



# Asymmetric polysilazane-derived ceramic structures with multiscale porosity for membrane applications



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## ABSTRACT

Novel ceramic structures with multi-scale porosity were developed using a single preceramic poly(vinyl)silazane to generate asymmetric Si-C-N-based membranes through pyrolytic conversion. Macroporous supports in planar-disc configuration were prepared through a sacrificial filler approach, intermediate structures and microporous layers were deposited via dip-coating. Microporosity in the selective layer was generated through a controlled thermal decomposition of the precursor component in nitrogen atmosphere at temperatures up to 600 °C, resulting in micropores with average pore sizes of 0.8 nm, as investigated by nitrogen adsorption and small-angle X-ray scattering (SAXS). The general feasibility of the single-precursor approach towards selective permeation of gaseous species was demonstrated by the investigation of gas permeances of the generated structures using single-gas permeance testing of He, N<sub>2</sub>, Ar, C<sub>2</sub>H<sub>6</sub>, and CO<sub>2</sub>. By variation of the deposition sequence during preparation of the selective layer by dip-coating, asymmetric structures with ideal permselectivities exceeding predicted Knudsen values were obtained. At 500 °C, He/N<sub>2</sub> and He/CO<sub>2</sub> permselectivities of up to 3.1 and 4.1 were found, respectively, at He permeances up to  $3 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ . The new single-material system is a first step towards the potential establishment of new, alternative membrane materials systems, circumventing thermal and chemical incompatibilities between constituents, and increasing material performance due to the applicability under extreme operating conditions.

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## 1. Introduction

Recent global challenges leading to the development of more sustainable processes, calls for energy conservation as well as the increased utilization of renewable energy sources have resulted in increasing interest in the application of membranes for filtration and separation processes.

Ceramic membranes present an alternative to conventional polymer-based membranes due to superior thermal, chemical, and mechanical properties, facilitating applications at temperatures beyond 300 °C or in harsh chemical environments. In contrast to dense membranes, porous ceramic membranes exhibit different mechanisms governing the transport of species through the

membrane depending on the pore size. In macro- and mesoporous materials, the main gas transport mechanisms include molecular diffusion, viscous flow, and Knudsen diffusion [1,2]. While offering high permeabilities, membranes operating under the Knudsen flow regime generally show low selectivities. Therefore, there is interest in developing microporous membrane materials with pore sizes <2 nm, exhibiting increased selectivities. In this case, micropore diffusion is the predominant form of gas transport [3]. A variety of microporous materials have been under investigation for this purpose, including SiO<sub>2</sub> [4], zeolites [5,6], carbon-based compounds [7,8], metal-organic frameworks [9,10], and titanosilicates and related materials [11–13]. Common problems limiting the application of these materials are structural instability, especially in presence of humid atmospheres in case of SiO<sub>2</sub>, high costs and reproducibility problems in case of zeolites, and poor mechanical properties and sensitivity towards oxidative environments in case of carbon-based structures [14,15].

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The generation of microporous ceramic compounds from pre-ceramic polymers has gained increasing scientific interest in the recent past. Polymer-derived ceramics (PDCs) are generally obtained by a controlled thermal conversion (pyrolysis) of mainly organosilicon preceramic polymers into Si-based ceramic materials [16–18]. Owing to the polymeric nature of the precursors and the resulting ability to use processing techniques otherwise not feasible for ceramics, the PDC route represents an alternative to traditional powder-technology based ceramic processing. Pre-ceramic polymers have been used for obtaining a wide variety of complex ceramic structures for energy-related applications, including coatings, fibers, bulk materials, and composites [19]. Scientific interest in polymer-derived cellular ceramics has demonstrated the potential for obtaining macroporous materials with uniform, graded, or hierarchical pore systems [20–22].

Microporosity in PDCs is generally produced during the polymer-to-ceramic conversion of the precursor [23,24]. Both the evolution of gaseous by-products as a result of the decomposition of organic groups as well as molecular rearrangements within the three-dimensional network structure lead to the development of an intrinsic micropore network [25]. However, further increase in temperature results in a closing of micropores, most likely due to viscous flow processes driven by a reduction in surface energy [26,27]. For instance, microporous compounds derived from pre-ceramic polysiloxanes show a significant reduction in microporosity starting at temperatures as low as 450 °C, with an almost complete collapse of the micropore network at temperatures beyond 700 °C [24].

