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The influence of the functional group density on gas flow and selectivity: Nanoscale interactions in alkyl-functionalized mesoporous membranes

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Mesoporous inorganic structures with mean pore diameters of 26 nm are prepared by extrusion based on a yttria stabilized zirconia nanopowder. The sintered capillary membranes serve as model structures to investigate the influence of an alkyl-chain (C_{16}) surface functionalization on the gas diffusion kinetics of argon (Ar), nitrogen (N_2) and carbon dioxide (CO_2) in mesopores. The density of the C_{16} alkyl-chains immobilized on the membrane surface has an effect on both, gas flow as well as gas selectivity. For low functional group densities (<4 groups nm^{-2}), the gas flow is reduced without having an effect on the selectivity. In contrast, for high alkyl-chain densities (>4 groups nm^{-2}) the mean distance between the C_{16}-chains is reduced to the order of magnitude of the gas molecules leading to a reduction in gas flow and a significant change of the gas selectivity. The selectivity is found to be influenced depending on the molecular diameter of the gas species, being more evident for CO_2 compared to Ar and N_2, suggesting a separation mechanism more comparable to molecular sieving than to surface diffusion.

1. Introduction

Gas-solid interactions within porous materials are important for many processes and applications such as solid oxide fuel cells, catalysis, gas chromatography, gas separation or gas adsorption on solid sorbents [1–7]. The pore size of the material can be very different ranging from several micrometers to nanometers. Nevertheless, the performance of a process and its characteristics are often defined or driven by nanoscale interactions of gas molecules with the solid material surface, for example in the capillary of a gas chromatography column or at the pore walls of an inorganic membrane. Depending on the pore size and the Knudsen number (*Kn*), various transport mechanisms dominate inside the porous structures. Asymmetric inorganic membranes are a very good and well known example of porous materials where different transport mechanisms can occur simultaneously. They usually consist of a macroporous support structure (>50 nm, usually 1–10 μm), one or two mesoporous intermediate layers (10–50 nm) and a micro- or mesoporous top layer with pores <10 nm [8,9]. Determined by the structural proportions, the gas transport is dominated by viscous flow in the macropores of the support structure ($Kn > 1$), Knudsen diffusion in mesoporous intermediate layers ($Kn > 1$), and surface diffusion or molecular sieving in the top layer ($Kn > 10$) [10–16]. The transitions between the transport mechanisms are fluid, but under ambient pressure and room temperature (RT) viscous flow can be neglected in pores <50 nm and surface diffusion is negligible in pores >10 nm. In particular in gas chromatography as well as in membrane separation based on surface selective flow, the gas-wall interactions define the properties of the material [17–19]. Despite the difference in pore dimensions which are in the micrometer range for chromatography columns and in the nanometer range for membranes, in both cases the selective properties depend on the surface functionality. Therefore, different surface functionalization

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strategies with numerous functional groups are used to alter the surface chemistry and influence the gas-solid interactions [4,20–22]. For example, alkyl-functionalizations have been successfully applied in both, chromatographic applications [23] as well as membrane separation [24–28]. Especially in membrane separation, it is often observed that the membrane flux is reduced by several orders of magnitude as a result of the surface functionalization, independent of functional group type [20–22,24–30]. Usually this is explained by the reduction in pore size and porosity due to the functional groups immobilized on the pore walls. Surprisingly, the decrease in pore size and porosity is seldom in the order of magnitude of the decrease in flux. This indicates that the full impact of surface functionalizations on the gas flow through a porous material has not been completely understood yet. Asymmetric membranes are often used for the investigation of surface functionalizations and their impact on gas flow properties. But, the total gas flow of the membrane will be a superposition of multiple transport phenomena, because they consist of multiple layers with pore sizes over several length scales. For this reason, asymmetric membranes are not the most favorable structures for the analysis of transport phenomena depending on surface functionality as well as pore size. To achieve fundamental understanding about nanoscale interactions of gas molecules with functional layers and their relations to pore size and porosity, the gas transport mechanisms need to be studied separately for each length scale. This study aims to experimentally investigate the impact of the surface functional group density on the gas diffusion dynamics in mesopores between 10 and 50 nm, where Knudsen diffusion is dominating. The study is focused on the experimental determination of the gas transport with high accuracy, without the development of analytical or semi-empirical gas transport models. For this purpose, mesoporous ceramic capillary membranes are prepared by an extrusion process using yttria stabilized zirconia nanopowder. These membranes serve as model structures which are functionalized in a second step with varying amounts of an alkyl-silane showing a C_{16}-chain as functional group (hexadecyltrimethoxysilane, HDTMS). All membranes are characterized concerning their pore size, open porosity, specific surface area and alkyl-chain density on the surface. Single gas permeation measurements using argon (Ar), nitrogen (N_2) and carbon dioxide (CO_2) are performed to investigate the impact of the functional group density on the gas diffusion kinetics within the mesoporous structures.

