Hybrid silica nanofiltration membranes with low molecular weight cut-off values

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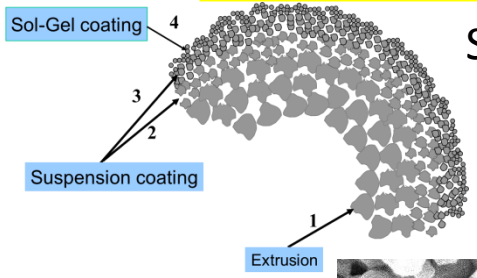
- Conclusions

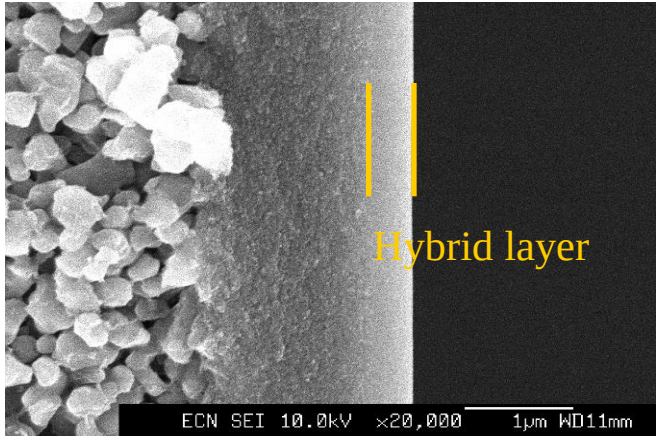
Introduction/background

- Wish for organic solvent stable NF membranes: sharp MWCO 200-500 Dalton
  - Now available: polymeric, ceramic, porous/non-porous, asymmetric, integrally skinned composites, however, not meeting all demands
  - No swelling, predictable and stable (but tunable) flux
  - Permeance at least 0.5 kg/barm^{2}h
  - Wide range of solvents (alcohols, ketones, aromatics, aprotics, solvent + water)
- Approach: apply a solvent stable hybrid silica layer on ceramic tubular support
- Basis is microporous HybSi® membrane:
  tailor pore structure to fit in with NF properties