A significant problem of oxygen-rich Si-based PDCs is the limited stability at high temperatures; furthermore, Si-O-C bonds are considered to be hydrothermally unstable [28]. Non-oxide PDCs such as polysilazane-derived silicon carbonitrides exhibit improved resistance against oxidation and creep at elevated temperatures [29]. As a result, the fabrication of these types of microporous non-oxide ceramics for a variety of fields, including catalysis and membrane applications, has gained increasing attention [23,27,30]. Dismukes and co-workers [23] reported on a variety of methods to generate microporous polysilazane-derived non-oxide ceramics, including the controlled thermal decomposition in a reactive atmosphere, in this case, ammonia (NH<sub>3</sub>), the use of inert, sub- $\mu\text{m}$  sized fillers, the formation of metal- or cermet-ceramic composites from polysilazane-stabilized metal colloids, or the thermal conversion of polysilazane mixed with metal-organic compounds. Using these methods, materials with specific surface areas  $>500\text{ m}^2\text{ g}^{-1}$  and micropore volumes  $>0.2\text{ cm}^3\text{ g}^{-1}$  were generated. A further increase in thermal stability of the micropore structure, i.e. the shift of the pore collapse onset towards higher temperatures, was reported by chemical modification of the preceramic polymer, e.g. by the addition of Ni [27,31], or by using a reactive gas atmosphere such as NH<sub>3</sub> during thermal decomposition [30]. Owing to the straightforward method of generating and controlling their micropore structure, microporous PDC-based SiO<sub>2</sub> [32], Si(O)-C [28,33–38], Si-C-N [39–41], and Si-B-C-N [42,43] have been investigated as selective layer structures in membrane systems.

In addition to the micro- or mesoporous selective layer structure, porous ceramic membranes generally require a macroporous support structure, responsible for the structural integrity of the component, resulting in an asymmetric structure with multi-scale porosity. Often, additional intermediate layers are present to suppress formation of pinhole defects in the selective layer. The most commonly used material for macroporous supports in PDC-based gas-separation membranes is Al<sub>2</sub>O<sub>3</sub> [2], but the use of other ceramics such as SiC has also been reported [44,45]. The choice of mesoporous intermediate layer depends on the materials involved.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, obtained through sol-gel techniques, is a common material

used on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-based supports [46]. An alternative method for the application of intermediate layers is the combination of preceramic polymers (in this instance, acting as a binder) with particulate fillers, e.g. SiC or Si<sub>3</sub>N<sub>4</sub> [28,39]. However, the use of different materials within a single membrane leads to a variety of problems. A mismatch of coefficients of thermal expansion between support and deposited layers decreases the ability to withstand repeated heating and cooling cycles without stress-induced damage. Furthermore, increased chemical reactivity between the constituents at elevated temperatures places a limit on the maximum operation temperature of the membrane systems.

Recently, we reported on a novel method for the preparation of porous ceramic support structures based on preceramic polymers, including polysilazane [47]. The supports, comprising a well-defined macropore structure obtained through a sacrificial template approach, were found to exhibit tailorable strength and permeability characteristics [48], rendering them potentially suitable as membrane supports. Based on these findings, we propose a new strategy for the generation of completely novel structures derived from a single preceramic polymer, exhibiting pore sizes ranging from the nanometer- to the micrometer-range.

The specific objectives of this work are the development of asymmetric ceramic structures with multi-scalar porosity, composed solely of a polymer precursor-derived non-oxide ceramic, as well as the proof-of-concept for potential applications in membrane processes, in particular an evaluation of the selective permeation of a variety of gaseous species at elevated temperatures, with the aim of obtaining permselectivities exceeding selectivities determined by Knudsen flow. The preceramic polymer used has to fulfill a variety of requirements, including the potential for the production of both macro- and microporous ceramics, as well as adequate properties of the derived material itself, including sufficient stability at high temperatures in oxidizing and reducing atmospheres and hydrothermal stability. To fulfill these requirements, we chose a commercially available poly(vinyl)silazane (PVS) as precursor.

With respect to the objectives of this work, we first present a methodology for the generation of microporous ceramics with pore sizes  $<1\text{ nm}$ , thus being, e.g., in the range of the kinetic diameter of gases typically encountered in energy production. In the second part of this contribution, we report on the generation of novel asymmetric porous structures potentially suitable for membrane applications, all sub-structures of which are derived from a single polysilazane-based precursor, including a microporous top layer, a macro-/mesoporous intermediate layer, as well as a macroporous support. Finally, we present the proof-of-concept of our single-precursor approach, demonstrating the general feasibility of these novel structures for the permeation of gases with selectivities above values limited by Knudsen diffusion, at temperatures up to 500 °C.

By following our novel single-precursor approach, we expect to circumvent potentially detrimental effects caused by thermal or chemical incompatibilities between constituents, thus leading to the development of completely new membrane or nanofiltration systems suitable for harsh chemical and thermal environments.

## 2. Experimental

### 2.1. Preceramic polymer

As precursor material, a commercially available poly(vinyl)silazane (PVS; HTT1800, AZ Electronic Materials, USA) was used. The pure, liquid polymer has a viscosity of 22 mPa s at 25 °C [49], and is sensitive towards hydrolytic decomposition in ambient atmosphere. As a result, processing was conducted inside a high-purity

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