



# A comparative experimental study on the deviation of the ideal selectivity in HDTMS-functionalized and untreated ceramic structures with pores in the upper mesoporous range



Benjamin Besser<sup>a</sup>, Thomas Veltzke<sup>b</sup>, Jochen A.H. Dreyer<sup>c</sup>, Julia Bartels<sup>a</sup>, Michael Baune<sup>b</sup>, Stephen Kroll<sup>a, d, \*</sup>, Jorg Thöming<sup>b, d</sup>, Kuroschi Rezwan<sup>a, d</sup>

<sup>a</sup> Advanced Ceramics, University of Bremen, Am Biologischen Garten 2, 28359 Bremen, Germany

<sup>b</sup> Center for Environmental Research and Sustainable Technology (UFT), University of Bremen, Leobener Strasse 1, 28359 Bremen, Germany

<sup>c</sup> School of Energy and Environment, City University of Hong Kong, 11 Science Park West Avenue, Shatin, Hong Kong Special Administrative Region

<sup>d</sup> Centre for Materials and Processes (MAPEX), University of Bremen, Am Fallturm 1, 28359 Bremen, Germany

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## ABSTRACT

Mesoporous ceramic capillary membranes with mean pore sizes of about 20 nm are prepared as model structures to investigate the influence of an altered surface chemistry on the flow behavior of gases. To modify the membrane surface, a wet chemical silanization process with hexadecyltrimethoxysilane (HDTMS) is used to gain an alkyl-functionalized surface. Structural and surface characterizations show that the surface chemistry is altered without affecting the mean pore diameter. For the non-functionalized membrane, single gas permeation measurements at 20 °C reveal ideal permselectivities which are in good agreement with the Knudsen theory. In contrast, the HDTMS-functionalized membrane shows permselectivities regarding carbon dioxide (CO<sub>2</sub>) which deviate about 20% from Knudsen theory. The gas permeation measurements further indicate a relative flow enhancement for CO<sub>2</sub> in comparison to nitrogen (N<sub>2</sub>), argon (Ar) and methane (CH<sub>4</sub>). Adsorption and desorption isotherms of CO<sub>2</sub> and N<sub>2</sub> at 20 °C show a decreased specific adsorption capacity for both gases, while the adsorption selectivity for CO<sub>2</sub>/N<sub>2</sub> is increased. This indicates a weaker interaction of gas molecules and membrane surface due to HDTMS functionalization. This weaker gas–solid interaction along with the increased adsorption selectivity is proposed as reason for the experimentally observed deviation of the permselectivities from Knudsen theory.

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## 1. Introduction

In microfluidic systems, biotechnology and separation science, surface modifications of inorganic substrates are an active field of research. Especially in membrane science, this concept is applied to develop new and improved materials, for example to enhance the selectivity of porous, inorganic membranes for gas separation [1]. Mass transport in such mesoporous membranes is mainly governed by Knudsen diffusion, which results only in small separation factors. To increase the separation beyond Knudsen limit, the principle

of surface-selective flow, which is attributed to selective adsorption and diffusion, can be utilized. Surface modifications are applied to increase the concentration of a specific adsorbable gas species on the surface to favor surface diffusion [2].

Processes using silane precursors provide a versatile tool to functionalize and tailor the membrane surface [3]. The surface functionality can be adjusted easily due to a broad spectrum of available silane molecules with different functional groups for example amino-, carboxyl- or alkyl-groups and spacer length, often ranging from C<sub>3</sub>–C<sub>18</sub> [4–6]. In particular, when focusing on CO<sub>2</sub> adsorption, amine-functionalizations show a high potential and are therefore subject in recent investigations [7,8]. For example, Stoltenberg and Seidel-Morgenstern [2], along with Ostwal et al. [9] and Sakamoto et al. [1] used an amine-modification to increase the CO<sub>2</sub>/N<sub>2</sub> selectivity of mesoporous silica membranes. Furthermore, the effect of a membrane

\* Corresponding author. Advanced Ceramics, University of Bremen, Am Biologischen Garten 2, 28359 Bremen, Germany. Tel.: +49 421 218 64933; fax: +49 421 218 64932.

E-mail address: [stephen.kroll@uni-bremen.de](mailto:stephen.kroll@uni-bremen.de) (S. Kroll).

functionalization with organosilanes showing different alkyl-chain lengths on the selectivity of especially heavier hydrocarbons [3,10,11] or for purification of aggressive gases such as chlorine [12] has been investigated.

According to Koros and Mahajan [13], the key requirements for membranes are durability, productivity and separation efficiency. The aimed performance optimum for membranes is therefore a high flux combined with a high selectivity. In general, a bigger pore size and a higher porosity results in a higher flux (permeability). Nevertheless, the contribution of surface diffusion is decreasing with increasing pore sizes, thus limiting an optimization. Therefore, the used membranes in the aforementioned studies possess pore sizes in the lower mesoporous region around 2–10 nm, since high separation factors are aimed. According to the general opinion in the literature, surface diffusion is supposed to be negligible in pores in the upper mesoporous range (10–50 nm) as well as macropores (>50 nm) [12,14,15]. In fact, solely Knudsen diffusion is considered as the main governing transport mechanism in the upper mesoporous region >10 nm [16].

