Experimental investigation of the transport mechanism of several gases during the CVD post-treatment of nanoporous membranes

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Modification of ceramic membranes

- Fabrication of highly Hydrogen-permeable and Hydrogen-selective ceramic membranes.

i. Modification of ceramic membranes by application of the Chemical Vapor Deposition process (CVD) technique.

ii. Investigation of the pore structure evolution of the modified membranes with the progress of deposition.

iii. Elucidation of the transport mechanisms of a variety of probe gases in the studied membranes.

iv. Evaluation of the permeation properties and separation efficiency of the studied membranes with respect to Hydrogen gas.

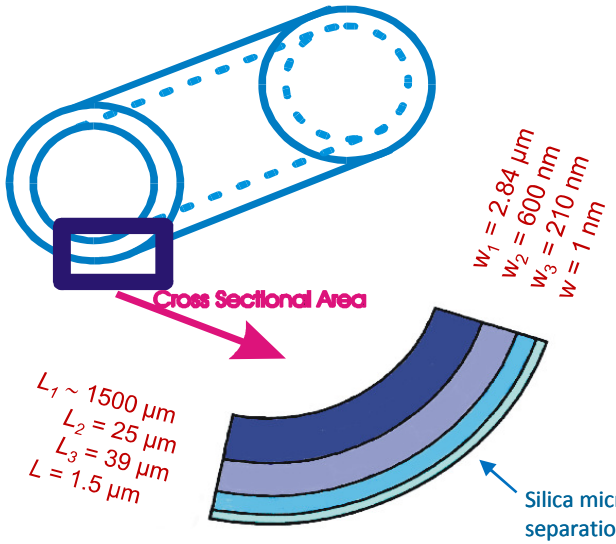
Applications of membranes for Hydrogen separation

- *Hydrogen membrane separation technologies have the potential to reduce costs, improve efficiency, and simplify Hydrogen production.*
- *Hybrid membrane reactors combining H_2 separation membranes with water–gas shift reactor can drive the equilibrium of water shift reaction forward (e.g. in coal gasification, methane partial-oxidation or steam reforming processes), thereby increasing the H_2 yield and resulting in significant cost reductions in the generation of H_2.*

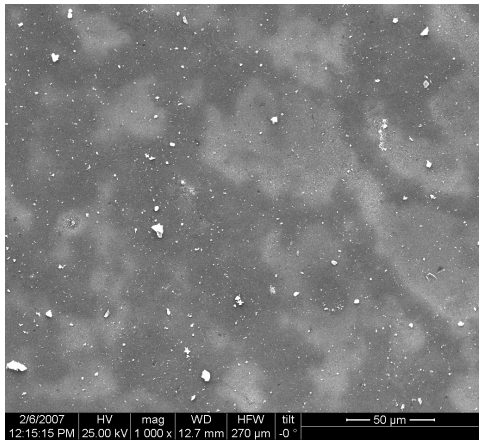
i. *Separation of Hydrogen from synthesis gas so as to be used as a clean fuel or feedstock.*
ii. *Paraffins dehydrogenation for production of olefins.*
iii. *Separation of Hydrogen from Nitrogen in Ammonia production.*
iv. *Separation of Hydrogen from Hydrocarbons.*

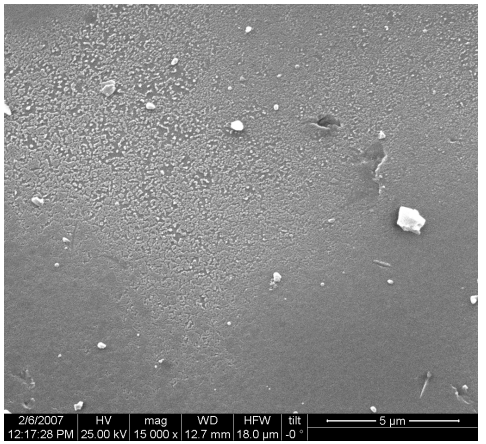
Ceramic membranes for modification: structural features and morphology

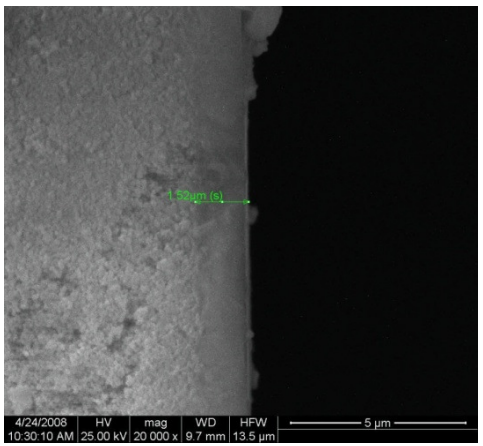
Type of ceramic membranes	Tubular composite nanofiltration membranes Outer side: support. Interior side: separation layer.
Support	α-Al_2O_3 (thick coarse outer macroporous layer), α-Al_2O_3, (two macroporous intermediate layers).
Separation layer	SiO_2 (thin microporous layer, w = 1 nm).
Outer diameter	10 mm
Inner diameter	7 mm

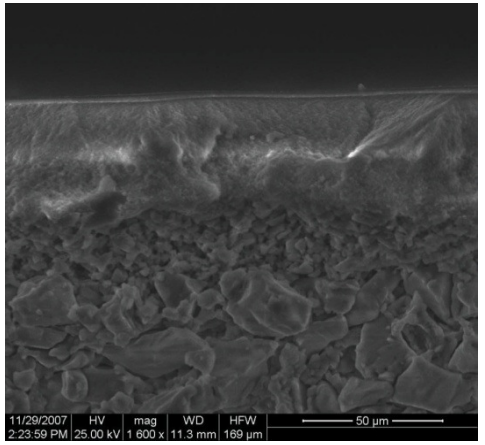


Schematic multilayered membrane support





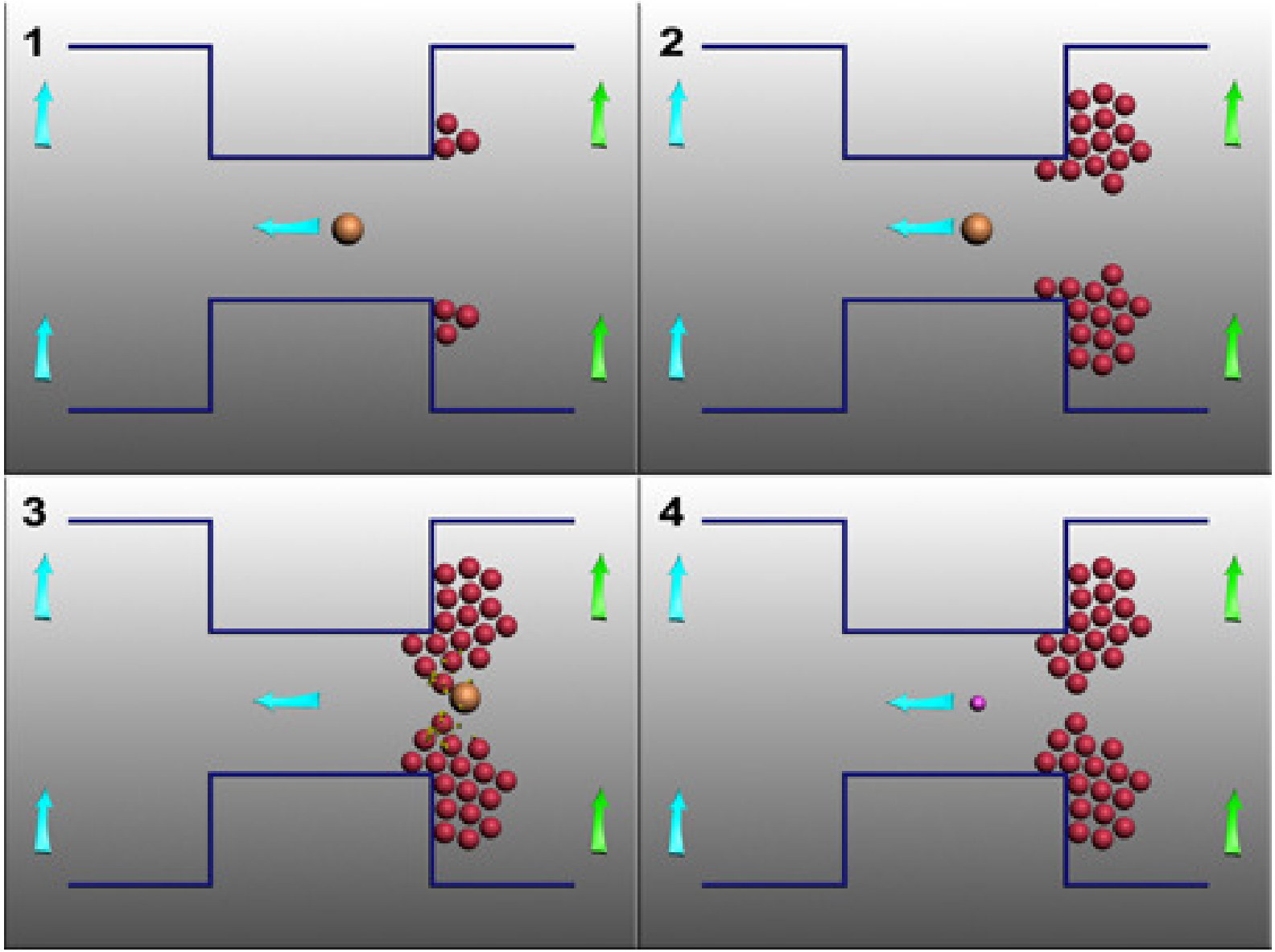




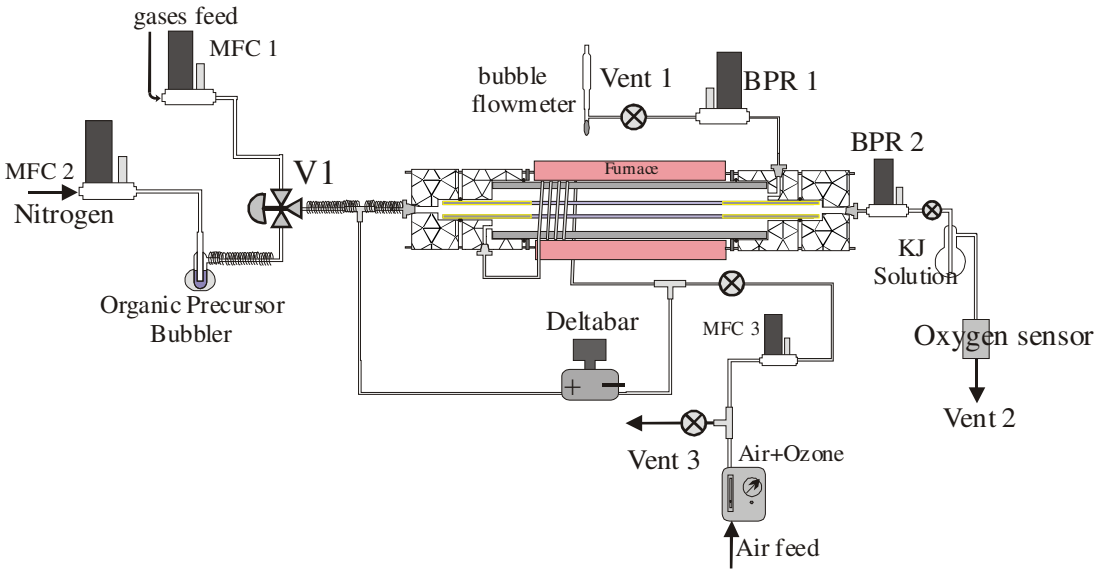
FEG-SEM images of the microporous separation layer surface (inner side) and cross sectional area

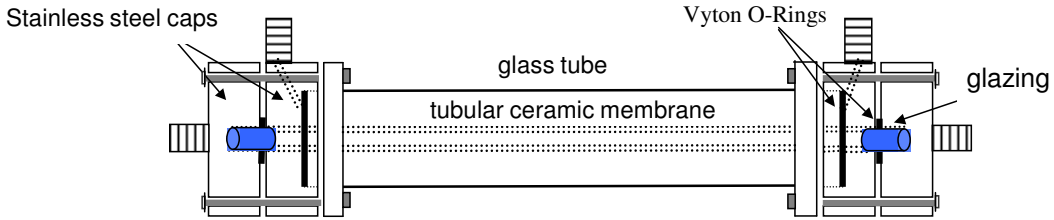
Untreated composite ceramic membrane

Chemical Vapor Deposition process (CVD)



