Corresponding author.
E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

http://dx.doi.org/10.1016/j.memsci.2015.10.049
0376-7388/

operational cost for gas separation and, moreover, membrane operations are more scalable than conventional separation unit operations in the chemical industry [1,2]. Several important industrial processes would benefit from the use of membranes, such as air separation (N_2/O_2) [3], recovery of hydrogen from mixtures (H_2/N_2, H_2/CO, H_2/CO_2, H_2/hydrocarbons) [4], hydrocarbon separations (olefins/paraffins, linear/branched isomers, etc.) [5], and CO_2 capture from natural gas, flue gas, biogas and syngas (CO_2/air, CO_2/CH_4, CO_2/H_2) [6,7].

Membranes are usually categorized in four main groups based on the nature of the membrane material: polymeric, inorganic, mixed-matrix and liquid membranes. Polymeric membranes currently dominate the global membrane separation market [8], because of their good processability, economic competiveness, scalability and tuneability [9,10]. On the other hand, polymeric membranes suffer from several limitations such as their inherent permeability/selectivity trade-off [11,12] and low thermal and chemical instability limiting, respectively, the overall performance and the range of operation conditions. Similar issues disturb industrial implementation of liquid membranes [13–16]. Mixed matrix membranes (MMM) are obtained when selective inorganic fillers are introduced into a polymeric matrix. The advantage of the MMM concept is that it combines the ease of polymer film processing with the high selectivity and permeability of inorganic materials. Several inorganic materials have been explored in this approach such as carbon molecular sieves [17,18], zeolites [19,20] and metal-organic frameworks [21–23].

Inorganic membranes are particularly interesting, as these materials can usually withstand high temperature and pressure. Several materials have already been explored for the preparation of dense and porous inorganic membranes. Dense structures conduct only particular gases or ions by solution-diffusion or mixed ionic-electronic conductivity mechanisms. Examples of such membranes are thin metallic (palladium, vanadium, iron, etc.) films for recovery of hydrogen [4,24] and ceramics (perovskites, fluorites) for oxygen separation [25]. The advantages of dense inorganic membranes are high selectivity (approaching infinity for high quality membranes) and thermal stability. On the other hand, low permeability and/or sensitivity to poisoning of dense membranes are their main drawbacks. Porous inorganic membranes, including those made of carbon, amorphous silica, zeolites and metal-organic frameworks, generally offer much higher fluxes and chemical stability.

Microporous amorphous silica membranes are usually thermally stable supported films with a thickness of several tens of nanometers capable of separating gases with very high fluxes. Such films can be prepared by sol–gel or chemical vapor deposition (CVD) techniques [26,27]. Low hydrothermal stability is, however, often a major weakness of silica membranes. Some methods including surface grafting (silylation) [28,29] and preparation of hybrid silica membranes [30,31] have been explored to improve hydrothermal properties of amorphous silica.

Carbon membranes are prepared by conversion of polymer layers by pyrolysis or carbonization at high temperature in inert atmosphere [32]. In general, pore sizes and adsorption properties of carbon membranes may to a certain extent be tuned by varying pyrolysis conditions and/or the polymeric precursor [33–35]. Unfortunately, carbon membranes are usually brittle, sensitive to strongly adsorbing components and possess pores of random size distribution, which make them difficult to apply for many relevant separations.

Metal-organic frameworks (MOFs) constitute a relatively new class of materials, which already have been extensively studied for membrane applications [36]. MOFs are porous coordination polymers consisting of metal ions (clusters) interconnected by polytopic organic linkers to form ordered porous structures. The number of possible MOF structures is only limited by synthetic imagination, as there are myriads of cluster-linker combinations. Accordingly, it is possible, within certain limits [37], to tune structure properties for a particular separation [38]. There are many examples of the preparation and application of MOF membranes. The interested reader is referred to recent review papers describing in detail state-of-the-art techniques, concepts and achievements in the field [39–42].

Finally, zeolites, owing to the uniform system of pores with molecule-sized dimensions, high porosity, excellent thermal and chemical stability, are particularly promising for fabrication of molecular sieving membranes, capable of separating gases at industrially relevant conditions.

Several reviews discussing advances in zeolite membrane fabrication and their separation properties are available. These include contributions of Caro and co-workers [43,44] and, more recently, the work of Pera-Titus [45] that reviewed the performance of zeolite and other porous inorganic membranes in CO_2 capture. Tsapatsis, Caro and co-workers discussed the preparation of ultra-thin and oriented zeolite films and also compared the separation properties of MOF and zeolite membranes [46]. The current review focuses on gas separation applications of zeolite membranes. First, we discuss general aspects of gas separation by zeolite membranes, including separation mechanisms, the influence of the porous membrane support and the main issues involved in the preparation of high-quality membranes. Second, zeolites and zeotypes of different topology and chemical composition are reviewed in terms of potential for membrane applications; post-synthesis modifications of such membranes to enhance separation performance are highlighted as well. Finally, we summarize our work by providing some general conclusions about the state of the art and an outlook on important development directions.

2. Zeolite membranes: general aspects

2.1. Permeation: adsorption

Any zeolite membrane separation starts with the adsorption of the molecules from the gas phase onto the zeolite pore surface. Accordingly, adsorption affinity plays an important role in overall separation performance. At low to moderate operation temperatures (up to 100–200 °C depending on zeolite structure and polarity) zeolite membranes usually exhibit adsorption selectivity. That is, the more strongly adsorbing component of a mixture disturbs or blocks permeation of other components for which zeolite channels remain (partially) inaccessible. Adsorption based separations are particularly effective for dewatering and CO_2 capture, namely when a strong adsorbates needs to be removed. Adsorption of certain gas molecules on the surface of a given zeolite material depends on the adsorbate and the adsorbent. The most important adsorbate parameters are polarizability and dipole and quadrupole moments (see Table 1). These parameters determine the strength of the interaction between the adsorbing molecule and the zeolite surface. For instance, H_2O and CO_2 are usually the strongest adsorbed species on zeolites among the compounds considered in Table 1, because of their large dipole and quadrupole moments. As an example, Fig. 1 provides ambient temperature adsorption isotherms of CO_2, CH_4 and N_2 on high-silica SSZ-13 zeolite.

As for zeolite adsorbents, such properties as polarity, topology and flexibility of the framework, the type of counter cation compensating for possible negative framework charges and the zeolite pore size determine adsorption behavior. One of the most important parameters is polarity, which in turns depends on the