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Micro-/Mesoporous polymer-derived ceramic structures using molecular porogens

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Abstract. Micro- and mesoporous ceramics demonstrate promising properties for applications in energy- and environment-related fields. Due to their high thermal and chemical stability, they are particularly suited for separation in harsh thermal or chemical environments, e.g. as membrane materials for the separation of gas mixtures. In this work, we present the use of a preceramic poly(vinyl)silazane in combination with organic molecular porogens for the generation of micro-/mesoporous non-oxide ceramic structures. Microporosity is generated during the pyrolytic conversion process, while the addition of molecular porogens, to be removed during the heat-treatment, enables further control of the micro-/mesopore structure. A systematic investigation of various porogens showed the suitability of polystyrene for this purpose. Based on these findings, the pore structure and pore connectivity of polysilazane/polystyrene-derived structures were evaluated using gas physisorption and small angle X-ray scattering techniques. This material was further investigated by preparing asymmetric membranes consisting of micro-/mesoporous polysilazane/polystyrene-derived layers on porous ZrO₂/TiO₂ supports. The potential for gas separation applications was then demonstrated by single-gas permeance evaluation of the generated structures at temperatures up to 300 °C.

Introduction

Microporous ceramic materials have gained increasing attention due to their prospective uses in various energy- and environment related fields such as separation processes or catalysis. A straightforward method to generate microporosity in ceramics is the use of the polymer precursor route, which involves the controlled thermal conversion (pyrolysis) of preceramic polymers such as

polysilazanes or polysiloxanes [1]. The precursor polymers, which are primarily Si-based, are cross-linked and subsequently heat treated in inert or reactive atmosphere at 400 °C to 700 °C to first yield ceramic-polymer hybrid materials (commonly referred to as ceramers [2]) and, at higher temperatures, to convert into amorphous ceramic structures [3]. Depending on the chemical constitution of the precursor compounds, the obtained ceramers can exhibit pronounced amounts of microporosity, which collapses upon further heating [4]. This phenomenon has been exploited, e.g., for the production of microporous compounds with proposed applications as adsorbents [2,5], as protective coating for sensors [6], in the field of catalysis [7,8], or as membrane materials [9,10]. In addition to the adjustment of process parameters during pyrolytic conversion, the addition of compounds acting as spaceholders and the selective removal of which during heat treatment, e.g., by evaporation of polymers, presents a method to control and tailor the resulting pore structure in the materials generated [11-13].

In a recent contribution, we reported on the generation of microporosity in polysilazane-derived ceramics by controlled thermal conversion. When pyrolyzed at 600 °C in nitrogen atmosphere, organic-inorganic hybrid materials with pore sizes of 0.8 nm and total micropore volumes of around 0.1 cm³ g⁻¹ were obtained, which exhibited promising characteristics for the prospective separation of gases, tested at temperatures up to 500 °C [14].

In this work, the focus is on the evaluation of the effect of an addition of a variety of molecular porogens to the preceramic polymer – including solvents, sacrificial polymers such as polystyrene, or organometallic compounds – in terms of micro- and mesopore development during thermal conversion, employing a variety of characterization methods to investigate the pore structure. One further aspect is the determination of gas permeance properties of a promising material combination in order to evaluate its feasibility for potential uses in gas separation applications at elevated temperatures.

Experimental

Materials. A commercially available poly(vinyl)silazane (*PSZ*; HTT 1800, AZ Electronic Materials, USA) was used as the precursor compound. This liquid compound converts into a Si-C-N-(O)-based ceramic material in the temperature range between 400 and 800 °C. Before further use, 1 wt.% of dicumyl peroxide (99 %, Acros Organics, USA) was added as cross-linking agent.

A variety of distinct molecular porogen systems were evaluated, including mixtures of *PSZ* with toluene (99.8 %, Alfa Aesar, USA; *PSZ_Tol*), polystyrene solutions (molecular weight of 13,000 g mol⁻¹, Alfa Aesar, USA; *PSZ_PS1* and *PSZ_PS5*), an aluminum acetylacetonate solution (99 %, Strem Chemicals, USA; *PSZ_Alacac*), and n-decane (99+ %, Alfa Aesar, USA; *PSZ_nDec*). Table 1 lists an overview of the initial compositions. Owing to the reactivity of the *PSZ* compound with moisture, all processing steps up to the pyrolytic conversion were conducted in inert atmosphere.