Apparatus for conducting cyclic modes of CVD processes and single gas permeance measurements for a variety of probe gases at several stages of deposition

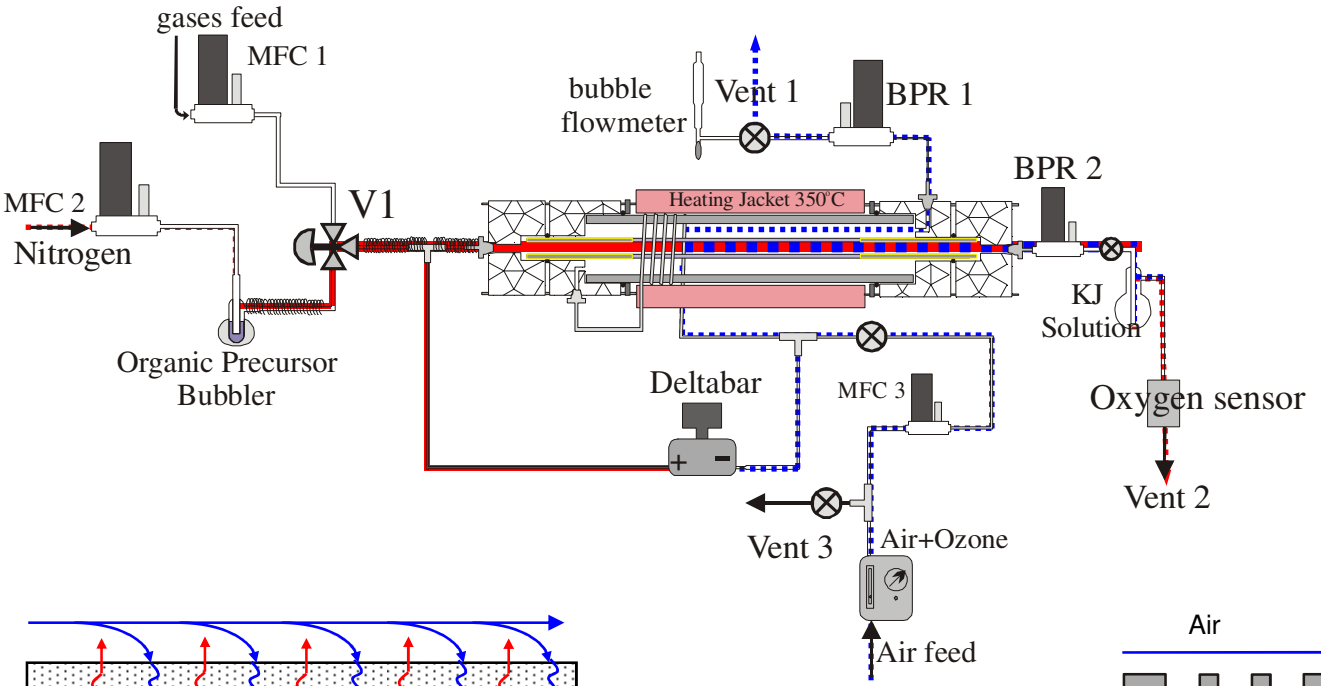


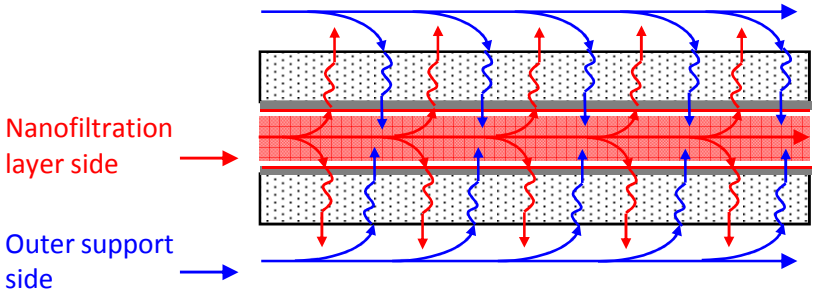


Mode of operation: opposing reactants configuration

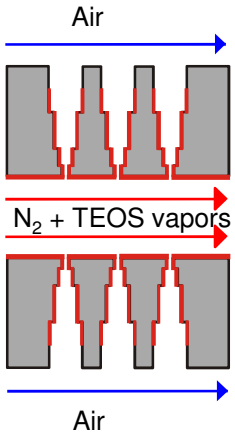
- Silica precursor: TEOS vapors
- Reaction system: TEOS/O_3
- Nitrogen used as sweep gas for TEOS vapors
- Air used as sweep gas for Ozone

Apparatus for conducting cyclic modes of CVD processes and single gas permeance measurements for a variety of probe gases at several stages of deposition

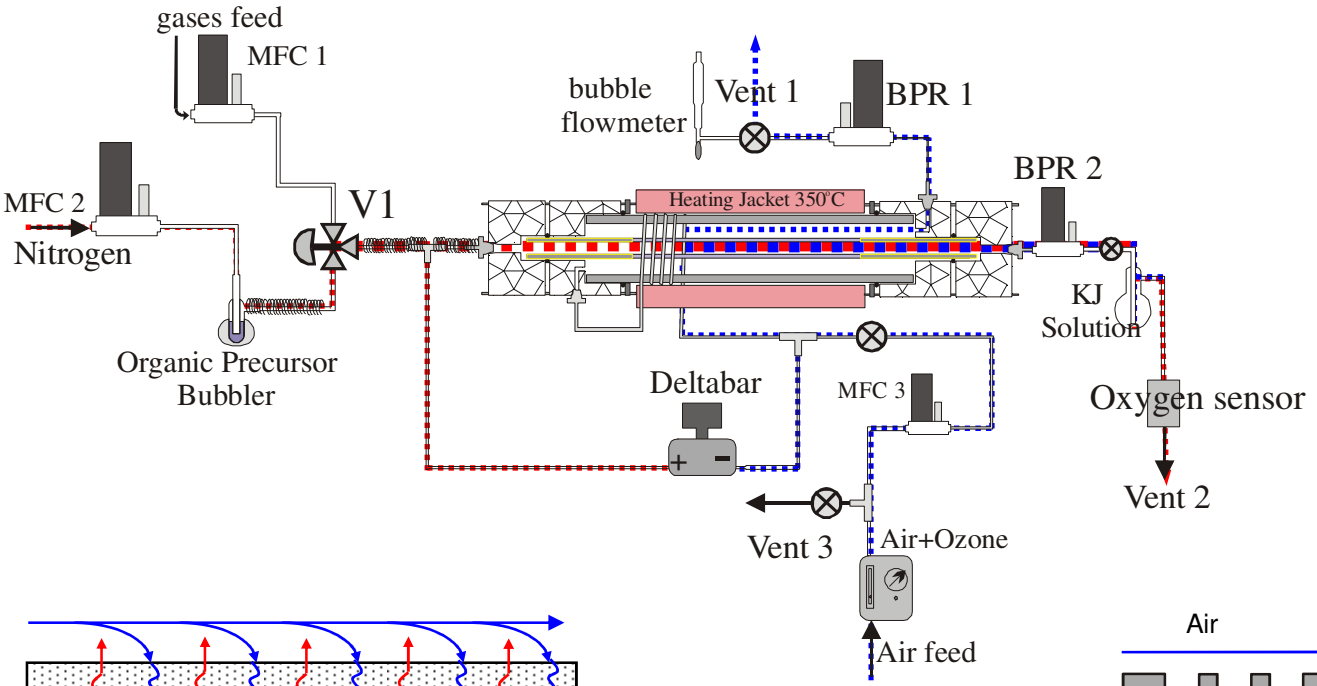


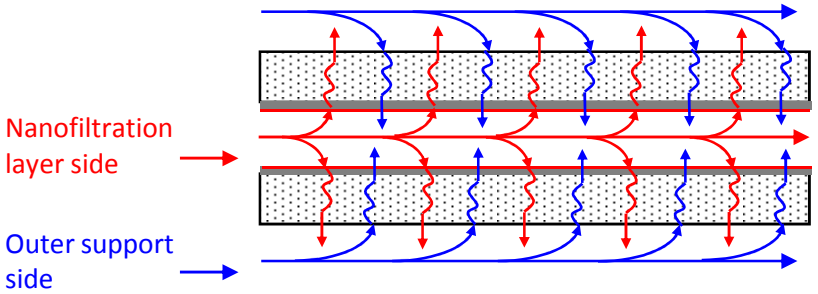


1. Introduction of the TEOS vapors - enriched Nitrogen stream from the (inner) nanofiltration layer side of the treated membranes.

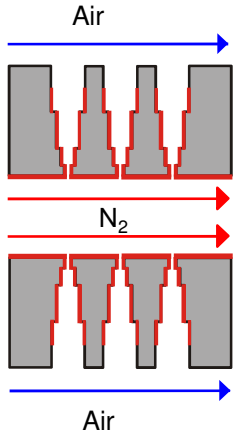


Apparatus for conducting cyclic modes of CVD processes and single gas permeance measurements for a variety of probe gases at several stages of deposition

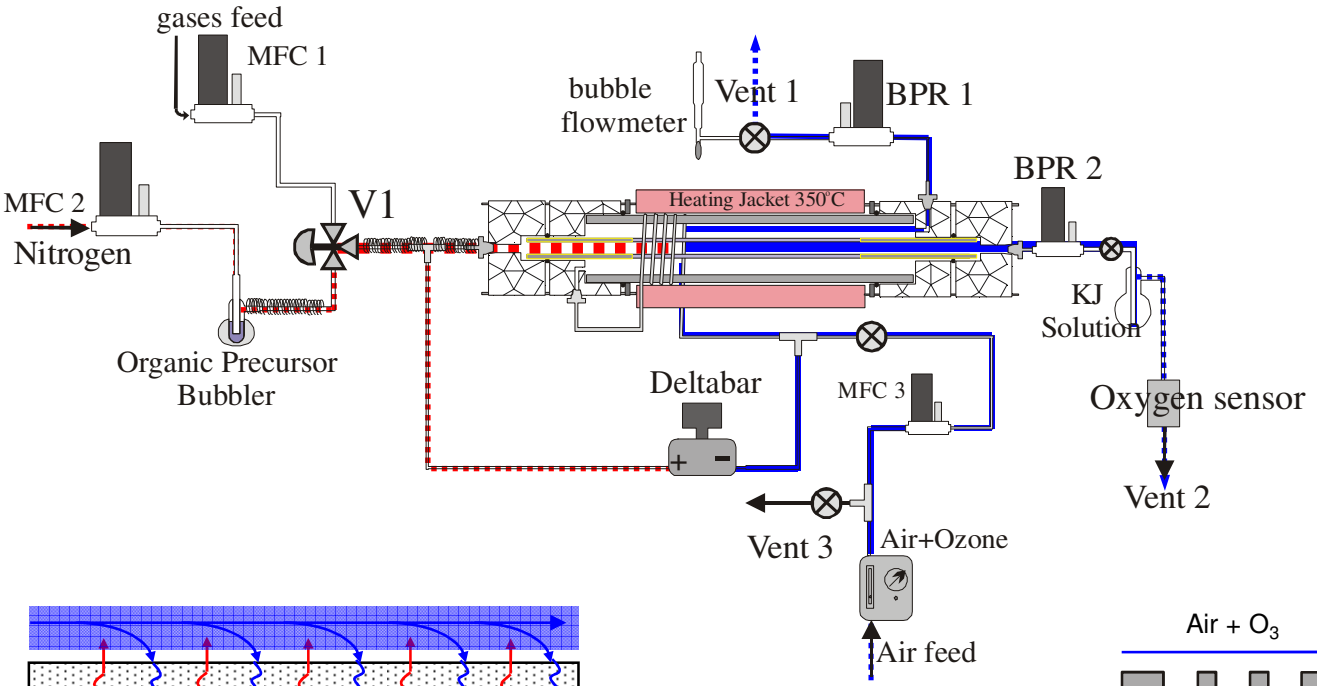


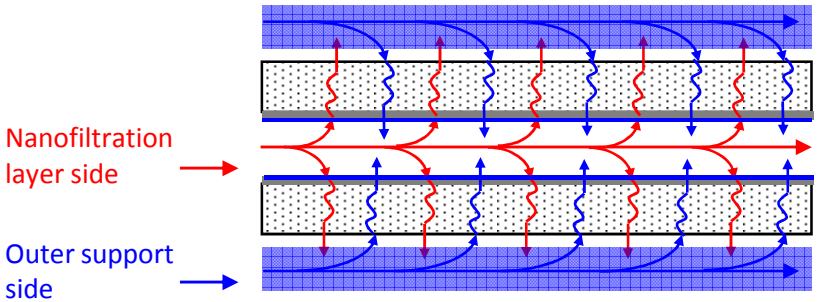


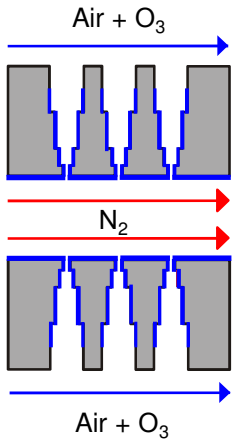
2. Purging with Air (support) and N_2 (nanofiltration side).



