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Polymer Derived Ceramic Membranes for Gas Separation

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Ceramic membranes based on polymer derived ceramics (PDCs) like silicon oxycarbide (SiOC) and silicon carbonitride (SiCN) offer an attractive combination of physical and chemical properties like chemical inertia, high mechanical strength and high temperature resistance. SiOC and SiCN membranes were deposited as thin layers by coating on top of tubular asymmetric porous ceramic substrates starting from a polymeric precursor solution followed by crosslinking and pyrolysis above 600 °C in inert atmosphere. High ideal permselectivities were achieved at 300 °C. SiOC membrane showed nearly ten times higher permeances of hydrogen to carbon dioxide and therefore possessed molecular sieving properties in separation of H_2/CO_2. A comparable SiCN membrane had a very low H_2/CO_2 ideal permselectivity but promising results for the other ideal permselectivities.

1. Introduction

Hydrogen is produced by steam reforming based on hydrocarbons (Kordesh and Simader, 1996). The by-products CO and CO_2 are separated by energy consuming adsorption or absorption processes. Combined methane reforming and purification at lower temperatures (~500 °C) shall be realized in membrane reactors (Mori et al., 2008). The H_2/CO_x separation is a challenge due to the small differences of the kinetic diameters of these gases (H_2 = 0.29 nm, CO = 0.37 nm and CO_2 = 0.33 nm) and require microporous inorganic membranes (Bernardo et al., 2009) like crystalline zeolites (Richter et al., 2003), amorphous silica or graphitic carbon. (Nenoff et al., 2006) Zeolites are limited in their performance considering the problems to synthesize a thin defect-free membrane. Amorphous silica membranes are hydrothermal unstable and therefore their application is limited as well (Dong et al., 2008). Carbon membranes with a turbustratic structure are more stable in comparison to zeolites and silica membranes but even their thermal stability is limited to 300 °C (Kaltenborn, 2010). Novel and interesting candidates appear to be polysiloxane-derived, polycarbosilane-derived (Li et al., 1996) and polysilazane-derived (Prasad et al., 2010) ceramics for high temperature applications (Riedel et al., 2006).

Kafrouni *et al*., 2009 worked in the field of SiCN membrane development using hexamethyl disilazane and *bis*(dimethylamino)-dimethylsilane precursors. The coating was performed on a porous alumina support by PECVD technique in ammonia or argon atmosphere. The so prepared membranes showed an ideal permselectivity of 2.4 at room temperature and 2.7 at 150 °C (Knudsen selectivity of He/N_2 = 1.87) (Kafrouni, 2010).

Tsotsis *et al.* uses chemical vapour deposition/infiltration (CVD/CVI) of triisoproylsilane to prepare SiC membranes on γ-Al_2O_3 substrates or by dip-coating of SiC substrates in allylhydropolycarbosilane (AHPCS). (Ciora, 2004) The ideal permselectivities of He/N_2 were around 22 at 200 °C.

In this paper the preparation, characterization and gas permeation measurements of nearly defect-free SiOC and SiCN membranes are reported derived from polycarbosilane and polysilazane precursors.

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2. Experimental

2.1 Synthesis

SiOC membranes

Polysiloxane XP RV 200 (Evonik Industries AG) was diluted (40 vol% anhydrous toluene) and directly used as precursor for the deposition of membrane 1.

The XP RV 200 had a low ceramic yield (~ 25 %) due to the low concentration of terminating vinyl groups. Small amounts of a thermal crosslinker containing silane groups could react via hydrosilylation reactions with the vinyl groups increasing the ceramic yield (membrane 2). In this regard, 0.5 wt% of AHPCS, 100 ppm of Pt catalyst and 10 wt% of XP RV 200 were diluted in toluene and used for membrane deposition. The thermal crosslinking occurred during the thermolysis of deposited membrane.

SiCN membranes

SiCN membranes were prepared using two different polysilazanes Ceraset PSZ 20 and HTT 1800 (Clariant Advanced Materials GmbH) solutions in toluene with varying concentration of the precursor (table 1).

2.2 Sample preparation

Monochannel Al_2O_3 tubes (O.D.: 10 mm, I.D.: 7 mm, L.: 100 mm) were used as supports. A γ-Al_2O_3 layer with a pore size of 5 nm and a ZrO_2 layer with a pore size of 3 nm located on the core side of the tube were applied as intermediate layers for SiOC or SiCN membranes. Both ends of the tubes were glas sealed.