Table 1: Overview of materials systems investigated, listing the initial sample compositions

Sample	Porogen	Porogen content (wt.%) [†]	Toluene content (Vol.%) [†]
<i>PSZ_Tol</i>	-	-	50
<i>PSZ_PS1</i>	Polystyrene (M.W. 13,000)	1	50
<i>PSZ_PS5</i>	Polystyrene (M.W. 13,000)	5	50
<i>PSZ_Alacac</i>	Aluminum acetylacetonate	15	50
<i>PSZ_nDec</i>	n-Decane	5	-

[†] with respect to *PSZ* compound

Micro-/Mesopore generation and characterization. After mixing of the respective compounds, the mixtures were cross-linked at 130 °C for 12 h in flowing N₂ (0.3 l min⁻¹). Subsequently, coarse pieces of the crushed cross-linked compounds were pyrolyzed at 600 °C for 4 h in flowing N₂ (0.3 l min⁻¹) from which residual O₂ and H₂O gases were removed using a purifier unit (GF-20A, MTI Corp., USA). The ceramized compounds were then crushed to powders and stored in inert atmosphere until characterization.

Nitrogen adsorption/desorption at 77 K was conducted to evaluate the specific surface area and micro-/mesopore size distribution (ASAP 2010, Micromeritics, USA). Before testing, the powders were degassed at 300 °C for 12 h. Specific surface areas were determined using the BET method. For selected samples, the micro-/mesopore size distribution was determined from adsorption/desorption isotherms in the p/p_0 range of 10⁻⁵ to 0.995, using a non-linear density functional theory (NLDFT) model for heterogeneous surfaces included in the SAIEUS software package (Micromeritics, USA). Complementary to physisorption, small-angle X-ray scattering studies were conducted to further clarify the micropore structure, following the procedures explained in detail in a recent contribution [14].

Gas permeance testing. Gas permeance characteristics of the PSZ_PS5 material were determined in order to evaluate its feasibility for prospective gas separation applications. A commercially available ceramic filter made of ZrO₂/TiO₂ with a top layer pore size of 200 nm (datasheet value; Sterlitech, USA) was used as membrane support. The selective membrane layers were applied via dip-coating (50 Vol.% PSZ/PS in toluene), using a withdrawal speed of 20 mm min⁻¹, and were subsequently cross-linked at 130 °C (2 h) and pyrolyzed at 600 °C (4 h) in flowing N₂. The coating/pyrolysis cycles was repeated twice using a coating solution with a reduced concentration (5 Vol.% PSZ/PS in toluene) before permeance testing. Gas permeances were determined using a custom-built single gas constant-volume/variable-pressure setup at testing temperatures up to 300 °C. Single-gas testing was conducted using He, N₂, Ar, C₂H₆ and CO₂ (high purity grade, Airgas, USA). After degassing, the feed side of the planar membrane (permeated area: 0.8 cm²) was exposed to a constant flow of the respective test gas at ambient pressure, while the permeate side was evacuated to 130 Pa. Upon reaching a steady-state permeation regime, evacuation of the permeate side was terminated, and the pressure rise rate on the downstream side was recorded up to 660 Pa. Using the slope of the pressure increase, the permeance of each individual test gas was calculated. Subsequently, the permeance ratios between two test gases yielded the respective permselectivity values. A detailed description of both the testing setup and the typical testing and evaluation procedure can be found elsewhere [14].

Results and Discussion

Introduction of porogens. The porogen compounds were either introduced into a solution of the preceramic polymer compound in toluene or, in the case of n-decane, directly into the liquid polymer. Mixing of the starting materials as listed in Table 1 resulted in homogeneous starting solutions. During the cross-linking stage, both an evaporation of the toluene solvent as well as a curing of the polymer compound occurred, resulting in either transparent or slightly opaque polymer solids. After pyrolysis and a subsequent grinding step, dark yellow powders were obtained, which were further characterized. The pyrolytic conversion temperature was limited to 600 °C, as previous experiments showed a collapse of microporosity in poly(vinyl)silazane-derived compounds at higher temperatures [14].

Pore evolution during pyrolytic conversion. In a first step, the extent of pore development during the pyrolytic conversion stage was assessed based on the specific surface area of samples (Table 2). When compared to the reference sample PSZ_Tol, a slight decrease in specific surface area was found for all samples with the exception of PSZ_PS5, containing 5 wt.% of PS.