Apparatus for conducting cyclic modes of CVD processes and single gas permeance measurements for a variety of probe gases at several stages of deposition

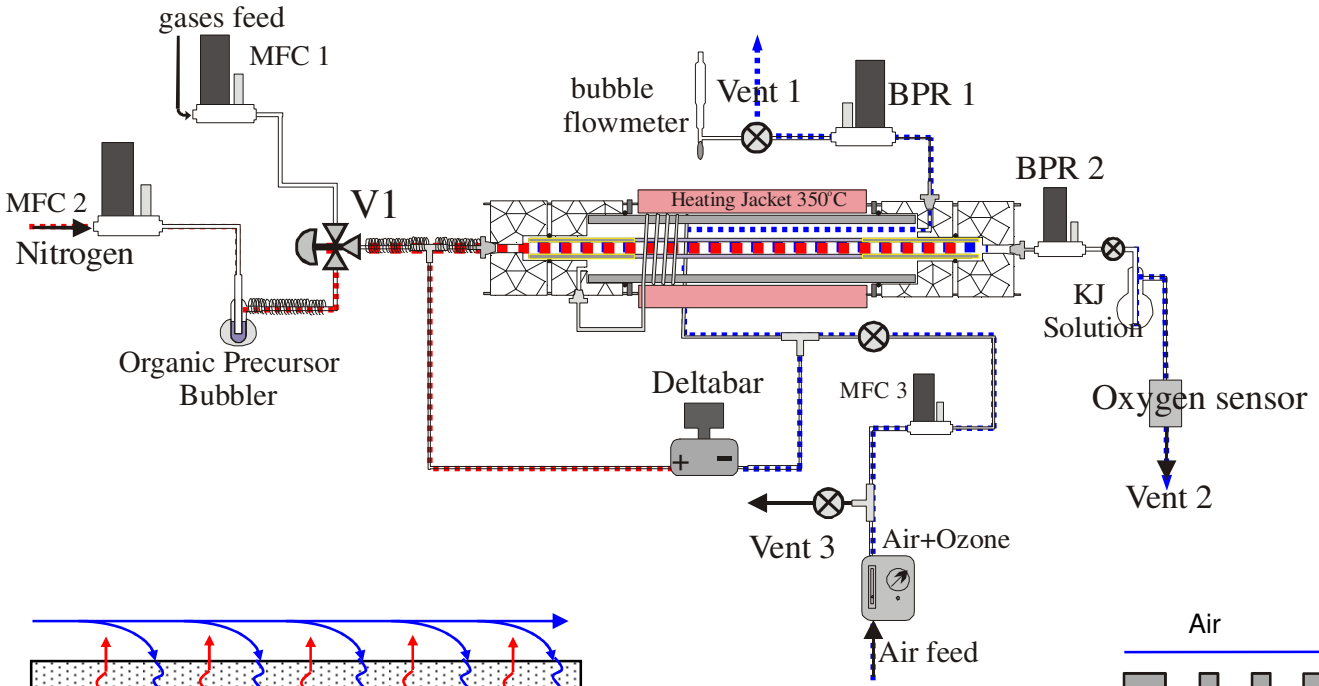


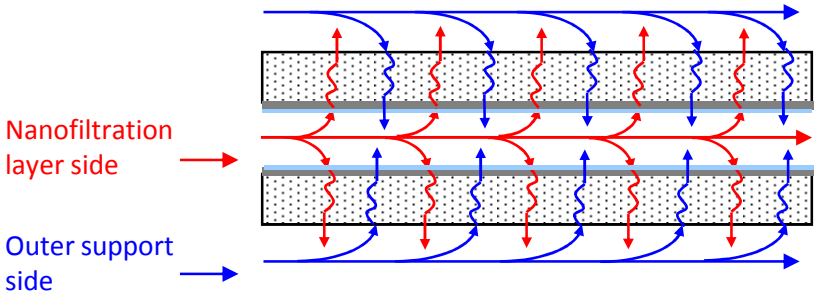


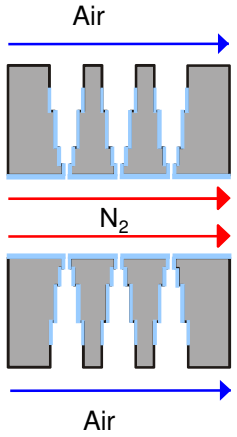


3. Simultaneous introduction of Air/O_3 stream from the outer side (support) and N_2 stream from the nanofiltration layer side of the treated membranes.
Oxidation of the chemisorbed alkoxy-silane molecules leading to growth of a silica deposition film within micropores.

Apparatus for conducting cyclic modes of CVD processes and single gas permeance measurements for a variety of probe gases at several stages of deposition



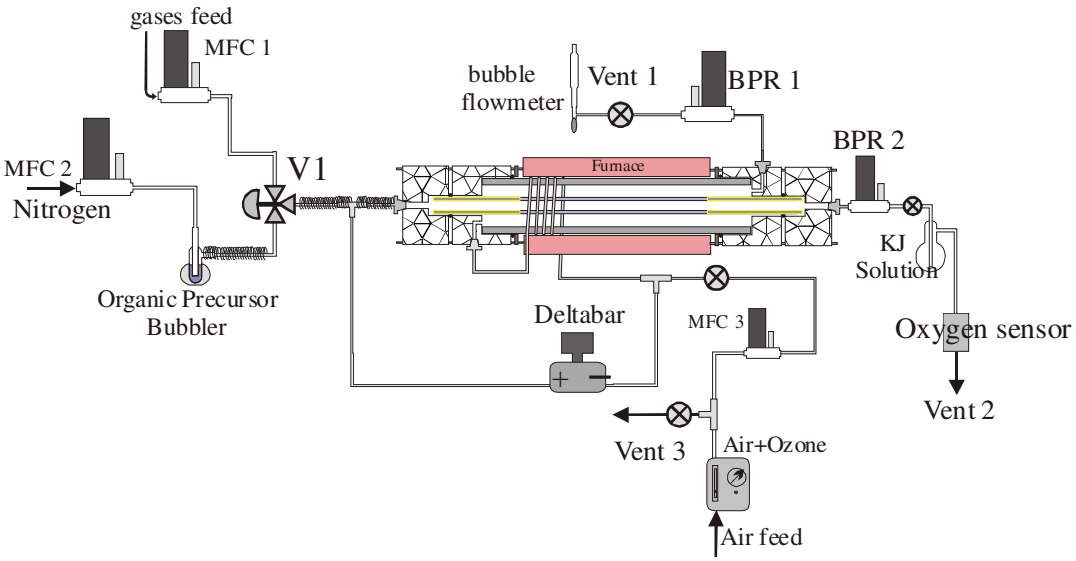


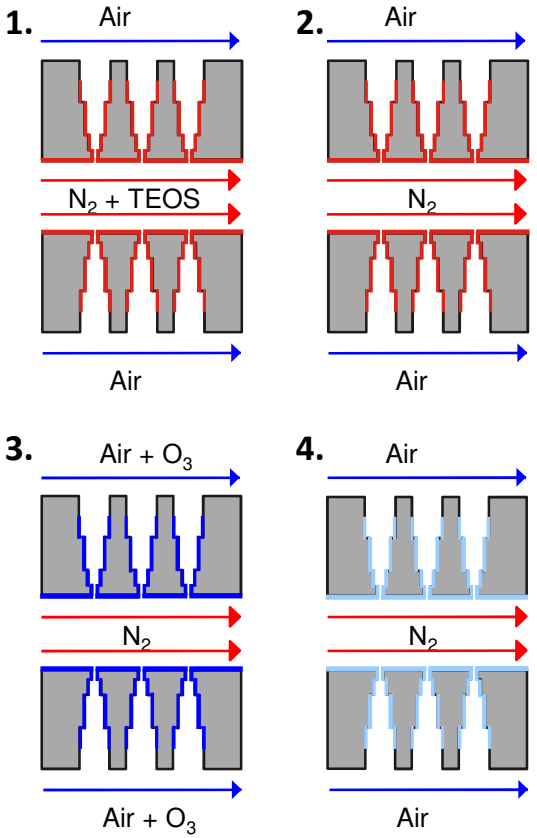


4. Purging with Air (support) and N_2 (nanofiltration side).

❑ **Completion of the individual deposition cycle of the CVD process.**

Apparatus for conducting cyclic modes of CVD processes and single gas permeance measurements for a variety of probe gases at several stages of deposition