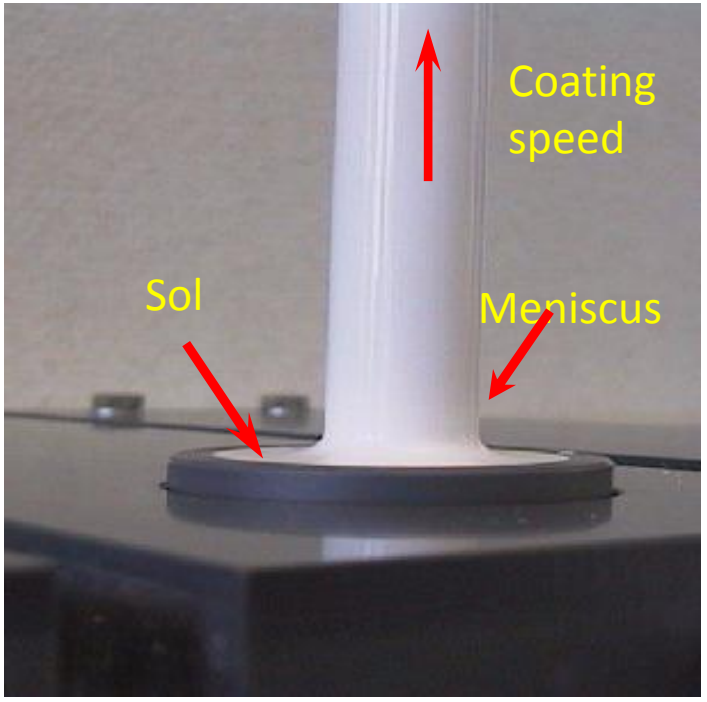
HybSi® and hybrid membranes

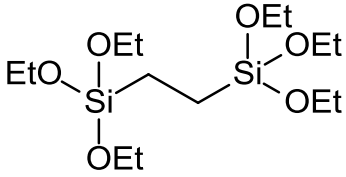


Sol – gel technology



Coating step

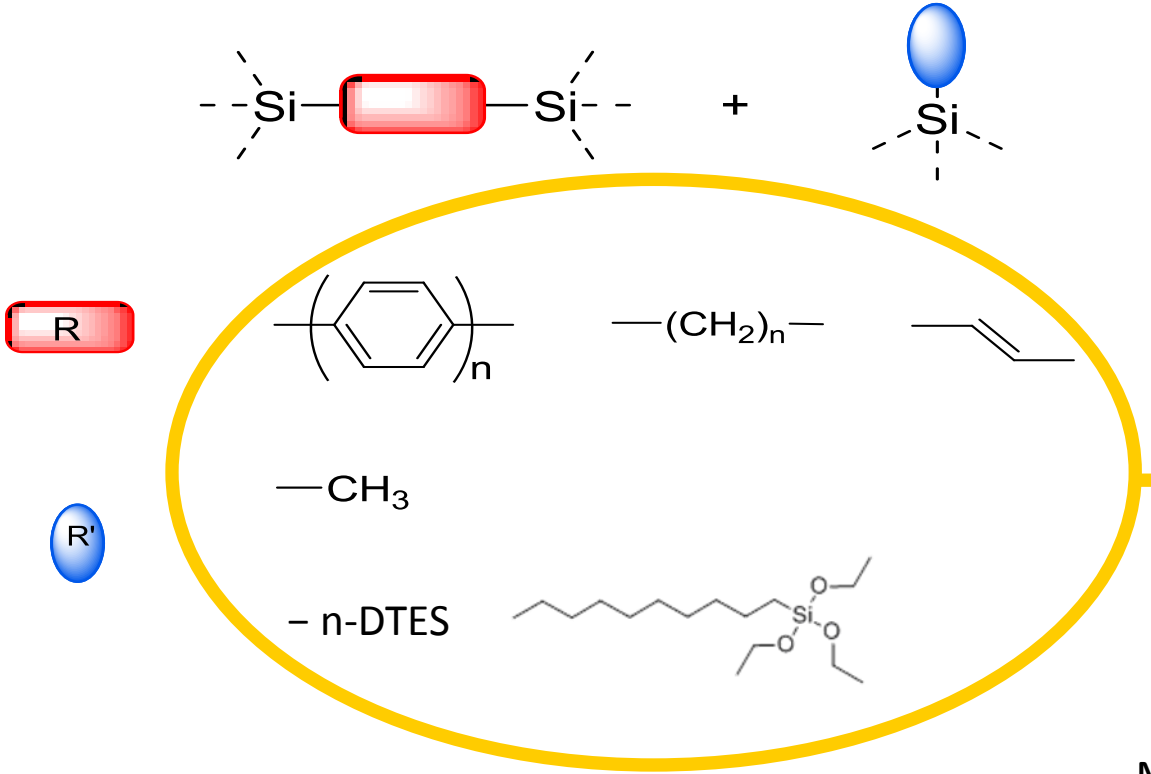




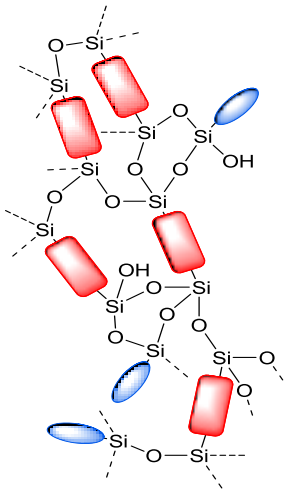
BTESE

HybSi® Pervaporation Membranes

HybSi® and hybrid membranes



Tailored network

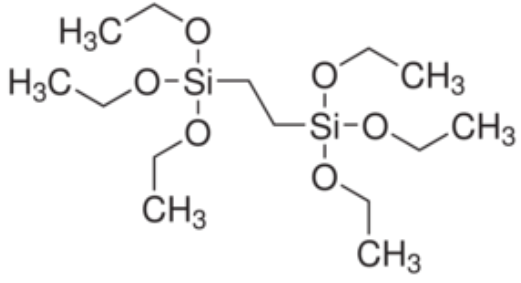


Microporous pervaporation membrane

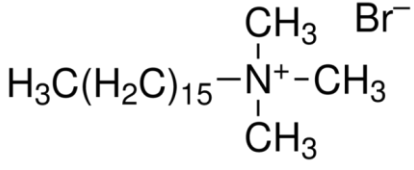
HybSi®
Pervaporation Membranes

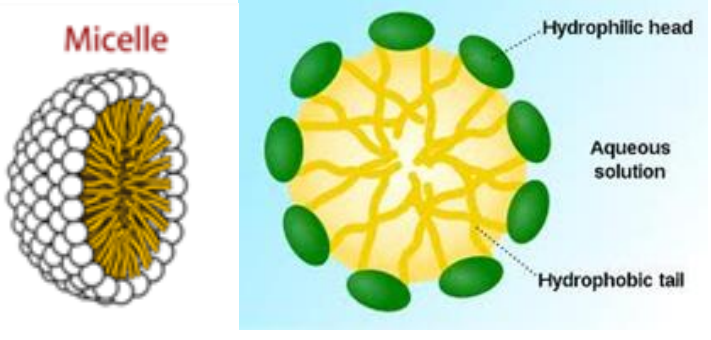