However, during physisorption testing of microporous materials, special care has to be taken in order to avoid the unwanted adsorption of gas species such as He into micropores prior to testing, interfering with the controlled adsorption of N₂ species. Therefore, more detailed physisorption experiments were conducted with the most promising samples (Fig. 1). The resulting adsorption/desorption isotherms were identified as Type I isotherms (IUPAC nomenclature), indicating the presence of microporosity. Based on the adsorption branches, the micro-/mesopore size distributions were obtained through NLDFT models. Even though the maximum of the differential pore size distribution curves remains rather stable at a pore diameter of 0.8 to 0.9 nm, a decrease in total micropore volume was found for PSZ_PS samples. This leads to the assumption that two distinct pore types are present in PSZ_PS samples; the first being intrinsic porosity developed during the pyrolytic conversion of the preceramic polymer in the sub-nm range, and the second being porogen-derived porosity mainly in the low mesopore range around 2-5 nm, stemming from the decomposition of the polystyrene compound.

Table 2: Specific surface areas (SSA) of porogen-containing PSZ after pyrolytic conversion at 600 °C (BET method)

Sample	SSA (m ² g ⁻¹)
PSZ_Tol	115.8
PSZ_PS1	101.9
PSZ_PS5	132.6
PSZ_Alacac	95.7
PSZ_nDec	98.3

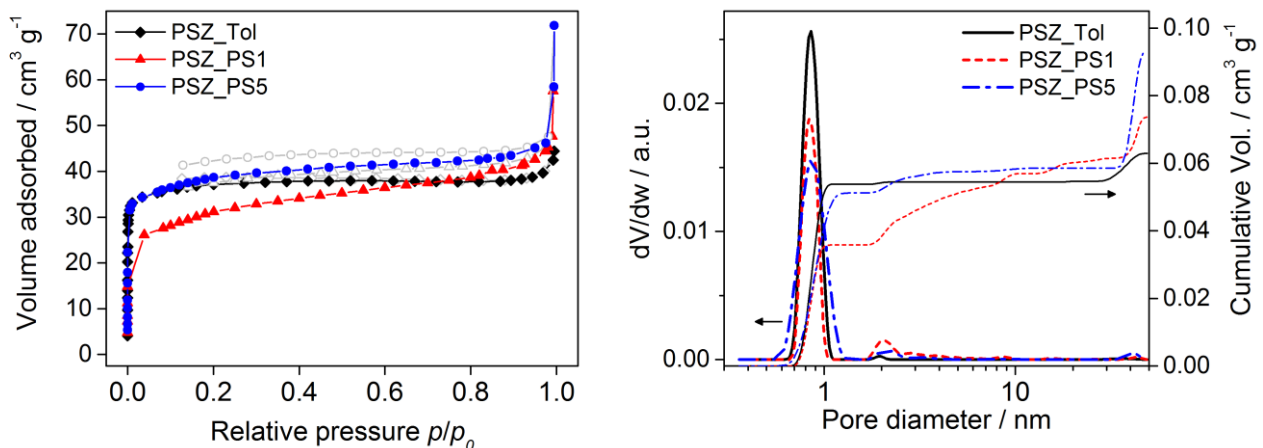


Fig. 1: N₂ adsorption/desorption isotherm of PSZ_Tol, PSZ_PS1, and PSZ_PS5 (left, desorption branches shown in grey), and the corresponding micro-/mesopore size distributions obtained by NLDFT (right)

In order to verify the results from physisorption experiments, small-angle X-ray scattering studies were performed. By applying a fit function for aggregated spherical objects to the experimental scattering data shown in Fig. 2 (as described in more detail in [14]), several descriptors for microstructural features of the pores could be obtained (Table 3). The radius of gyration R_g , a measure of the pore radius, is in agreement with the maximum of the pore size distribution curve obtained by physisorption testing, being between 0.6 and 0.8 nm. The fractal dimension D is close to 4 for all samples, indicating a smooth (not rough) surface of the pores, and also no noteworthy differences were found for the hard sphere radius R_{hs} (a measure of inter-pore distance). In contrast,

values of the hard sphere volume factor η , interpretable as the packing density of pores, differ slightly, with higher values for the porogen-free PSZ_Tol sample.

