Microporous and Mesoporous Materials 154 (2012) 148–152

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

An attempt to alter the gas separation of mesoporous glass membranes by amine modification

Daniel Stoltenberg [a,*], Andreas Seidel-Morgenstern [a,b]

[a] *Max-Planck-Institute for Dynamics of Complex Technical Systems, D-39106 Magdeburg, Germany*
[b] *Otto-von-Guericke-University, D-39106 Magdeburg, Germany*

ARTICLE INFO

Article history:
Received 30 May 2011
Received in revised form 7 November 2011
Accepted 9 November 2011
Available online 18 November 2011

Keywords:
Surface modification
Porous glass
Gas separation
Carbon dioxide

ABSTRACT

Mesoporous glass membranes were synthesised and used to study the influence of an altered surface chemistry on adsorption and diffusion properties. A modification with a silane possessing high amine content was conducted to enhance the interaction with adsorbable gases. The obtained membranes were characterised by their adsorption equilibrium properties and their permeabilities for the gas pair carbon dioxide and nitrogen in single gas and binary mixture permeation experiments. The modified surface induced a reversal in the temperature dependence of the membrane selectivity. The strong adsorption on the modified surface led to a hindered carbon dioxide transport at lower temperatures and an accelerated transport at higher temperatures. Due to the limited amount of grafted adsorption sites on the modified membranes this effect was pronounced at low partial pressures of carbon dioxide.

1. Introduction

A post-synthesis chemical modification of the surface of known materials is an attractive possibility to enhance the properties of well defined structures and adapt them to new applications. The use of such modified materials in gas separation attracted much attention in the recent literature. Because of large surface areas and the possibility to modify the surface functionality easily by making use of the present surface silanol groups [1], porous silica is regarded as a potential material class to benefit from the chemical surface modification. The functionalisation of silica surfaces, for instance with amine groups, was already used in various studies for carbon dioxide sequestration by adsorption as well as membrane separation [2–5].

The mass transport in mesoporous media is mainly governed by the Knudsen diffusion mechanism. The maximum separation factor of a gas mixture in the Knudsen region is depending on the molecular masses of the diffusing gases. Compared to carbon dioxide, nitrogen has a smaller molecular weight and is therefore transported preferentially. To obtain a separation beyond the Knudsen value, additional effects have to be introduced to the mass transport. Higher concentrations of the adsorbable gas carbon dioxide on the surface of the membranes can result in an increased surface diffusion [6]. This effect can be exploited to generate separation performances beyond the Knudsen selectivity and was intensively studied in the last years in materials possessing hydrophobised surfaces modified with alkyl chains of different length ranging from methyl to octadecyl [7,8]. Hydrophobisation-procedures reduce the polarity of the surfaces and lead to non-specific interactions with nonpolar adsorbates. Modifications of the surfaces with amines which are supposed to cause specific interactions with the adsorbate were mainly applied in adsorption studies [2,3].

In this study, mesoporous glass membranes [9,10] were modified to influence and possibly enhance the carbon dioxide selectivity over nitrogen. The separation of carbon dioxide and nitrogen is of special interest because carbon dioxide is regarded as one of the main reasons for the current green house effect and is mainly emitted in combustion processes accompanied with nitrogen. Controlled pore glass was chosen as the membrane material due to the possibility to adjust pore sizes and the known adsorption potential for carbon dioxide [11].

2. Experimental

2.1. Membrane preparation

The mesoporous porous glass membranes were synthesised using a phase separation and a subsequent leaching process [9]. The glass was formed to round flat plates of 15 mm in diameter and 0.5 mm thickness by a core drill and a diamond saw and subsequently heat-treated at 813 K for 24 h to obtain the desired degree of phase separation. Afterwards, the glass was slowly cooled to room temperature and leached in 3 M hydrochloric acid for 24 h at 363 K. Finally, the prepared membranes were washed with water, aged in water for several days and dried in air.

---

[*] Corresponding author. Tel.: +49 391 6110 323; fax: +49 391 6110 501.
E-mail address: stoltenberg@mpi-magdeburg.mpg.de (D. Stoltenberg).

1387-1811/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2011.11.013

Nomenclature

m_{Mem}	mass of the membranes [g]
p_{eq}	equilibrium pressure [Pa]
p_0	initial pressure in the reference cell [Pa]
P	single gas permeability [mol m^{-1} s^{-1} Pa^{-1}]
q	loading of the membranes [mol m^{-3}]
R	universal gas constant [J mol^{-1} K^{-1}]
S^{single}, S^{mix}	ideal selectivity, separation factor [–]
T	temperature [K]
V_1, V_2	cell volumes of the adsorption device [m^3]
x, y	mole fractions in permeate and feed [–]
ρ	skeletal density of the glass membranes [g cm^{-3}]

2.2. Surface modification

The surface modification of the membrane was conducted by approved surface grafting methods [12]. 3-[2-(2-Aminoethylamino) ethylamino]propyltrimethoxysilane (Acros Organics) was reacted with the hydroxyl groups on the membrane surface in dry toluene. Prior to the modification the membrane was dried for 1 h at 390 K to desorb moisture. The dried membrane was put into a 0.01 M solution of the modifier in dry toluene and boiled under reflux for 6 h. It was finally washed thoroughly with toluene and dried at 350 K overnight. The total amount of the modifier used per membrane surface was calculated to give a grafted concentration of 7 μmol m^{-2}.