Membrane preparation

Precursor + structure directing agent for OSNF



BTESE, 1,2-bis(triethoxysilyl)ethane



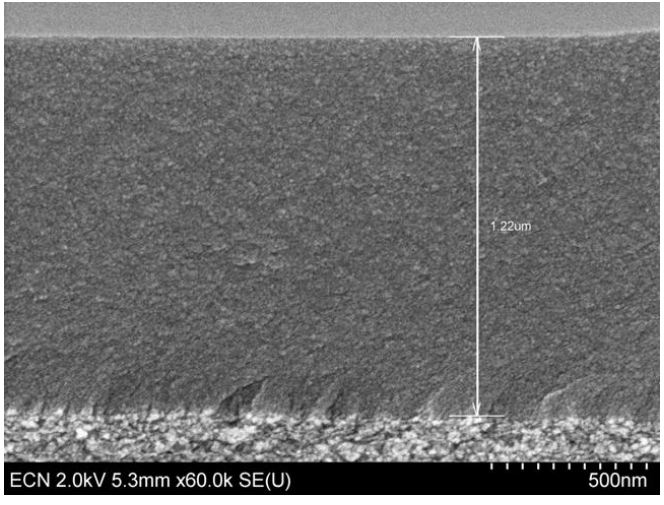


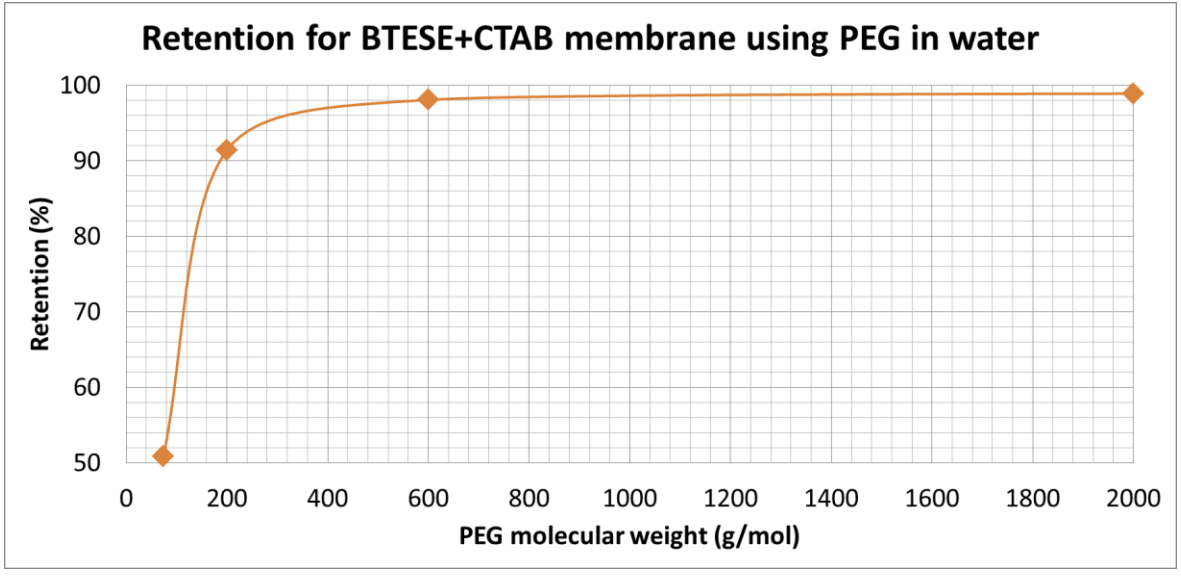
IDEA

CTAB forms micelles which create a more open structure after removal from during the calcination

CTAB, Cetyltrimethyl ammonium bromide (ionic surfactant as template)

First results BTESE - NF membrane





90% retention: 180 Dalton
Thickness: 1220 nm
Water permeance: 0.006 l/barm^{2}h (measured at 32 bar P_{feed})