The preparation of the membranes took place under inert atmosphere using a glove box. The tubular asymmetric substrates were in vertical position by dip coating of the substrates in solutions containing the preceramic polymer followed by the subsequent pyrolysis at a temperature between 600 – 900 °C under inert atmosphere (table 1). To ensure the preparation method and the subsequent results two samples (membranes) were produced under identical experimental parameters each time.

Table 1: SiOC and SiNC membrane samples.

No.	Membrane	Precursor	c(Precursor) [wt%]	Substrate	T(Pyrolyse) [°C]
1	SiOC	XP RV 200	40	γ-Al_2O_3	700
2	SiOC	XP RV 200	10+0.5 AHPCS +100 ppm Pt	ZrO_2	800
3	SiCN	Ceraset PSZ 20	5	γ-Al_2O_3	900
4	SiCN	Ceraset PSZ 20	10	γ-Al_2O_3	900
5	SiCN	Ceraset PSZ 20	20	γ-Al_2O_3	900
6	SiCN	HTT 1800	10	γ-Al_2O_3	900
7	SiCN	HTT 1800	15	γ-Al_2O_3	900
8	SiCN	HTT 1800	35	γ-Al_2O_3	900
9	SiCN	HTT 1800	15	γ-Al_2O_3	600

2.3 Membrane characterization

Gas permeance and permselectivity

Single gas permeance of the SiOC and SiCN membranes was measured using gases with different kinetic dimensions: He (0.26 nm), H_2 (0.29 nm), CO_2 (0.33 nm), O_2 (0.35 nm), N_2 (0.36 nm), CH_4 (0.38 nm), n-propene (0.44 nm), n-propane (0.43 nm), n-butene (0.45 nm), n-butane (0.47 nm) and SF_6 (0.50 nm) at different temperatures. The single gas permeance measurements were based on the pressure rise technique in a dead end cell. After evacuating feed- and permeate-site and tempering the module and gas pipes at the specific temperatures the gas streamed into the feed room and pressure increase on permeate site was measured. From linear part of the pressure increase massflow was determined. Gas permeance J could be calculated from massflow Q per membrane area A_M and partial pressure difference Δp. Ideal permselectivity was calculated as the ratio of the permeances of two gases.

The single gas permeation was carried out once for each membrane. To ensure the H_2 permeance values a second measurement was performed after half a year for at least one membrane.

Pore size distribution (permporometry)

The basic concept of permporometry is to use a non-condensable, less adsorbing gas (He, N_2) and a well adsorbing vapour like n-hexane to fill step by step the membrane pores. The remaining flux of the gas is attributed to defect pores in the macro pore range.

Hydrothermal stability tests

Boths tests were carried out in an autoclave. The conditions of first test were 180 °C and 30 bar in presence of 10 g water for 24 h. The second test was performed at 300 °C and 30 bar in presence of 5 g water for 5 days. Before and afterwards the membrane was characterized by single gas permeation.

3. Results and discussion

3.1 SiOC membranes

Membrane 1 prepared without crosslinking agent showed at room temperature a H_2 permeance of 0.56 $m^3/(m^2hbar)$ (table 2). With increasing temperature the permeance enhanced to 1.44 $m^3/(m^2hbar)$ (figure 1). In contrast to the H_2, the permeances of CO_2, C_3H_8 and SF_6 decreased but the drop was much higher and therefore the ideal permselectivities increased drastically. Membrane 1 showed a nearly ten times higher permeance of hydrogen to carbondioxide and nearly hundred times higher permeance to n-propane (table 2). The high ideal permselectivity of H_2/SF_6 indicated the membrane was free of defects and the separation mainly based on molecular sieving.