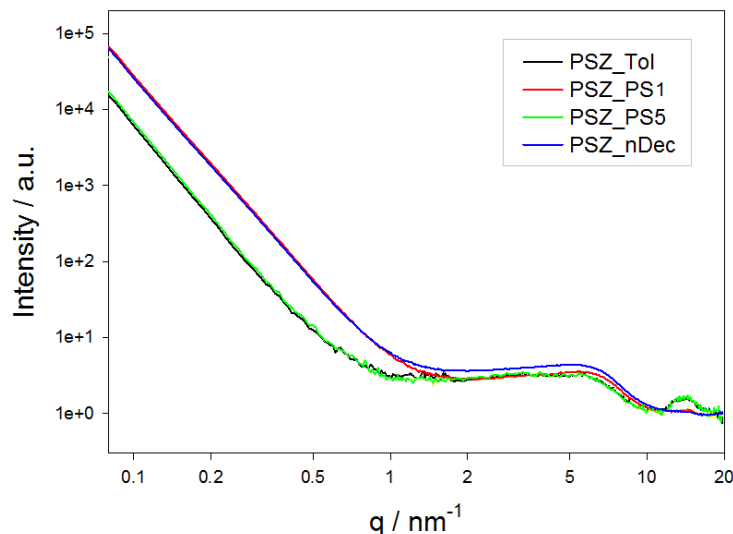


Fig. 2: Experimental data from SAXS experiments for PSZ-based specimens containing various molecular porogens, pyrolyzed at 600 °C.

Table 3: Descriptive parameters obtained from the fit model to experimental SAXS data

Sample	$2 R_g$ (nm)	D	$2 R_{hs}$ (nm)	η
PSZ_Tol	0.82	4	0.91	0.24
PSZ_PS1	0.64	3.6	0.90	0.19
PSZ_PS5	0.76	4	0.95	0.22
PSZ_nDec	0.65	4	0.91	0.19

Membrane preparation and gas permeation characteristics. Based on the promising pore size and total pore volume properties of the PSZ_PS5 material, its prospective suitability in membrane-based gas separation applications was evaluated. A commercially available $\text{TiO}_2/\text{ZrO}_2$ -based filter material with asymmetric porosity was chosen as membrane support (Fig. 3, left), onto which the PSZ_PS5 compound, dissolved in toluene, was deposited via dip-coating. After deposition and pyrolytic conversion of the first top layer, two additional layers were applied in order to reduce the number of potential defects in the membrane layer. For the final two layers, a coating solution with a reduced polymer concentration was used to minimize the final coating thickness and to facilitate higher permeances. After the final pyrolysis step, a continuous PSZ-derived selective layer closely connected to the supporting structure was obtained. (Fig. 3, right).

Permeance testing was conducted up to 300 °C for a variety of test gases. The range of permeances was in the range of 10^{-8} to slightly above 10^{-7} mol m^{-2} Pa $^{-1}$ s $^{-1}$, the highest values of which were found for the smallest gas, He (Fig. 4a). With the exception of CO_2 , permselectivities with respect to He clearly exceeded the values of theoretical permselectivities described by pure Knudsen diffusion (Fig. 4b), indicating a distinct contributing effect of the microporosity to the selectivity behavior of the PSZ-derived membrane material. The deviating behavior of CO_2 can potentially be explained by surface diffusion phenomena, resulting in increased CO_2 permeances at lower temperatures.

It has to be noted that, while demonstrating promising gas permeance characteristics, only a single specimen was tested for screening purposes, which does not suffice to clearly indicate a

distinctive behavior. Nonetheless, the general trends of permeance and permselectivity values observed for this material were subsequently observed for comparable material combinations, suggesting the general validity of the approach.