2.3. Characterisation

The pore structure of the controlled pore glass membranes was characterised prior to modification by low temperature nitrogen adsorption (Sorptomatic 1990, ThermoFinnigan). The surface area was calculated according to the Brunauer–Emmet–Teller (BET) [13], the mean pore diameter by the method of Barrett, Joyner and Halenda (BJH) [14] and Density Functional Theory (DFT) [15]. The pore volume was determined at $p/p_0 = 0.99$.

X-ray photoelectron spectroscopy (XPS) [16] was used to evaluate the success of the modification procedure. The membranes were cleaned with acetone in an ultrasonic bath and dried afterwards. After mounting the glass membrane on a C-tape to reduce charging effects the membrane was held in vacuum for 12 h. Measurements were performed in ultra-high vacuum using Mg Kα-radiation (1253.6 eV) and a hemispherical analyser (Phoibos 150, SPEC).

A simple volumetric method was used to determine the adsorption isotherms of carbon dioxide at different temperatures. The sorption device consisted of two separated cells of known volume and was heated by a thermostat. One of the cells was filled with the membrane, the other one was used as reference cell. Prior to each measurement, the membranes were activated in vacuum to desorb moisture and pollutants. The reference cell was filled with carbon dioxide at the desired pressure and subsequently connected to the membrane cell. The initial pressure in the reference cell and the equilibrium pressure in both cells after reaching a steady state were measured by pressure sensors (CTE8005AL4, SensorTechnics). The adsorption isotherms were recorded at temperatures up to 350 K and equilibrium pressures up to 2 bar. The adsorbed amounts were calculated using the measured pressures and the known cell volumes (Eq. (1)) and were related to the solid volume of the membranes, assuming a solid density of 2.2 g cm^{-3}. Nitrogen was assumed to be nearly non-adsorbable:

$$q = \frac{p_0 V_2 - p_{\mathrm{eq}}(V_1 + V_2)}{R T m_{\mathrm{Mem}}} \rho_{\mathrm{Mem}} \tag{1}$$

The diffusion measurements were performed in a modified Wicke–Kallenbach-cell (Fig. 1) conducting a "transient single gas" experiment [11] and a "steady state binary gas" experiment. The membrane was used to divide the device into two compartments. Chamber 1 was open to the atmosphere, chamber 2 was shut (transient measurement, volume known) or open to the gas chromatograph (Shimadzu GC17A, steady state measurement), respectively. Before measurement, the whole device including the membrane was heated in vacuum to 420 K to desorb the moisture and pollutants. For transient measurements, chamber 1 was flooded with the single test gases (CO_2, N_2) and subsequently opened to atmospheric pressure. To avoid boundary layers in front of the membrane, the test gas was supplied through a tube directly in front of the membrane (see Fig. 1). The resulting pressure increase in chamber 2 was recorded with a pressure sensor (CTE8005AL4, SensorTechnics). The derivative of the pressure increase over time was used to calculate the flux and the permeability of the membrane.

To measure the diffusion of binary mixtures in the steady state, chamber 2 was connected to the gas chromatograph and flushed with helium as carrier gas at atmospheric pressure. Similarly to chamber 1, the gas flow was directed to flush the membrane surface to avoid boundary layers at both sides of the membrane. The resulting streams of carrier gas and permeate gases were measured by a film flow metre (SF2, Stec) and analysed by the GC. For both methods temperatures up to 430 K were realised.

3. Discussion

According to the characterisation of the pore structure by nitrogen adsorption the unmodified porous glass membranes exhibit a relatively narrow pore size distribution with a mean pore diameter of 3.3 nm, calculated by BJH-method and 6.1 nm according to the DFT-calculations, respectively. The specific surface area by BET

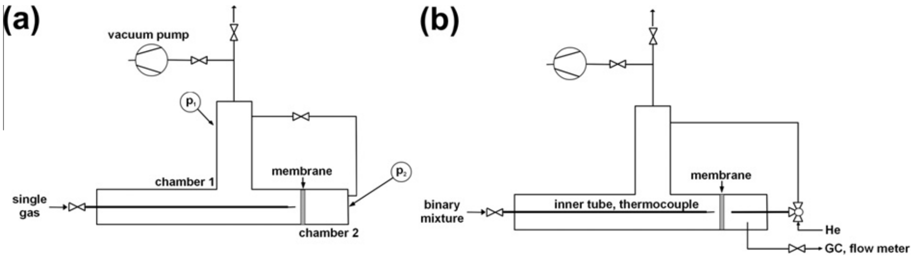

Fig. 1. (a) Experimental setup for transient single gas measurements; (b) setup for steady state binary mixture measurements.