Table 2: H_2 permeance ($P(H_2)$) and ideal permselectivities (PS) of SiOC membranes at different temperatures (T_M); membrane 2A and 2B after hydrothermal stability test

Membrane	Hydroth. stab. test [No.]	T_M [°C]	$P(H_2)$ [$m^3/(m^2hbar)$]	Ideal Permselectivity (PS) H_2/CO_2	H_2/C_3H_8	H_2/SF_6
1	-	25	0.56	0.94	3.67	24.9
1	-	100	0.72	2.3	9.2	65.8
1	-	200	0.84	4.6	38.2	152
1	-	300	1.44	9.1	92.8	320
2	-	300	49.8	3.7	3.7	8.2
2A	1	300	15.45	4.5	4.2	7.7
2B	2	300	11.49	4.3	3.9	7.1

Membrane 2 prepared with a crosslinking agent in the presence of Pt catalyst showed a H_2 permeance of 49.8 $m^3/(m^2hbar)$ at 300 °C (table 2, figure 2) and the calculated ideal permselectivities were obviously very low compared to membrane 1. The outcomes established membranes coated on ZrO_2 substrate resulted in membranes with very high gas fluxes and low permselectivity indicating the presence of bigger pores or defects. In comparison with the single gas permeances shown in figure 1 the presence of a viscous flux was more likely.

The reason why membrane 2 was shown here was the result of a hydrothermal stability test. A first test (membrane 2A) took place in an autoclave at 30 bar, 180 °C and 10 g water for 24 h. Beneficial, after the test the ideal permselectivities for H_2/CO_2 and H_2/n-propane mixture were nearly the same, except the statistically failure of the single gas permeation measurement. A second hydrothermal stability test was performed under even harsher conditions (30 bar, 300 °C for 5 d, membrane 2B). Again the ideal permselectivities of each gas mixture showed the same tendency as before. The permeances of each single gas were decreased after the hydrothermal tests. This indicated no appearance of pore widening instead a kind of pore blocking seemed to take place. Both, permeance and permselectivity suggesting that the membrane 2 was hydrothermal stable under all tested conditions.

3.2 SiCN membranes

Membranes 3 – 5 prepared using different concentrations of the polysilazane Ceraset PSZ 20 as precursor showed H_2 permeances which were one order of magnitude higher compared to SiOC membranes (table 3). An increase of the concentration of the precursor solution resulted in an enhancement of permeances (figure 3). The different concentrations of precursor solutions had no influence on the permselectivity of H_2/CO_2, which was below Knudsen selectivity (H_2/CO_2 = 4.67, H_2/C_3H_8 = 4.69, H_2/SF_6 = 8.51). In contrast to that the ideal permselectivity of H_2/C_3H_8 as well as H_2/SF_6 decreased with higher precursor concentration, indicating that the separation was controlled by adsorption.

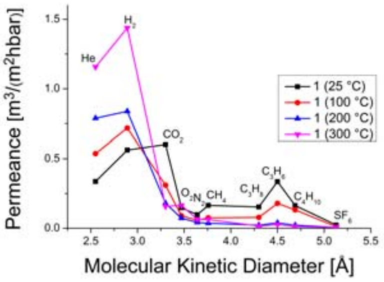

Figure 1: Single gas permeance of membrane 1 at different T_M.

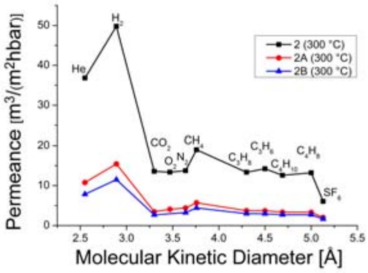

Figure 2: Single gas permeance of membrane 2 before and after hydrothermal stability test.

Membranes 6 – 8 prepared using different concentrations of the HTT 1800 as precursor compared with membranes 3 – 5 showed different results (table 3). Membrane 6 and 8 seemed to be comparable corresponding the H_2 permeances (figure 4) and ideal permselectivities (table 3). The ideal permselectivity was near to Knudsen selectivity. In contrast to that membrane 7 possessed a higher ideal permselectivity in case of H_2/C_3H_8 and H_2/SF_6.

Table 3: H_2 permeance ($P(H_2)$) and ideal permselectivities (PS) of SiCN membranes at different concentrations

Membrane	T_M [°C]	$P(H_2)$ [m³/(m²hbar)]	Ideal Permselectivity (PS)		
			H_2/CO_2	H_2/C_3H_8	H_2/SF_6
3	300	11.88	4.4	14.7	30.3
4	300	15.28	4.6	8.0	15.4
5	300	23.56	4.6	4.2	8.1
6	300	16.42	4.4	4.6	8.6
7	300	11.23	4.3	24.5	46.9
8	300	17.87	4.5	4.6	8.5
9	RT	25.62	1.5	1.8	22.7
9	300	19.08	3.2	29.7	103

Using Ceraset PSZ 20 as precursor a lower concentrated solution seemed preferable. As for HTT 1800 the optimal concentration was 15 wt%. The differences in the polymeric structure of both precursors explained perhaps the findings.