2. Experimental

2.1. Materials

The mesoporous ceramic structures are fabricated using a yttria (3 mol%) stabilized zirconia nanopowder (YSZ, primary particle size 30 nm, VP Zirkonoxid 3-YSZ, Lot. 3157061469) purchased from Evonik Industries, Germany. 3-aminopropyltriethoxysilane (APTES, ≥98%, product number A3648, Lot. WXBB5181V) and polyvinyl alcohol (PVA, fully hydrolyzed, product number P1763, Lot. SLBD2875V), used as additives, are obtained from Sigma-Aldrich Chemie GmbH, Germany. For the surface functionalization, sulfuric acid (H_2SO_4, 95–97%, product number 30743, Lot SZBF0330V) as well as hydrogen peroxide ((H_2O_2, ≥35%, product number 95299, Lot SZBE2740V) are provided from Sigma-Aldrich Chemie GmbH, Germany, whereas acetone (≥99%, product number 20063.365, Lot. 16E041994) is obtained from VWR International, Belgium, and hexadecyltrimethoxysilane (HDTMS, 90%, product number AB111166, Lot. 1270013) is purchased from ABCR, Germany. For all experiments, double deionized water with an electrical resistance of 18 MΩ (Synergy®, Millipore, Germany) is used. All materials are used as received and without further purification.

2.2. Processing and functionalization

2.2.1. Membrane preparation

Mesoporous membrane model structures are prepared based on an established extrusion process [31,32]. In short, using water as solvent (21 wt%), the YSZ nanopowder (79 wt%) is mixed with APTES (5 dwb.%) serving as dispersant as well as sintering additive and PVA (6 dwb.%) serving as temporary binder. All ingredients are mixed and homogenized using a planetary ball mill (PM400 from Retsch, Germany). Prior to milling, the PVA is dissolved in hot water ($\approx 80\ ^\circ C$) using a microwave (MD14482 Studio, Medion, Germany) to ensure a homogeneous slurry and avoid membrane defects due to PVA granules. The preparation process is schematically shown in Fig. 1A. After mixing, the homogeneous slurry is shaped into capillaries using a self-made lab extruder with a 2 mm die and a 1 mm pin [33]. After drying the green bodies for 2 days at room temperature, the membranes are finally sintered for 2 h at 1050 °C (the sintering program is given in Ref. [34]).

2.2.2. Surface functionalization

To alter the surface chemistry of the membrane, the surface is functionalized with HDTMS (C_{16}-chain) molecules based on a wet chemical functionalization process [35]. The process consists of the surface activation by acidic hydroxylation followed by a chemical functionalization using the silane HDTMS as indicated in Fig 1B. The surface activation is carried out by immersing the membranes into freshly prepared Piranha solution (95–97% H_2SO_4:35% H_2O_2, 3:1, v/v). After 30 min of incubation the membranes are washed with double deionized water until reaching neutral pH and subsequently dried at 70 °C for 30 h. For the drying process, the membranes are placed in an open glass petri dish which is finall$_{0.15}$y put into a drying oven. It should be pointed out at this point, that it is of high importance for the functionalization process that all membranes are completely dry before continuing with the surface silanization. After successful drying of the membranes, the membranes are immersed into a HDTMS solution with an acetone-water mixture (95:5, v/v) as solvent. The surface functionalization is carried out by boiling under reflux for 16 h aiming at monolayer formation of HDTMS molecules. In this study, the HDTMS concentration of the solution is varied from 0.01 to 0.2 M to adjust the loading capacity of immobilized alkl-chains on the surface. Finally, the membranes are washed with acetone and dried for 2 h at 70 °C. The samples are named according to the HDTMS concentration of the stock solution used as subscript, namely $M_{0.01}$, $M_{0.05}$, $M_{0.1}$, $M_{0.125}$, M and $M_{0.2}$, samples without a surface functionalization are named M_{non-f}.

2.3. Membrane characterization

2.3.1. Structural characterization

Nitrogen adsorption/desorption measurements as well as thermogravimetric analysis (TGA) are carried out to obtain information about the porous membrane structure (i.e. pore size distribution, pore volume and porosity) and the functional group density of immobilized alkyl-chains per membrane surface area as schematically shown in Fig. 1C. Nitrogen adsorption measurements are performed at −196 °C using a BELSORP-mini II (Bel Japan Inc., Japan). Prior to the measurement, the samples are degassed at 120 °C for at least 3 h under reduced pressure (≤2 Pa) followed by cooling to RT under argon atmosphere. Based on the adsorption isotherms, the mesopore size distribution and mean pore diameter are determined according to the BJH-method [36]. Furthermore, the specific surface area is calculated according to BET-method [37] and the open porosity is obtained based on the true density determined by helium pycnometry (Pycnomatic ATC, Porotec, Germany). All measurements are performed three times to ensure