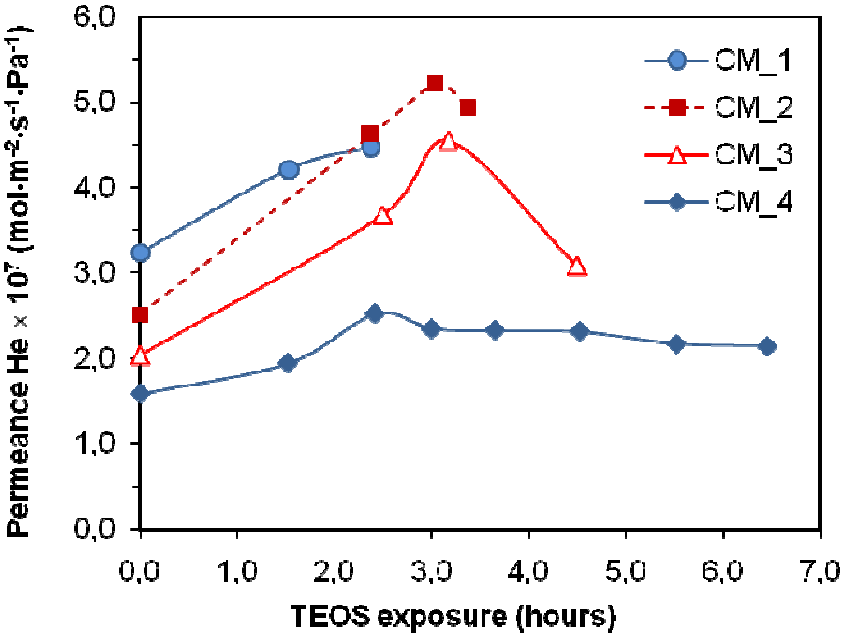


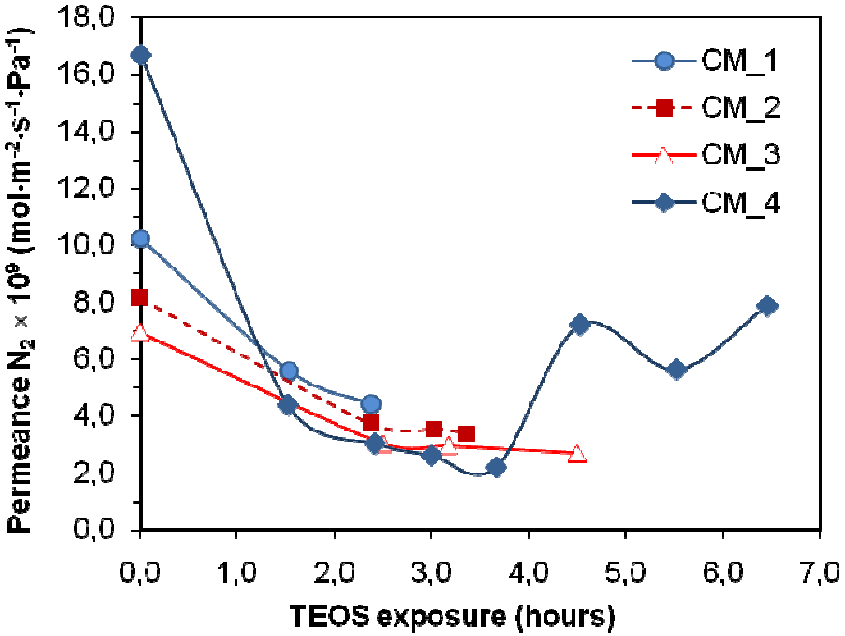


CVD conditions

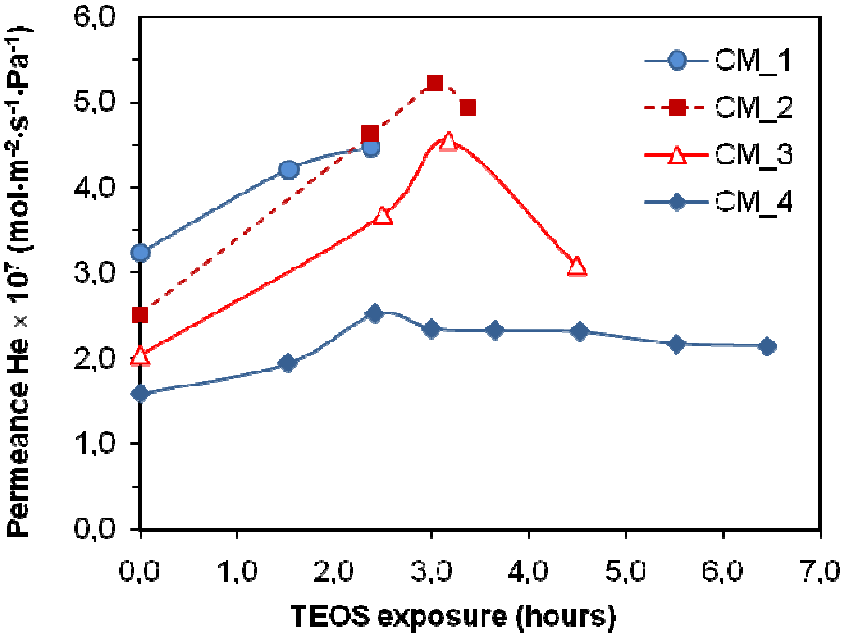
Sample code	T (K)	OM concentration ($mol \cdot m^{-3}$)	O_3 concentration ($mol \cdot m^{-3}$)	Number of CVD cycles	Hours of exposure of NF layer to silane vapors	Total silane mmols facing the NF layer
CM_1	573	0.11	0.29	3	2.37	0.47
CM_2	573	0.11	0.29	5	3.03	0.60
CM_3	573	0.11	0.29	6	3.37	0.67
CM_4	573	0.11	0.29	14	6.46	1.28

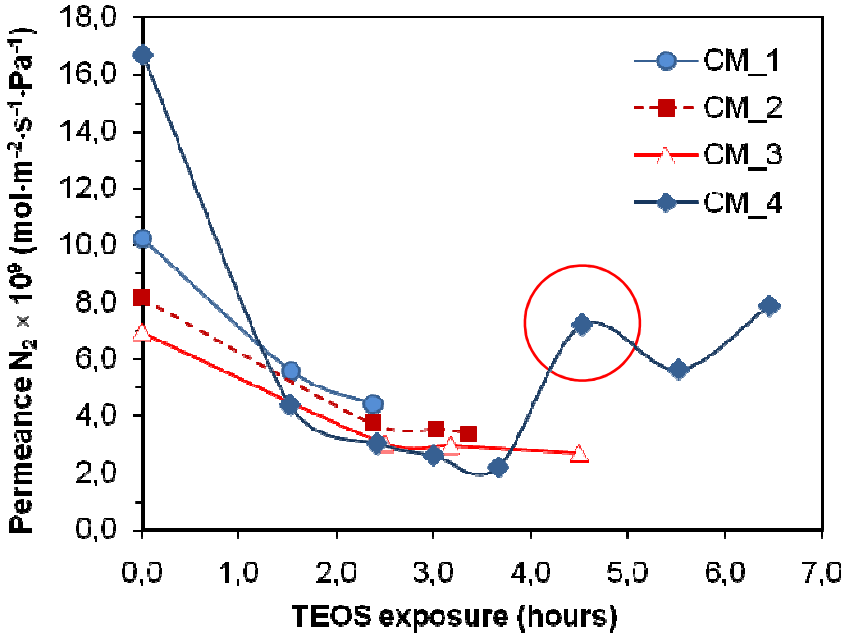
Evolution of He and N_2 permeance at 300°C with the progress of deposition



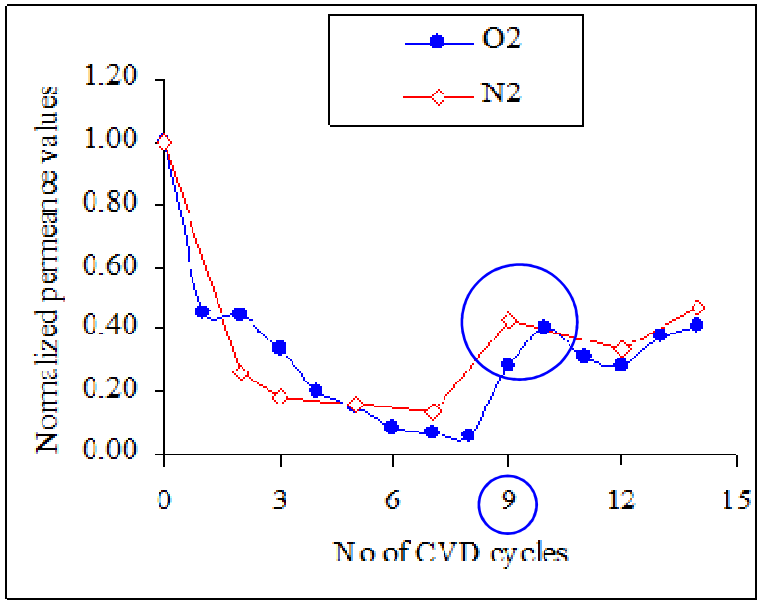


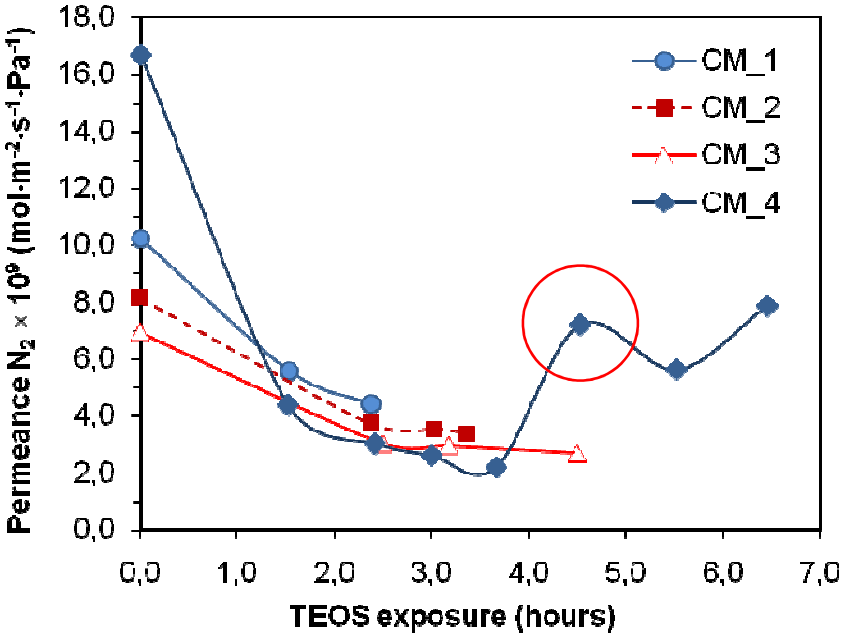
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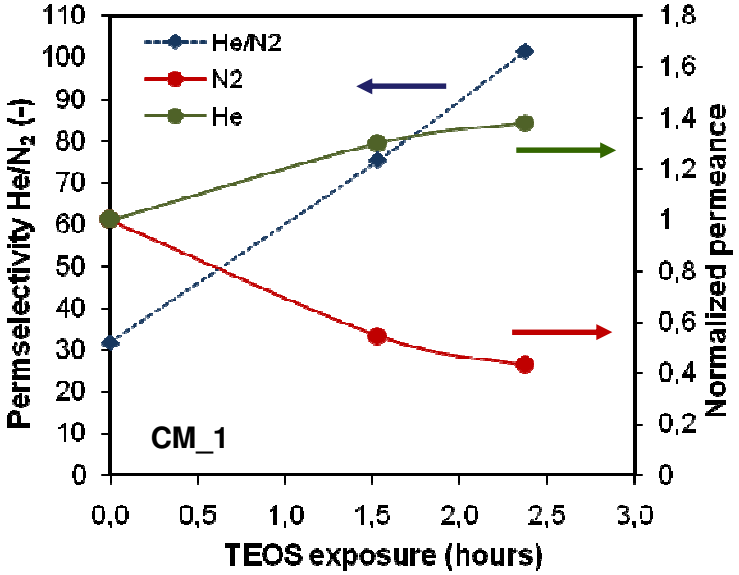


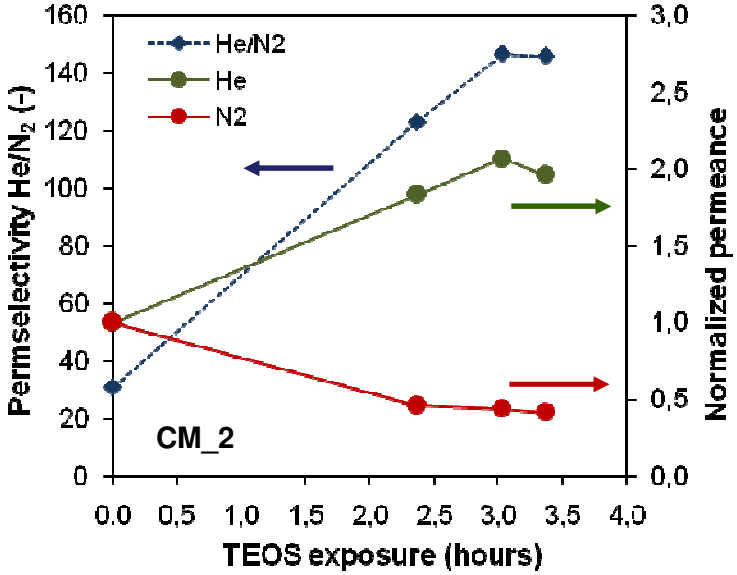
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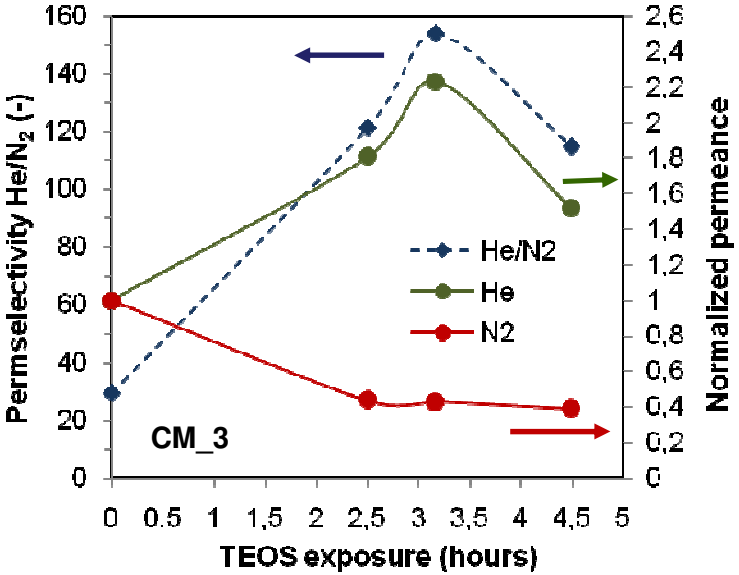