Testing different pyrolysis temperatures results in membrane 9 (table 3, figure 5). The permselectivities of H_2/C_3H_8 and H_2/SF_6 were significantly increased at 300 °C indicating the successful preparation of a membrane with molecular sieving properties. On the other side the permselectivity of H_2/CO_2 was surprisingly low and remarkable below the Knudsen selectivity. In contrast to membrane 1 the hydrogen permeance was higher than the permeance of carbon dioxide. Even so, there is a presence of adsorption effects of carbon dioxide. Moreover, the hydrogen permeance was decreasing with enhanced measurement temperature as well as carbon dioxide permeance and therefore the ideal permselectivity could not be increasing so much as compared to membrane 1.

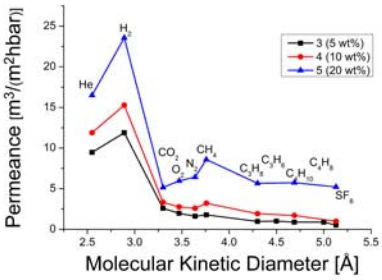

Figure 3: Single gas permeance of membrane 3 – 5 with different Ceraset PSZ 20 concentrations.

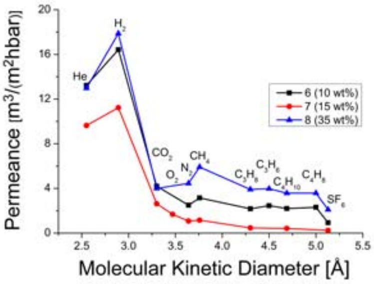

Figure 4: Single gas permeance of membrane 6 – 8 with different HTT 1800 concentrations.

The membrane was further characterized by measuring the permporometry (figure 6). The dry nitrogen flux was nearly 13 $m^3/(m^2hbar)$. From 1.5 nm on a saturation seemed to be achieved at a permeance of 0.39 $m^3/(m^2hbar)$. This correlated with a relative permeance of 3.1 %, which was called defect flow. The reasons of the defect flow were bigger pores or cracks in the membrane layer which could be detected by SEM (figure 7). The crack in figure 7b started from the surface of the membrane and continued through all intermediate layers deep down to the pure Al_2O_3 support. It looks like the membrane got a lot of stress during pyrolysis process.

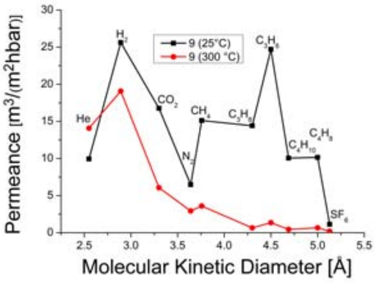

Figure 5: Single gas permeance of membrane 9 at 25 and 300 °C

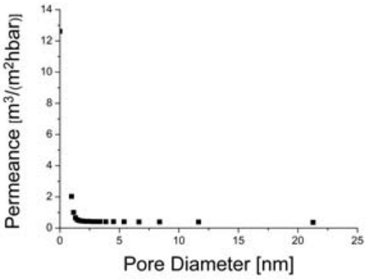

Figure 6: Permporometry of membrane 9; N_2 as feed gas and hexane as blocking agent.

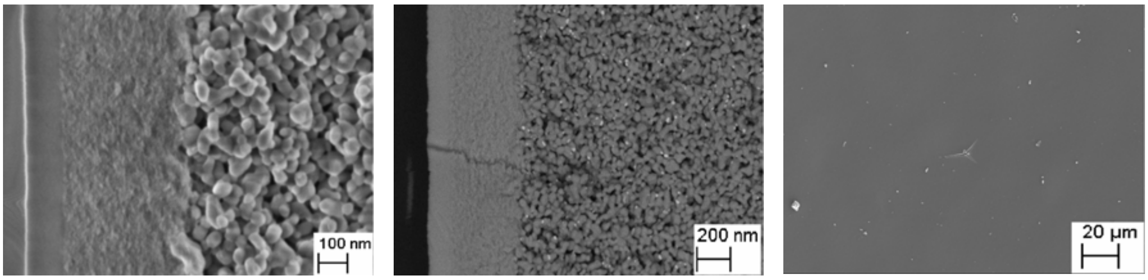

Figure 7 a – c: SEM images of a SiCN membrane using polysilazane, a) cross section without crack, b) cross section with a crack, c) surface with a crack.

