



Hybrid organosilica membranes and processes: Status and outlook



Ion Agirre^a, Pedro L. Arias^a, Hessel L. Castricum^{b,c,d}, Madriana Creatore^e, Johan E. ten Elshof^b, Goulven G. Paradis^d, Patrick H.T. Ngamou^e, Henk M. van Veen^d, Jaap F. Vente^{d,*}

^aChemical and Environmental Engineering Department, Engineering School of Bilbao (UPV-EHU), Alameda Urquijo s/n, 48013 Bilbao, Spain

^bMESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

^cVan't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

^dEnergy research Centre of the Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands

^eDepartment of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Available online 8 August 2013

Keywords:

Hybrid silica membranes with organic links
HybSi[®]

Gas separation

Pervaporation

Sol–gel technology

Plasma enhanced chemical vapor deposition

ABSTRACT

In the past, the research in molecular separation membranes prepared through sol–gel technologies has been dominated by ceramic membranes. Especially, silica membranes have been studied in great depth. Steps towards hybrid organosilica membranes were taken by using pendant organic groups. However, only with the appearance of organically bridged silica, stable and reliable membranes that are suitable for large scale industrial utilization have become available. In this paper, we provide an overview of recent development of hybrid silica membranes that contain organic bridges. The freedom of choice in precursor allows for a flexible approach towards tailoring of the membrane properties. New support materials can be used by applying alternative deposition methods, such as expanding thermal plasma chemical vapor deposition. The robustness of the membrane concept allows for the design of novel separation process concepts in which the demonstrated stability is required.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Molecular separation membranes are expected to play an important role in reaching the environmental goal to reduce CO₂ emissions by approximately 50 Gt per year by 2050 [1]. Membranes can be applied as effective and energy-efficient separation systems to dehydrate wet bio-based fuels [2,3]. Also application in the (petro)chemical industry is widely considered to significantly enhance the energy efficiency of key processes. Although exact numbers are missing, separation processes are known to be one of the more energy-intensive steps in a chemical production plant. Molecular separation membranes can play a crucial role here [4–6].

In this paper, the status and potential of hybrid organosilica membrane materials, and their use in different molecular separations are presented. An outlook is given towards further developments. Pure inorganic silica membranes have a low hydrothermal stability [7,8], reducing the application window for dehydration of organic liquids by pervaporation to temperatures not exceeding ~75 °C [9]. The incorporation of methyl groups

[10] in the silica structure allows an increase of the application temperature to 95 °C [9]. This results in an application window with a temperature range that is similar to that of polymeric membranes like PVA [11] and polyimides [12]. Ceramic membranes will only have a value in the market when clear advantages over the commercially produced polymeric ones can be obtained. These advantages may include a higher performance, i.e. a higher selectivity and permeance, and an increased stability. As a result the application window can be broader than the more commonly used polymeric membranes. Envisaged application extensions are a higher application temperature, higher chemical stability towards strong organic solvents, acids and water, and a smaller sensitivity to swelling. The increase of operation periods under a wider range of applications will result in a positive business case for all industrial parties involved.

The focus of this review will be the preparation of membranes bridged polysilsesquioxanes precursors and their application in processes. Other types of hybrid membranes are reviewed elsewhere [13]. These current class of materials is characterized by covalent bonds between both oxygen and hydrocarbons to silicon. These materials are prepared by sol–gel processing [14] of monomers that contain an organic group that bridges typically two functional silyl groups [15]. A great variety of organic bridges can be used, including aromatic, alkyne, alkene, alkane, and functionalized moieties [16]. A general trend in mesoporous materials is that

* Corresponding author at: ECN, Westerdinweg 3, P.O. Box 1, 1755 ZG, 1755 LE Petten, The Netherlands. Tel.: +31 88 515 49 16, fax: +31 88 515 86 15.

E-mail address: vente@ecn.nl (J.F. Vente).

URL: <http://www.ecn.nl> (J.F. Vente).

the pore diameter increases with increasing length of the bridge [16–18]. Alternatively, organic templates can be used to direct the pore formation process [19]. The positive impact of the organic bridge on the hydrothermal stability for mesoporous materials has been recognized [20]. The application of similar microporous materials in molecular separation membranes was reported as recently as 2008 [21].

This review paper is structured in a number of chapters. We start with material and preparation considerations, which include structure–property relations. With respect to preparation, our focus is on sol–gel processes, in which bridging and pendant organic groups with various structures are incorporated. This is followed by a generic overview of possible applications of these membranes. While the main focus is on pervaporation, developments in gas separation and nanofiltration are discussed as well. A pervaporation process case study is presented for the production of an acetal, which can be used as a renewable diesel additive. The topics of the last chapters are recent developments in alternative preparation methods, new support options, new processes, and an outlook towards the requirements in fundamental knowledge needed to allow further applicability.