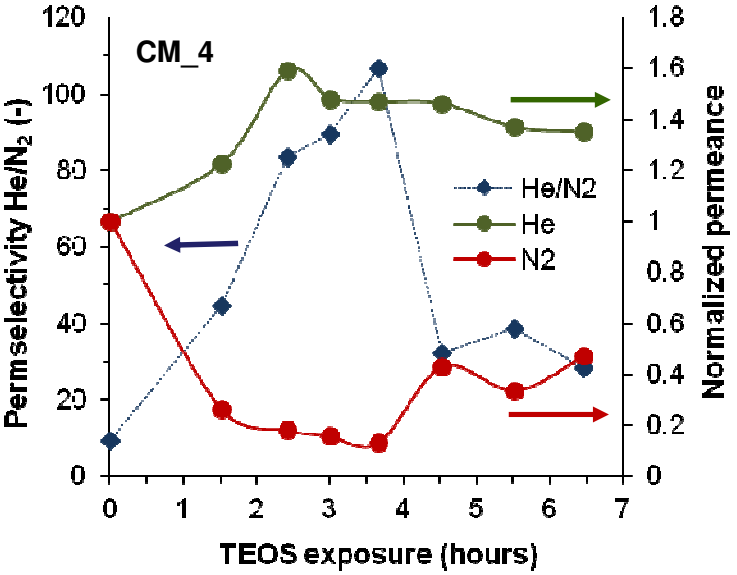


Evolution of He/N_2 ideal selectivity

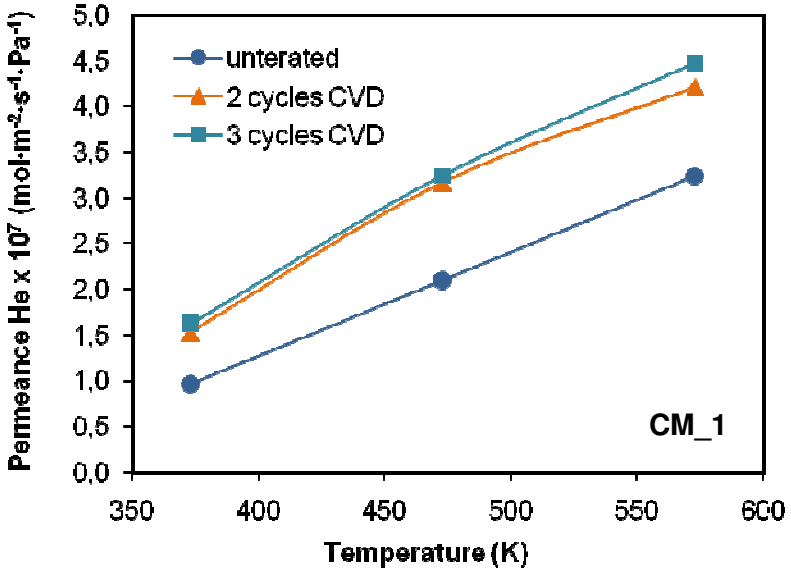


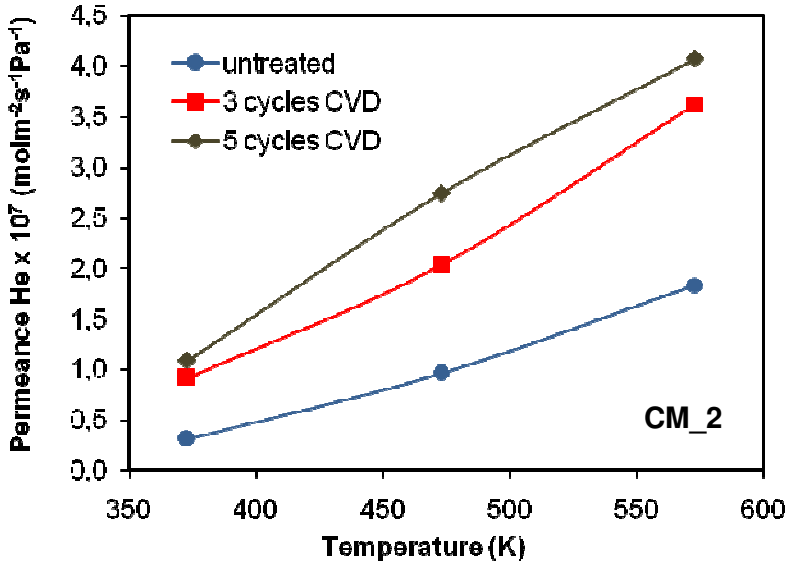


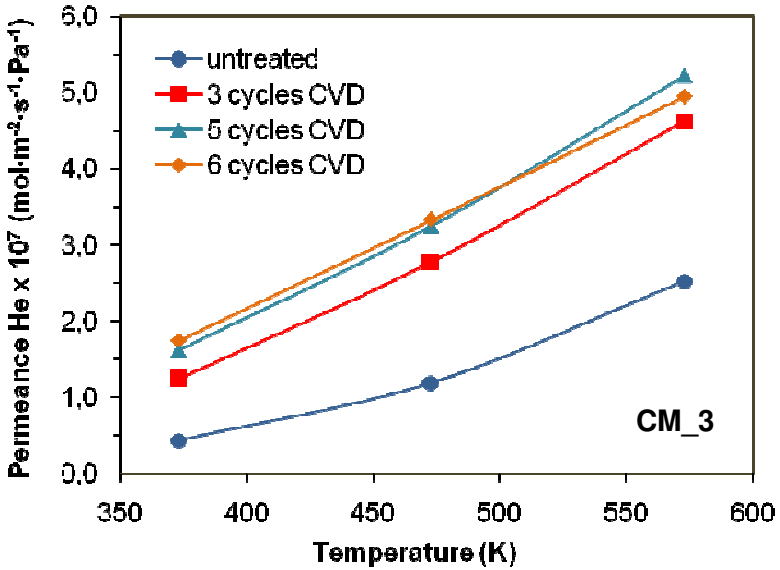


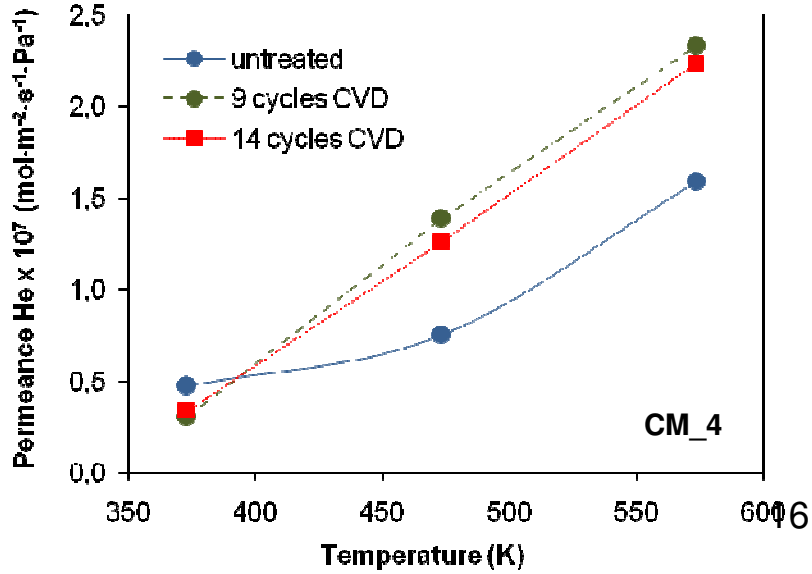


Evolution of the temperature dependence of He permeance

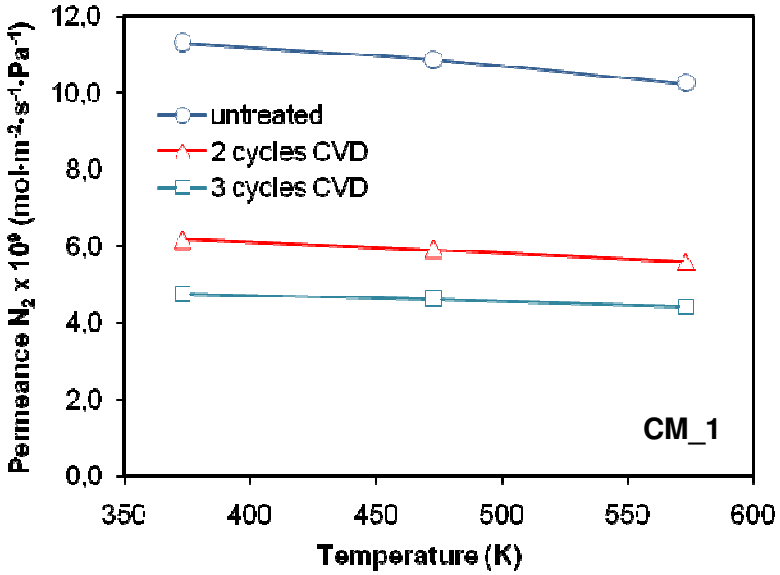


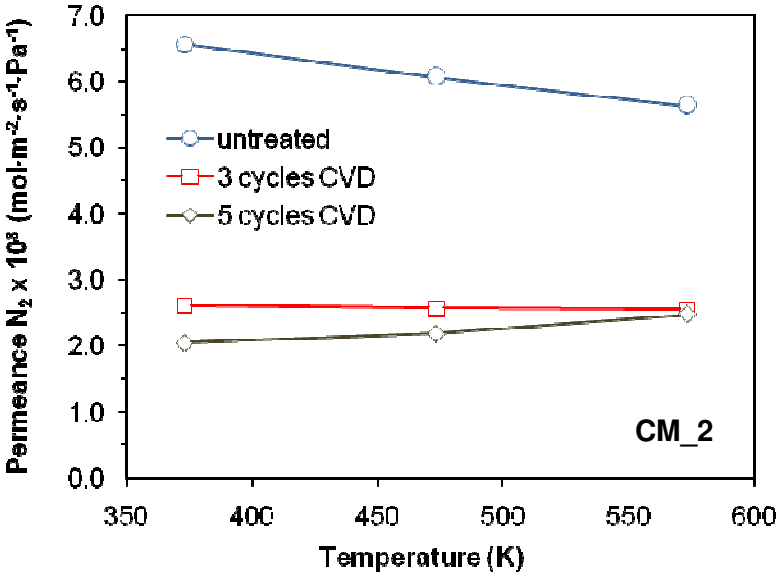


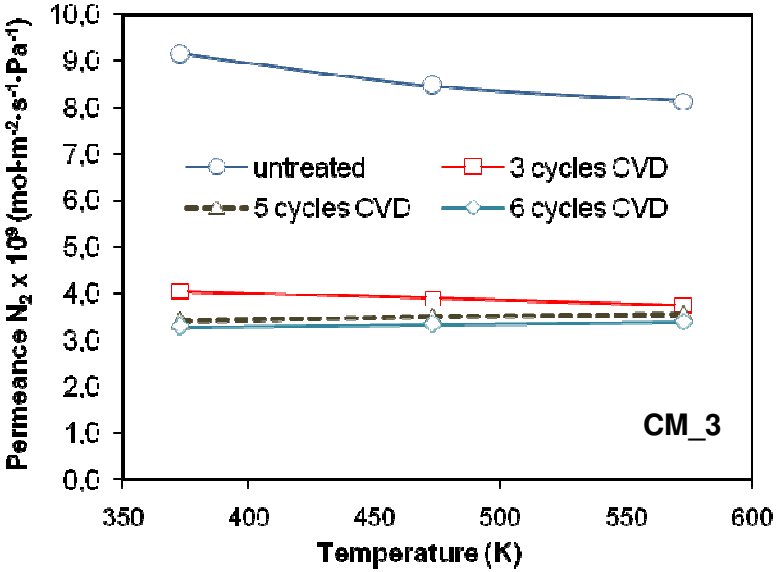


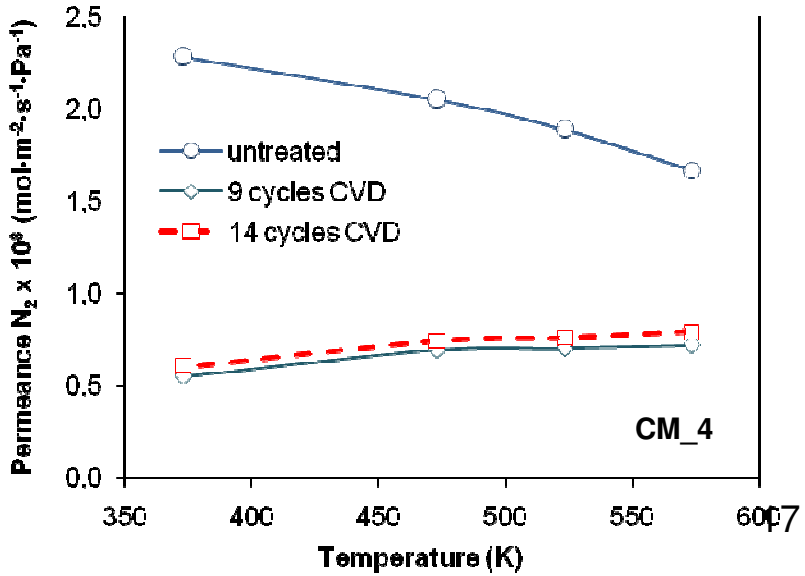


Evolution of the temperature dependence of N_2 permeance

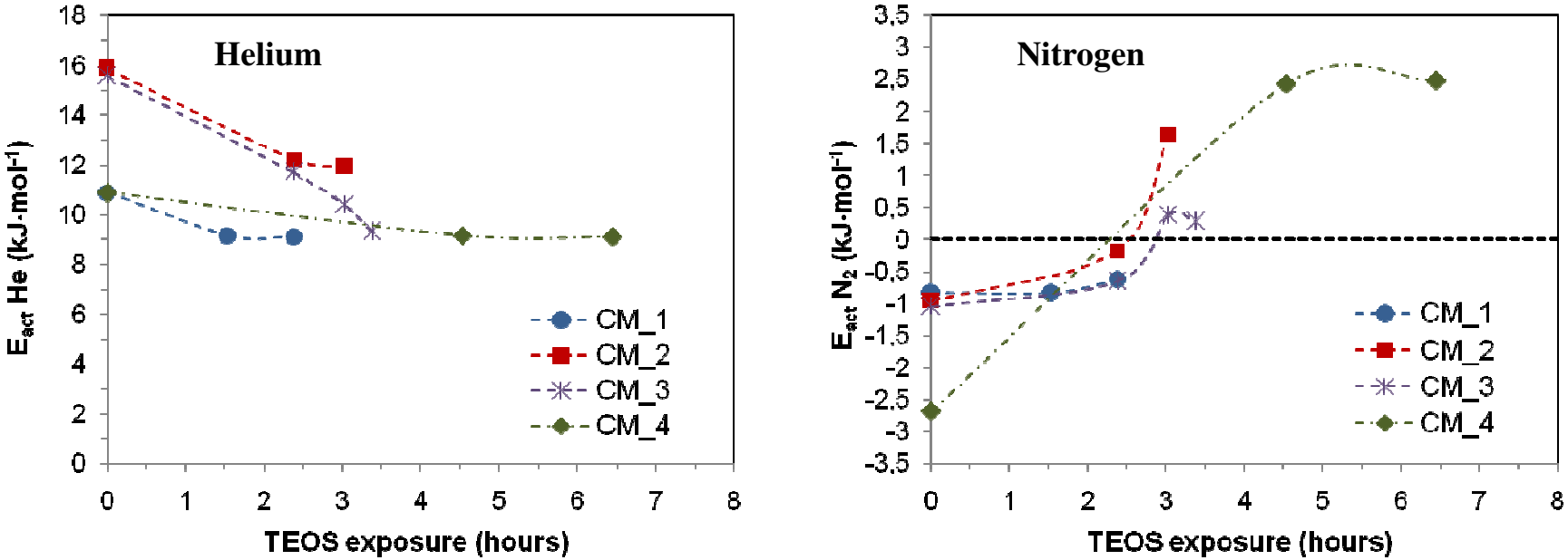








Evolution of He and N_2 apparent activation energy of diffusion



- The apparent activation energy is considered as the result of two contradicting mechanisms that is activated (or configurational) diffusion in micropores and sorption at different sites inside the pores, which reduces mobility.
($E_{act} = E_m - q^{st}$, where E_m: activation energy for activated diffusion, q^{st} : isosteric heat of adsorption).
- Gradual transition of N_2 transport mechanism from surface diffusion to activated diffusion.
- This transition has already occurred after the 9th cycle of CVD treatment on the membrane CM_4.

Permeance vs. temperature for an unmodified membrane and the membrane treated with 3 cycles of CVD process.