In the **Supporting Material** of asymmetric inorganic membranes gas transport usually occurs in pores >10 nm. Until now, adsorption effects such as surface diffusion are neglected in such pores. In this study, deviations from the general rule stated above are observed by investigating the gas diffusion in inorganic membranes with pore sizes in the upper mesoporous region (>10 nm). Here, yttria stabilized zirconia (YSZ) as ceramic material and a well-established extrusion process are used to fabricate capillary membranes serving as model structures for gas permeation measurements. To affect the gas transport, a wet-chemical silanization process is used to immobilize an alkyl silane (hexadecyltrimethoxysilane, HDTMS) onto the surface showing a C<sub>16</sub>-chain as functional group. Both, the non- and HDTMS-functionalized membranes are characterized by microstructural analysis with focus on pore size, porosity and specific surface area to ensure comparability. Single gas permeation measurements are conducted with argon (Ar) and nitrogen (N<sub>2</sub>) as representatives for inert gases, as well as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) as gases with a more complex molecule structure and a higher interaction potential. Furthermore, adsorption/desorption measurements using N<sub>2</sub> and CO<sub>2</sub> are performed at 20 °C.

## 2. Experimental

In this section the used materials are briefly presented, followed by an introduction into the processing and functionalization route. Afterwards, the used material characterization methods are described, including structural analysis, characterization of the surface functionalization, as well as gas permeation and adsorption measurements.

### 2.1. Materials

The zirconia powder and reagents were purchased from commercial sources and used without further purification. The yttria (3 mol%) stabilized zirconia powder (YSZ, VP Zirkonoxid 3-YSZ, Lot. 3157061469) was obtained from Evonik Industries, Germany. Furthermore, for slurry preparation, 3-aminopropyltriethoxysilane (APTES, 99%, product number 440140, Lot. SHBC8357V) as dispersant and polyvinyl alcohol (PVA, fully hydrolysed, product number P1763, Lot. SLBC9027V) as binder were obtained from Sigma–Aldrich Chemie GmbH, Germany. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95–97%, product number 30743, Lot SZBD2030V) as well as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, ≥35%, product number 95299, Lot SZBD2410V) for membrane surface hydroxylation were provided

from Sigma–Aldrich Chemie GmbH, Germany. For membrane surface modification acetone (≥99%, product number 00585, Lot. SZBB0100V) used as organic solvent was purchased from VWR International, Belgium, and hexadecyltrimethoxysilane (HDTMS, 90%, product number AB111166, Lot. 1010563) was provided by ABCR, Germany. Double deionized water with an electrical resistance of 18 MΩ (Synergy<sup>®</sup>, Millipore, Germany) was used for all experiments.

### 2.2. Capillary membrane preparation

To prepare YSZ capillary membranes an extrusion process is used as described by Werner et al. [17]. A schematic overview of the processing route for membrane fabrication is given in Fig. 1A. Four ingredients are used for slurry preparation, namely YSZ-nanopowder (79 wt.%, primary particle size 30 nm), double deionized water as solvent (21 wt.%), APTES as dispersant (5 dwb.%) and PVA as binder (6 dwb.%). Here, dwb refers to "dry weight basis" of the YSZ nanopowder. Accordingly, all additives are specified based on the powder content in relation to  $\text{dwb.}\% \equiv m_{\text{additive}}/m_{\text{powder}} \cdot 100$ . In contrast to Werner et al. [17], first, PVA is slowly dissolved in hot water (≈80 °C). Afterwards, YSZ powder, PVA-solution and APTES are mixed in a planetary ball mill (PM400 from Retsch, Germany) for 3 h at 350 rpm changing the rotation direction every 5 min. The obtained homogeneous slurry is then shaped into capillaries using a self-made lab extruder, equipped with an extrusion die of 2 mm diameter and a pin of 1 mm [18,19]. The resulting green bodies are dried at room temperature (RT) for at least two days, followed by final sintering for 2 h at 1050 °C (the detailed sintering program is given in [19]).

### 2.3. Membrane surface functionalization

The membrane surface modification is performed by a two-step, wet-chemical process consisting of surface activation by hydroxylation followed by surface functionalization via silanization as schematically shown in Fig. 1B. A silane molecule is supposed to condensate and bind covalently onto an existent surface hydroxyl group using a water molecule as reaction partner [4]. To increase the amount of available hydroxyl groups and therefore increase the amount of bonding sites on the membrane surface, the membranes are primarily treated with freshly prepared Piranha solution (95–97% H<sub>2</sub>SO<sub>4</sub>:35% H<sub>2</sub>O<sub>2</sub>, 3:1, v/v) for 30 min as suggested by Kroll et al. [20]. Afterwards, the membranes are washed with double deionized water until neutral pH is reached, subsequently followed by drying at 70 °C for 24 h.

Secondly, the activated membranes are functionalized with HDTMS according to previous works [21]. The modification is carried out using a 0.2 M HDTMS solution where a acetone-water mixture (95:5, v/v) served as solvent. The membranes are incubated for 16 h at 80 °C under reflux. After incubation, the membranes are washed three times with acetone followed by drying for 2 h at 70 °C.

### 2.4. Membrane characterization

#### 2.4.1. Membrane structure

To ensure the comparability between the untreated and the HDTMS-functionalized material, detailed structural analyses are carried out. Therefore, the membranes are characterized in terms of pore size distribution, mean pore size ( $d_{50}$ ), relative pore volume, open porosity and specific surface area. The pore size distribution and the resulting mean pore diameter, along with the

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