2. Precursors and preparations

2.1. Preparation of oxide membranes

Oxide microporous materials and membranes are typically prepared by conventional sol–gel approaches [14]. The mild synthesis conditions of sol–gel preparation allow the synthesis and control of nanoporous inorganic materials. Thin layers, $<1\ \mu\text{m}$, can be efficiently deposited onto a support by coating with the sol before the transition to the gel phase occurs. The first membranes prepared in this way were made from tetraethylorthosilicate (TEOS) [22–24]. A microporous, pore diameter $d_p < 2\ \text{nm}$, structure is formed upon acid-catalyzed hydrolysis and condensation of TEOS in mixtures with ethanol, water and nitric or hydrochloric acid. The basic degrees of freedom are the relative amounts of the four chemicals involved, the reaction temperature and time [14,25,26]. Variation in the preparative conditions leads to a great variety of membrane properties, which can be further enlarged through the use of pore forming agents [27]. The silica membranes can be doped with transition metal cations by the addition of a suitable alkoxy-functionalized metal precursor during sol preparation. Examples include Fe [28], Co [29], Zr [30], and Nb [31,32]. Inorganic membranes that consist completely of TiO_2 and ZrO_2 have also been prepared [33–36], although their dense atomic packing generally leads to low permeabilities [37]. The sol preparation part is followed by a coating step onto a multilayer support system. The most widely applied support system consists of a layer of mesoporous $\gamma\text{-Al}_2\text{O}_3$ [38], which in turn is supported by macroporous $\alpha\text{-Al}_2\text{O}_3$ [39]. After drying, the membrane preparation is concluded by calcination of the coated membrane.

2.2. Precursor choice for hybrid organosilica

The first membranes which did contain organic fragments were prepared by introducing alkyl-terminating groups into an otherwise inorganic membrane. Membranes have been made through the co-condensation of TEOS with mono-substituted R-trialkoxysilane precursors, with R = alkyl [9,40], phenyl [41], fluorine-substituted alkyl [42], unsaturated (alkene) [43], and amino groups [44,45]. Only recently, a bridging organic moiety was considered for the fabrication of a molecular separation membrane [21]. The precursor used for the preparation of the organically linked silica membranes was 1,2-bis(triethoxysilyl)ethane (BTESE,

$(\text{C}_2\text{H}_5\text{O})_3\text{-Si-C}_2\text{H}_4\text{-Si-(OC}_2\text{H}_5)_3$), which is still the most reported precursor molecule. The materials properties can be controlled by changing the structure of this bridging group [46,47]. Applying the BTESE precursor as a basis, other precursors can be added to modify the surface properties. The inorganic content can be increased by applying mixtures with TEOS [48]. Membranes with a higher organic content have been prepared with additives consisting of R-alkoxysilanes with R an alkyl [21,49] or amino side group [50]. The addition of Nb has led to a decreased permeance of CO_2 in SiO_2 -based membranes and an increased selectivity towards hydrogen [31]. This has inspired the addition of this precursor to BTESE-based membranes [51,52].

Organosilica precursors can also be used to synthesize inorganic silica membranes. Organic side groups [53,54] or bridging organic groups [27,55] are subsequently deliberately pyrolysed by high-temperature calcination. The organic groups thus served as pore formers and did not remain in the structure. This procedure is not further described in this review.

2.3. Sol preparation and coating

Control over the pore size distribution and defect concentration is essential in obtaining a high quality membrane [39]. Microporous and defect-free silica-based membranes with molecular sieving properties require acid-catalyzed hydrolysis and condensation, i.e. preparation conditions below the isoelectric point [14]. The reaction rate is determined by the temperature, the concentration of the reactants, the silsesquioxane precursor and water, and of the acid catalyst in the solvent. Condensation reactions lead to the formation of oligomeric colloidal structures and ultimately to the formation of a continuous network gel with high viscosity. NMR studies showed that BTESE hydrolyzes more rapidly than TEOS while condensation rates are of the same order [56]. The larger size and larger network-forming ability of BTESE, however, result in much faster colloidal growth than for TEOS. As thin-film coating requires low sol viscosity, lower reactant concentrations must be applied for BTESE than for TEOS [46,57].

The mean colloid hydrodynamic diameter can be applied as a measure for the suitability of a sol for membrane coating. A straightforward assessment can be done with dynamic light scattering [58]. A lower limit is set by the pore size of the mesoporous support layer, around 4 nm for $\gamma\text{-Al}_2\text{O}_3$, to prevent extensive infiltration of the sol into the substrate. At a particle size larger than 15 nm, growth is governed by colloid–colloid aggregation rather than the reaction of monomer species with colloids. Interaction between two large colloids for further-developed sols leads to broad colloid size distributions and viscous sols unsuitable for applying coatings [46].

Sol synthesis is usually carried out at 333 K or higher, with reaction times of several hours. An effective way to quench the reaction is to cool to room temperature and dilute the colloidal sol prior to coating. In this way, a stable sol is obtained with very limited ongoing condensation that can be handled easily. It can be used for coating during several hours, although the individual coating procedure does not take more than minutes. The coating procedure itself is preferably performed in a clean environment [40] to reduce the influence of the presence of dust particles which can adhere to the drying surface and create defects.

2.4. Calcination

The preparation of the membrane is finalized with a thermal treatment to consolidate the materials. The organic groups can be retained in the structure by applying mild thermal conditions, with temperatures between 250 and 300 °C and slow heating and cooling rates (0.5–1 K/min), in an inert atmosphere, usually

Download English Version:

<https://daneshyari.com/en/article/641415>

Download Persian Version:

<https://daneshyari.com/article/641415>

[Daneshyari.com](https://daneshyari.com)