- Single-gas permeance measurements conducted using the following gases: He, H_2, CO_2, Ar, O_2, N_2, CH_4, C_3H_8, n-C_4H_{10}, 1-C_4H_8, iso-C_4H_{10}, iso-C_4H_8 and SF_6.

- Temperatures of permeation rates measurements: 30, 50, 70, 100, 150, 200, 250, 300°C.

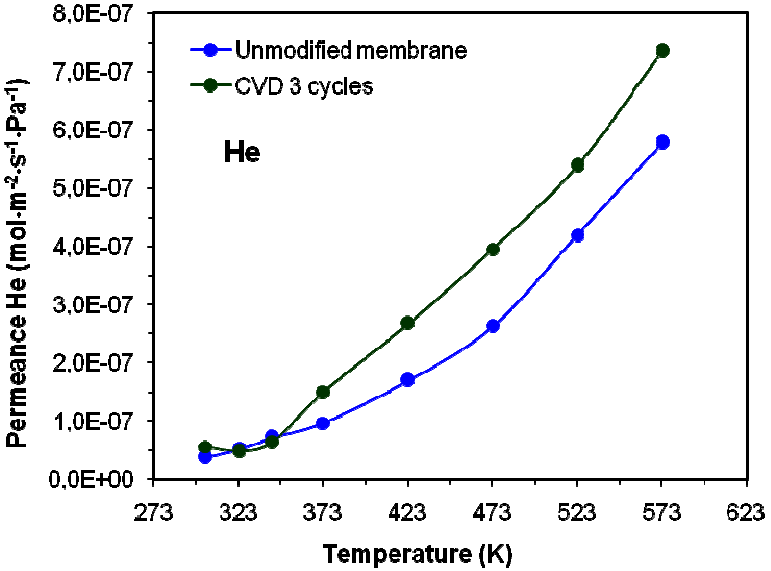
Gas	M [g·mol^{-1}]	σ_m [Å]	d_k [Å]	ε/k [K]	μ_e [Debye]	$Q_m \times 10^{26}$ [esu·cm^2]
He	4	2.551	**2.6**	10.22	0	0
H_2	2	2.827	**2.89**	59.7	0	0.637
CO_2	44.01	3.941	**3.3**	195.2	0	4.3
Ar	39.95	3.542	**3.4**	93.3	0	0
O_2	32	3.467	**3.46**	118.0	0	0.4
N_2	28.01	3.798	**3.64**	95.05	0	1.4
CH_4	16.04	3.758	**3.8**	148.2	0	0
C_3H_8	44.09	4.942	**4.3**	273.1	0.084	0
n-C_4H_{10}	58.12	5.405	**4.3**	305.1	0	0
1-C_4H_8	56.11	5.273	**4.8**	301.8	0.34	0
iso-C_4H_{10}	58.12	5.392	**5.0**	295.9	0.0132	0
iso-C_4H_8	56.11	5.273	**5.7**	302.6	0.5	0
SF_6	146.05	5.128	**5.5**	222.1	0	0

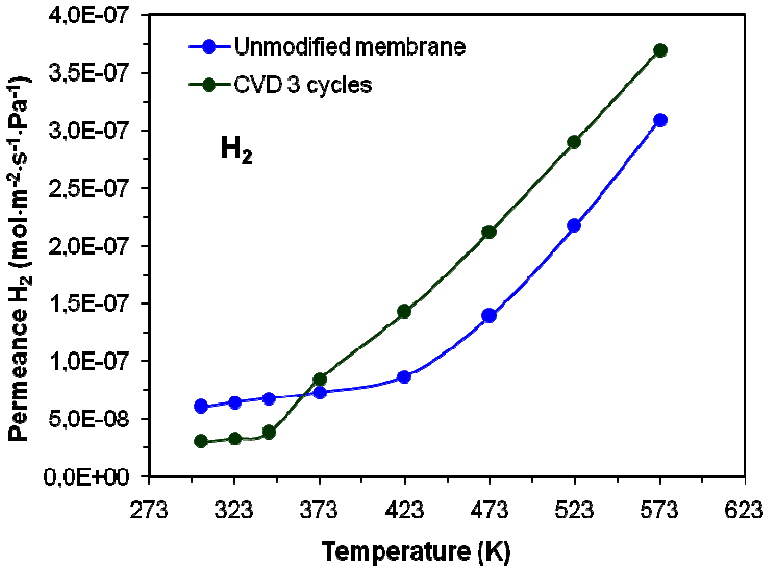
- The pressure in the permeate side was 1 atm.

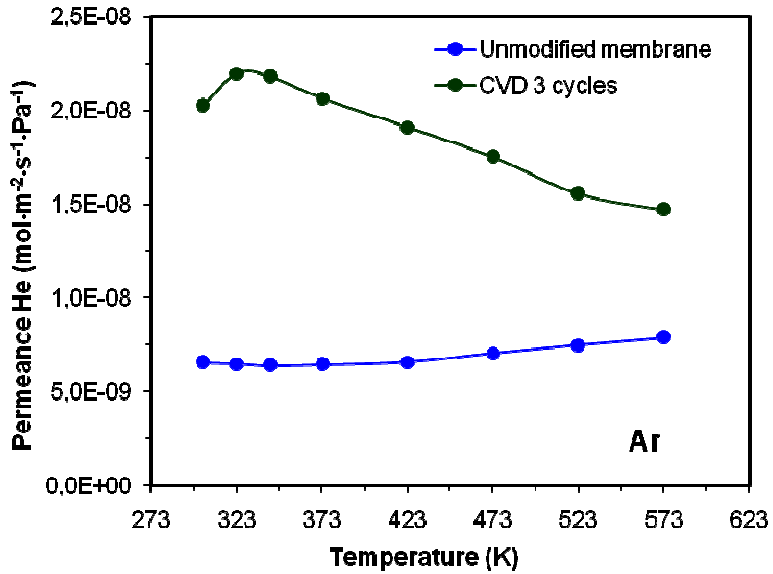
- The pressure in the feed side was by 500 – 1000 mbar larger than in the permeate side depending on the MFC feed flow rate and the supplied single gas.

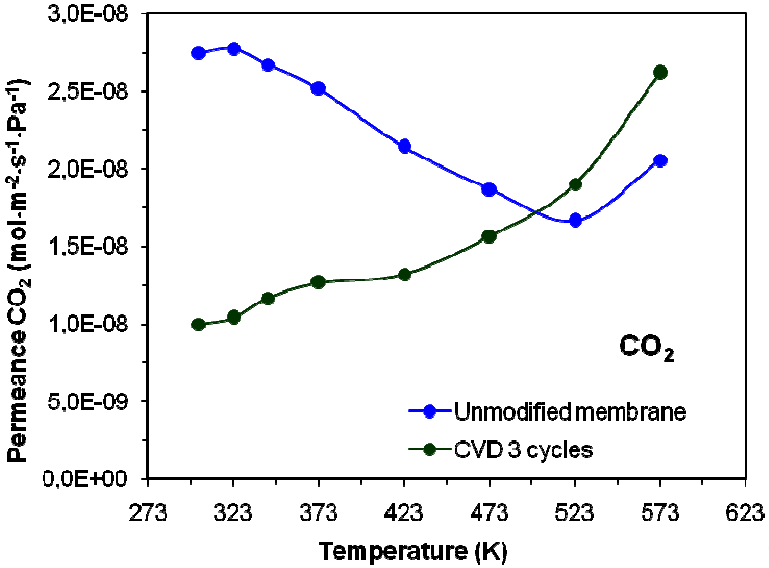
M: molecular weight,
σ_m: van der Waals diameter,
d_k: kinetic diameter,
ε/k: Lennard-Jones potential parameter,
μ_e: dipole moment,
Q_m: quadrupole moment.