4. Summary and conclusions

In summary, several amorphous SiOC as well as SiCN membranes had been realized and assessed with respect to hydrothermal stability, pore size distribution and single gas permeances.

SiOC membranes were prepared on γ-Al_2O_3 and ZrO_2 substrates by using different precursor mixtures. The best ideal permselectivities showed a SiOC membrane made on γ-Al_2O_3 possessing a high molecular sieving content. Membranes prepared on ZrO_2 were tested in hydrothermal conditions and seemed to be hydrothermal stable.

Two kinds of precursor for the preparation of SiCN membranes were tested. Firstly, the membrane preparation were optimized depending applied concentration of precursor solution as well as final pyrolysis temperature. The optimal precursor concentration seemed to be around 5 % for SiCN membranes based on Ceraset PSZ 20 and 15 % for membranes based on HTT 1800. The membrane prepared with 15 % HTT 1800 (membrane 9) showed excellent ideal permselectivities with the exception of the H_2/CO_2 permselectivity. The characterization of this membrane unveiled the presence of defect pores caused by stress during the preparation procedure. To develop a nearly stress-free preparation is more appropriate and in progress at the moment.

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References

Bernardo, P., Drioli, E., Golemme, G., 2009, Membrane gas separation: A Review/State of the art, Ind. Eng. Chem. Res., 48, 4638.

Ciora, R. J., Fayyaz, B., Liu, P. K. T., Suwanmethanond, V., Mallada, R., Sahimi, M., Tsotsis, T., 2004, Preparation and reactive applications of nanoporous silicon carbide membranes, Chem. Eng. Sci., 59, 4957-4965.

Dong, J., Lin, Y. S., Kanezashi, M., Tang, Z., 2008, Microporous inorganic membranes for high temperature hydrogen purification, J. Appl. Phys., 104.

Kafrouni, W., Rouessac, V., Julbe, A., Durand, J., 2009, Synthesis of PECVD a-SiC_xN_y:H membranes as molecular sieves for gas separation, J. Membr. Sci., 329, 130-137.

Kafrouni, W., Rouessac, V., Julbe, A., Durand, J., 2010, Synthesis and characterization of silicon carbonitride films by plasma enhanced chemical vapor deposition (PECVD) using bis(dimethylamino)dimethylsilane (BDMADMS), as membrane for a small molecule gas separation, Appl. Surf. Sci., 257, 1196-1203.

Kaltenborn, N., 2010, Nanoporöse Kohlenstoffmembranen auf asymmetrisch aufgebauten, porösen, keramischen Supporten für die Gastrennung, Freiberg.

Kordesh, K., Simader, G., 1996, Fuel Cells and Their Applications, Wiley-VCH, Weinheim, Germany.

Li, Z. Y., Kusakabe, K., Morooka, S., 1996, Preparation of thermostable amorphous Si-C-O membrane and its application to gas separation at elevated temperature, J. Membr. Sci, 118, 159.

Mori, N., Nakamura, T., Sakai, O., Iwamoto, Y., Hattori, T., 2008, CO-free hydrogen production by membrane reactor equipped with CO, Ind. Eng. Chem. Res., 47, 1421.

Nenoff, T. M., Spontak, R. J., Aberg, C. M., 2006, Membranes for hydrogen purification: An important step toward a hydrogen based economy, MRS Bull., 31, 735.

Prasad, R. M., Iwamoto, Y., Riedel, R. Gurlo, A., 2010, Multilayer amorphous Si-B-C-N/gamma-Al_2O_3/alpha-Al_2O_3 membranes for hydrogen purification, Advanced Engineering Materials, 12, 522-528.

Richter, H., Voigt, I., Fischer, G., Puhlfürß, P., 2003, Preparation of zeolite membranes on the inner surface of ceramic tubes and capillaries, Separation and Purification Technology, 1 – 3, 133.

Riedel, R., Mera, G., Hauser, R., Klonczynski, A., 2006, Silicon-based polymer-derived ceramics: synthesis properties and application – A review, J. Ceram. Soc. Jpn., 114, 425.