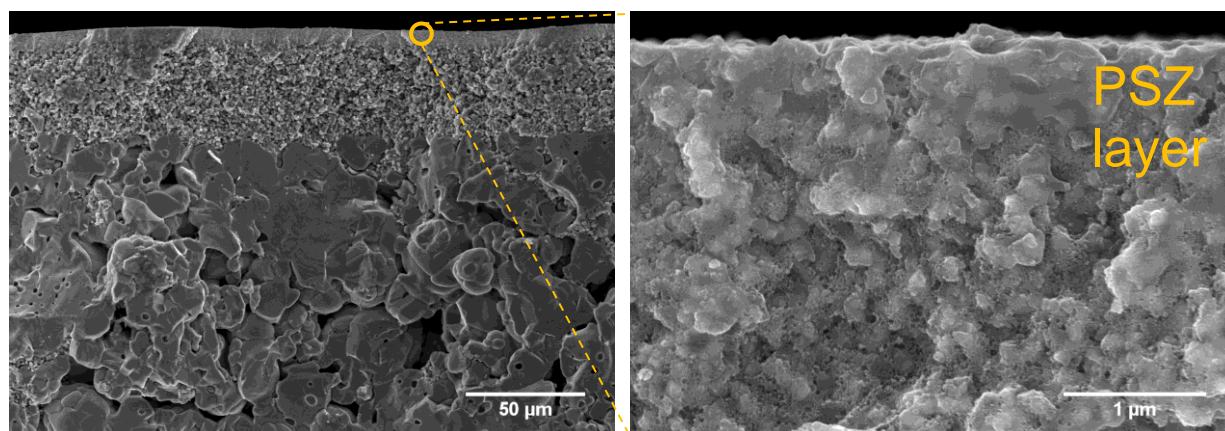


Fig. 3: Cross-sectional SEM images of a representative PSZ-based coating on a substrate with asymmetric porosity used for permeance testing, showing an overview of the three-layer support structure (left) and the magnified section of the indicated area showing the specimen surface including the deposited PSZ layer, partially infiltrated into the original support (right)

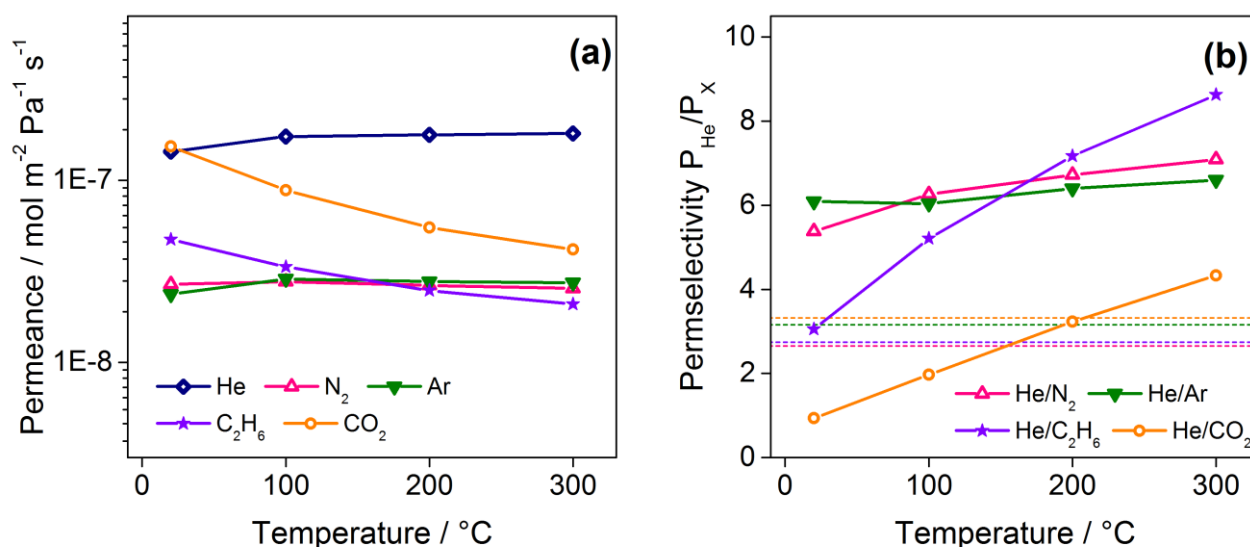


Fig. 4: Gas permeance characteristics of a membrane specimen prepared from PSZ_PS5 showing the permeance as a function of test gas and temperature (a), and the calculated permselectivity values (b) set in relation with permselectivity values achievable by Knudsen diffusion (dashed lines)

Conclusions

In this work, poly(vinyl)silazane was used in combination with a variety of molecular porogens to generate micro-/mesoporous organic/inorganic hybrid materials through pyrolytic conversion at 600 °C in N₂ atmosphere. It was found that among the molecular porogens investigated, polystyrene additions showed the most pronounced effect on the resulting pore structure. While not significantly affecting the intrinsic porosity generated in the polysilazane compound during the heat treatment, the emergence of mesoporosity, primarily in the range between 2 to 5 nm, was observed

after polystyrene addition. The polystyrene content in the initial mixture was found to correlate with the amount of mesoporosity. Single-gas permeance testing revealed the potential of this material class for the separation of gaseous species at elevated temperatures. By achieving permselectivity values exceeding the limits set forth by pure Knudsen diffusion, microporosity was shown to significantly affect gas permeance through the membranes investigated, even in the presence of mesoporosity. As such, the materials systems presented here possess the potential for broadening the application for polymer-derived ceramic and/or hybrid materials by further tailoring the pore structure through straightforward template approaches.

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