Permeance vs. temperature results

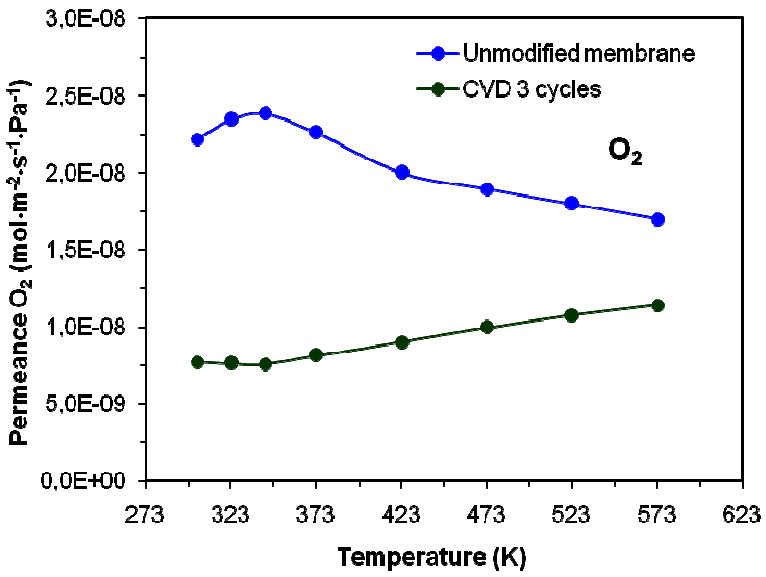


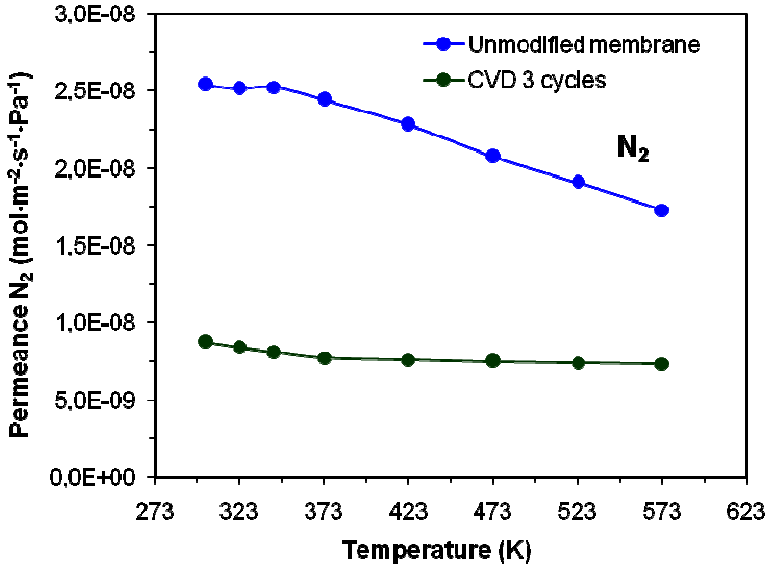


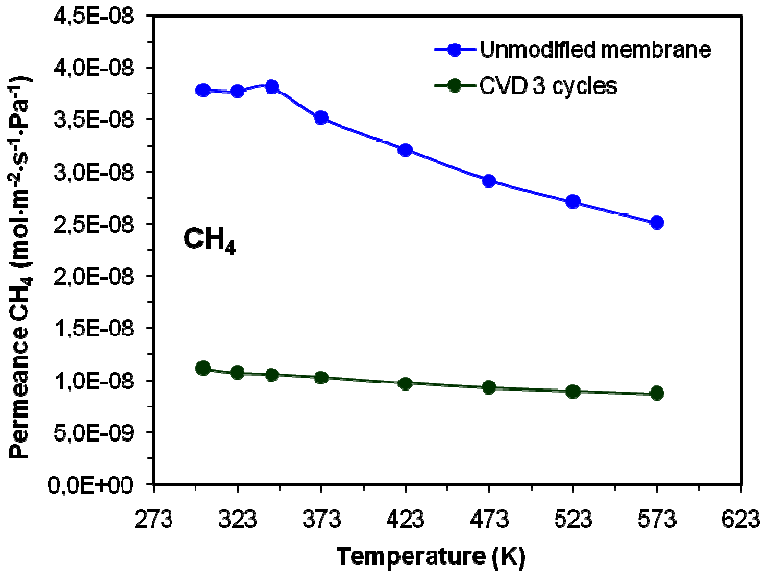


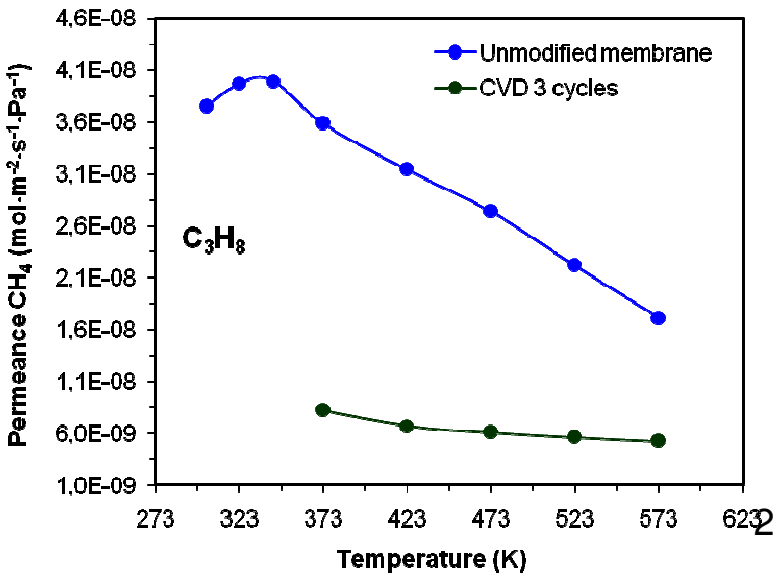


Permeance vs. temperature results

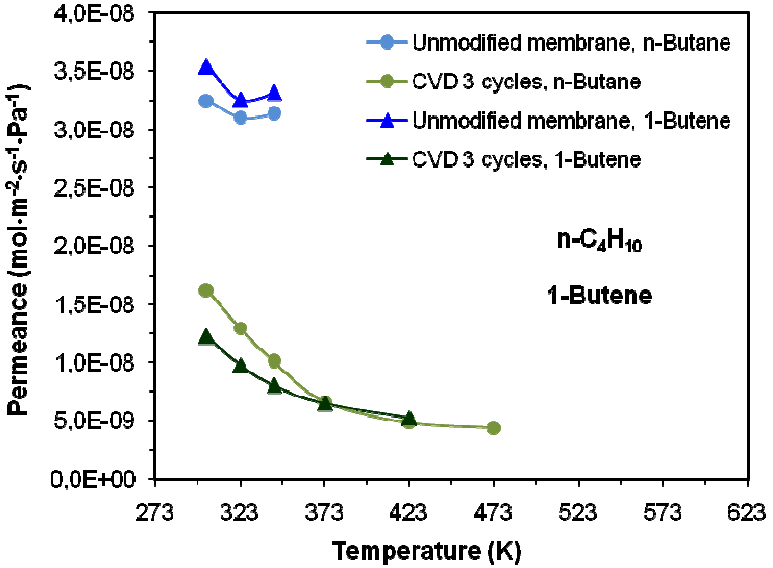


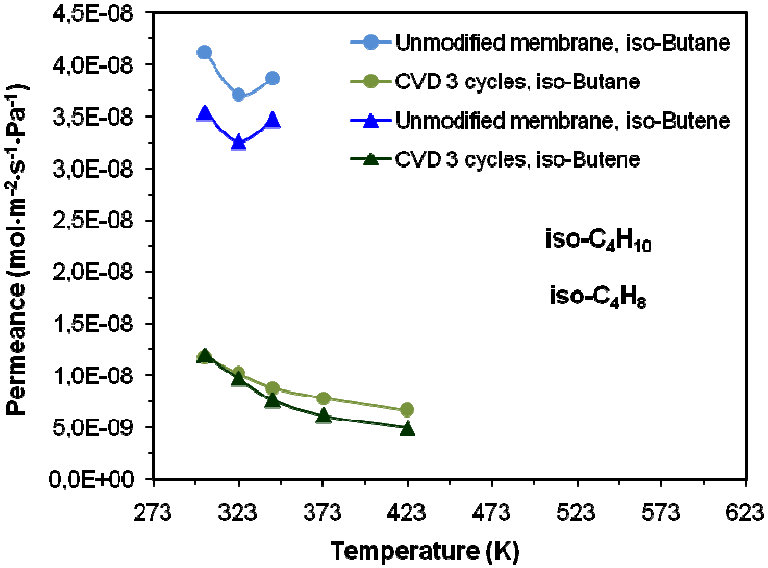


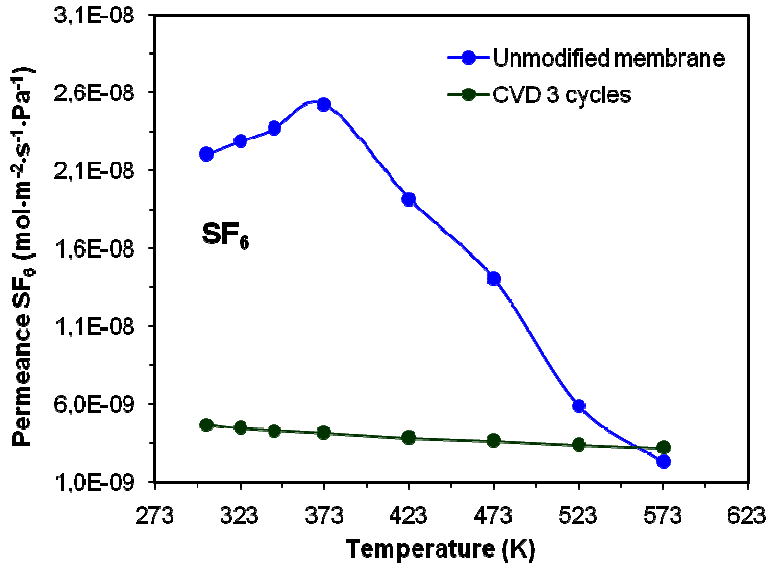




Permeance vs. temperature results



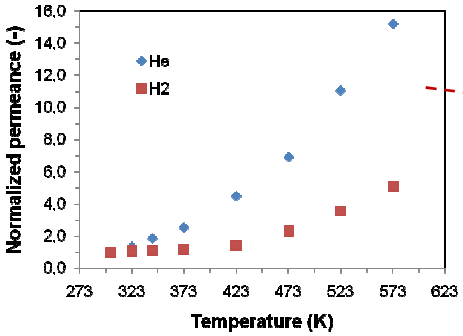


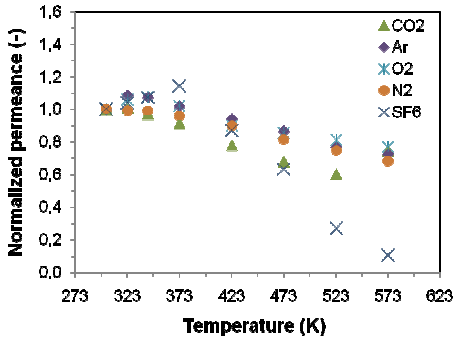


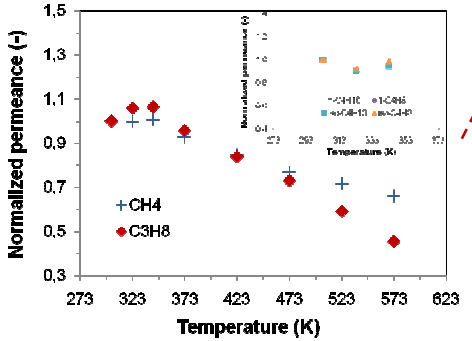
- In the unmodified membrane, a maximum peak of permeance can be determined in the case of Ar, O_2 and C_3H_8 gases at the range of 50–70°C whereas for SF_6 gas, this maximum has been shifted to 100°C.

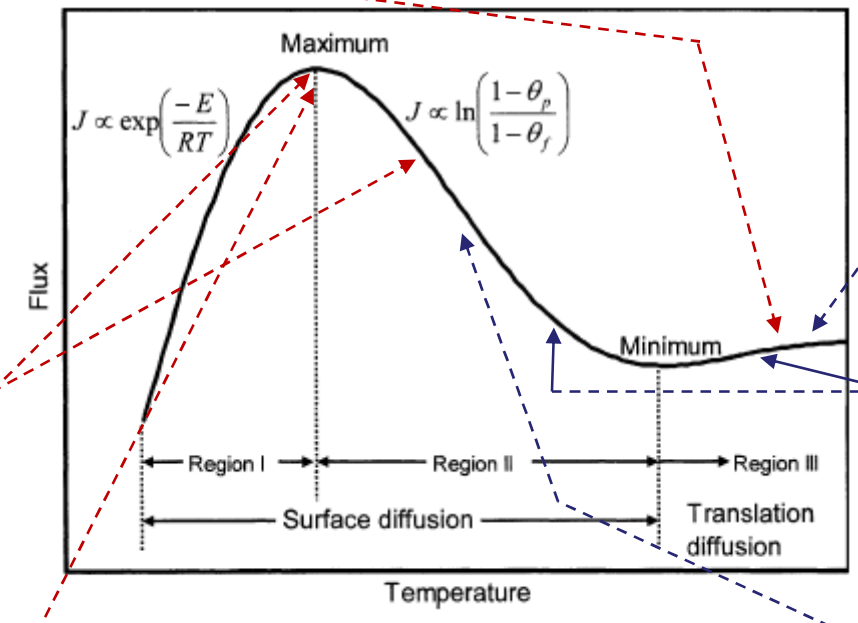
- A maximum peak is not clearly detectable in the case of N_2 and CH_4 even though the low temperature part of the graph is followed by a downward almost linear part up to 300°C, similar to Ar, O_2, C_3H_8 and SF_6 gases.

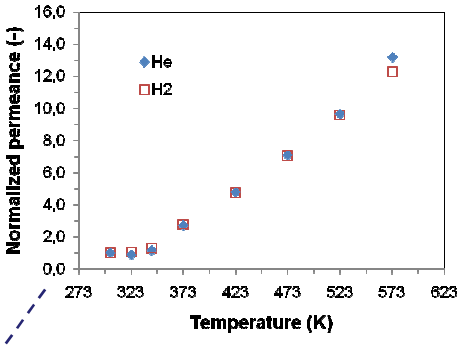
Permeance vs. temperature results

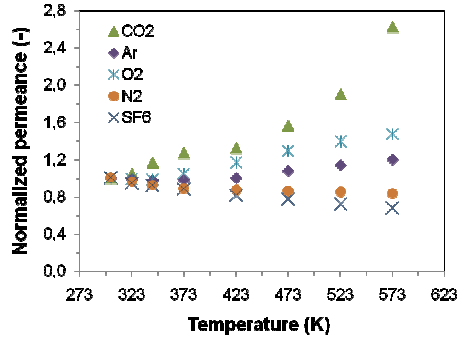


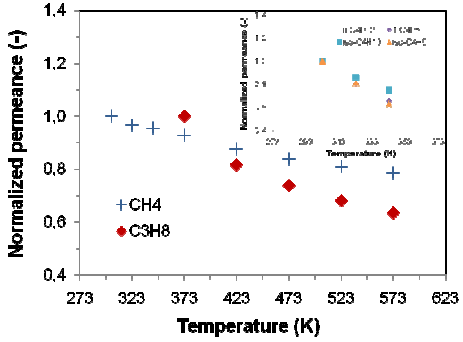












$$J = \frac{\rho n_{sat} D_{MS}}{\ell} \ln \frac{1-\theta_p}{1-\theta_f}$$

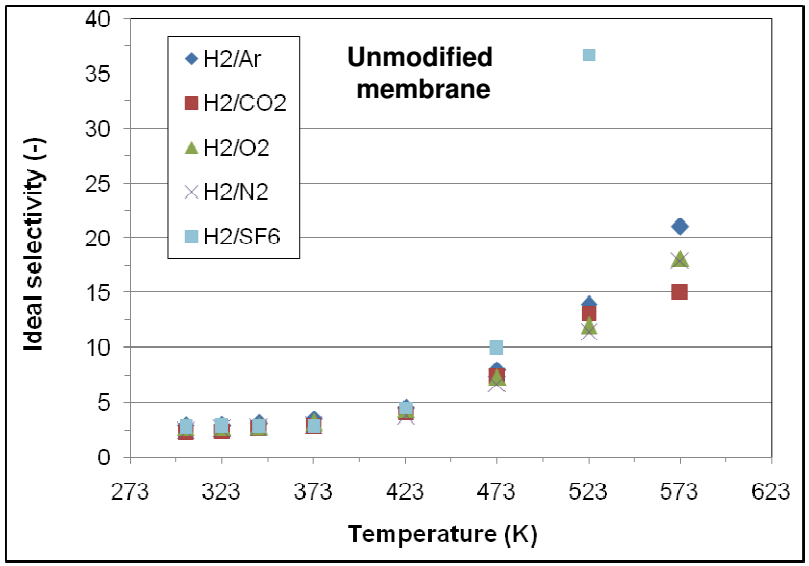
$$D_{MS} = D_{MS_o} \exp\left(-\frac{E_d}{RT}\right)$$

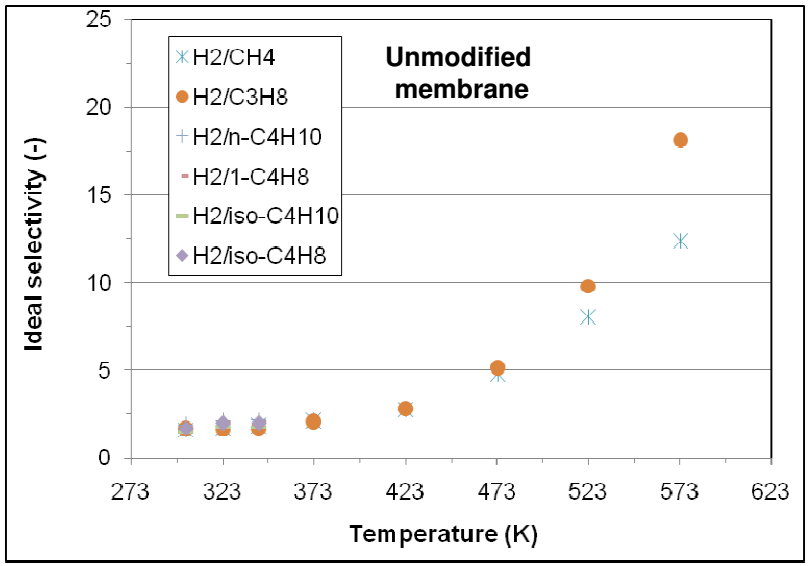
$$\Downarrow$$

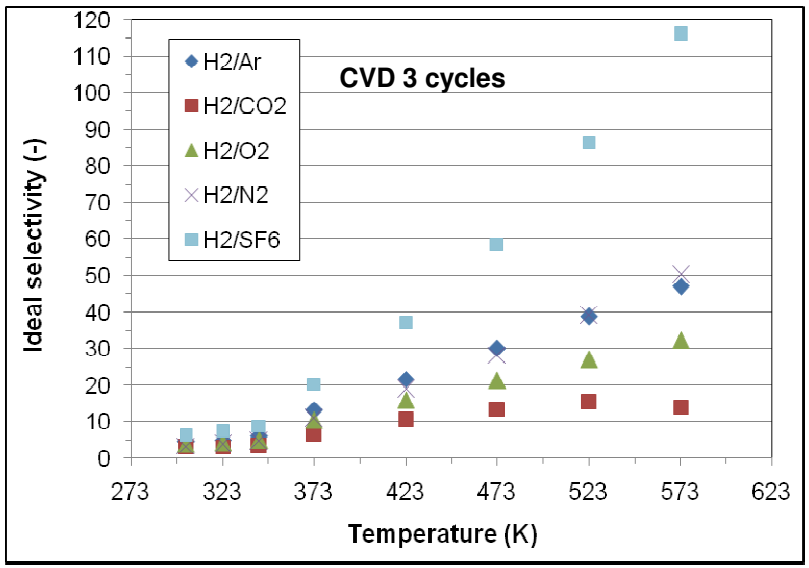
$$J = \frac{\rho n_{sat} D_{MS_o}}{\ell} \exp\left(-\frac{E_d}{RT}\right) \ln \frac{1-\theta_p}{1-\theta_f}$$

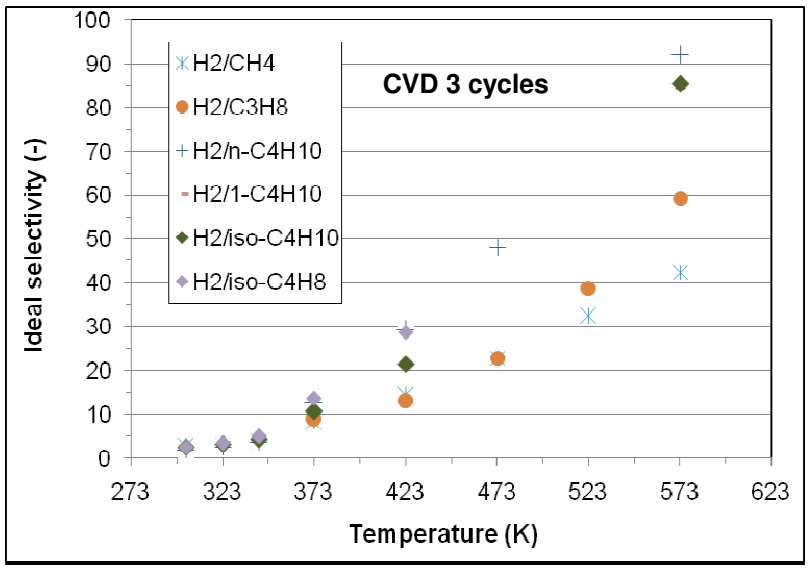
J: gas flux (mol·m^{-2}·s^{-1}),
ρ : zeolite density (Kg·m^{-3}),
n_{sat} : adsorbed amount at saturation coverage (mmol·g^{-1} zeolite),
D_{MS} : Maxwell–Stefan diffusivity (m^2·s^{-1}),
D_{MSo} : pre-exponential coefficient (m^2·s^{-1}),
l : effective thickness of the membrane (m),
E_d : activation energy for diffusion (kJ·mol^{-1}),
R : ideal gas constant (= 8.314 J·mol^{-1}·K^{-1}),
T : temperature (K),
θ_f : surface coverage in feed (-),
θ_p : surface coverage in permeate (-).

Ideal selectivity of gas pairs with respect to Hydrogen









Conclusions

• In the current investigation cyclic CVD modification processes were applied to composite tubular ceramic membranes with a silica nanofiltration layer of 1 nm pore diameter, in the opposing-reactants configuration. The TEOS/O_3 reaction system was used and the processes were carried out at 300^{o}C.

• He/N_2 permselectivity showed a tendency to reach to a maximum versus time of exposure to the supplied silane vapors. This tendency has been explained on the basis of the evolution of Helium and Nitrogen permeance in the course of the CVD processes and the estimations of the corresponding apparent activation energy values.

• H_2 permeance increases rapidly as the temperature is increased, as a result of its activated transport. Therefore, the CVD modified membranes have the potential to produce very high fluxes at elevated temperatures.

• The pore structure alteration with the progress of cyclic CVD treatment can be elucidated, by taking into account theoretical descriptions of gas transport through microporous media.

• By monitoring the evolution of He and N_2 single gas permeances as well as He/N_2 ideal selectivity at several temperatures during the CVD treatment, optimized process conditions can be estimated thereby enabling fabrication of selective and highly permeable – with respect to hydrogen gas – ceramic membranes.

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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

ΕΣΠΑ 2007-2013
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ΕΥΡΩΠΑΪΚΟ ΚΟΙΝΩΝΙΚΟ ΤΑΜΕΙΟ