Performance optimization

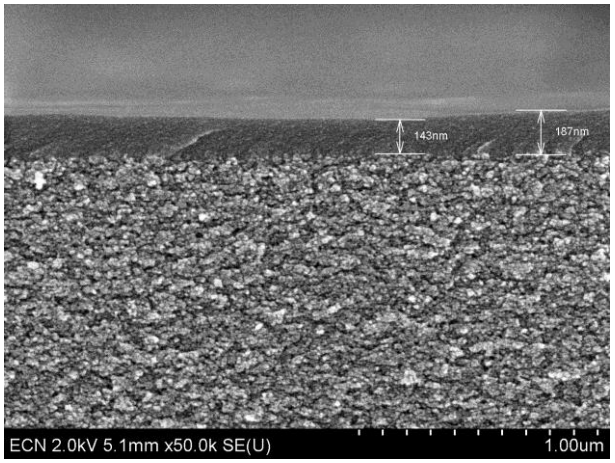
- Decrease of the membrane layer thickness
- Modify the pore structure by changing the sol recipe, like relative amounts of:
  - BTESE
  - CTAB
  - Acid
  - Water
- Design of experiment-like approach – total of 24 different recipes tested, trends will be shown

- Precursor chemistry (not presented here)

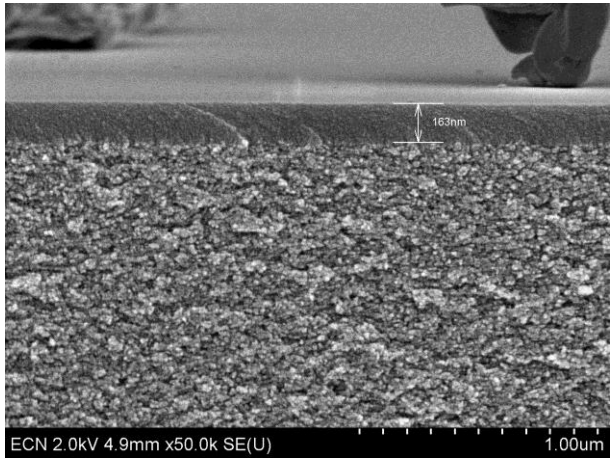
Thinner membrane layer

Sol concentration

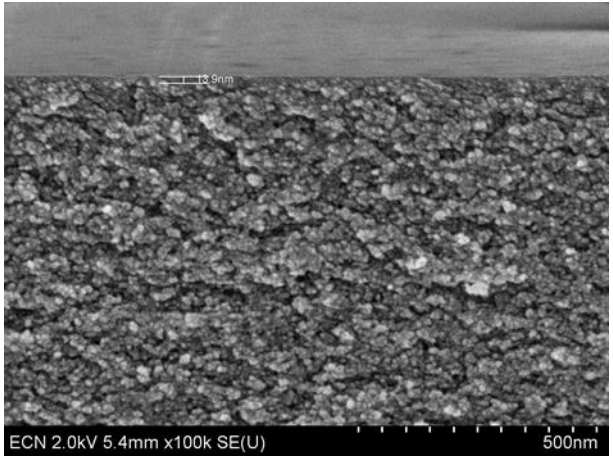
100%



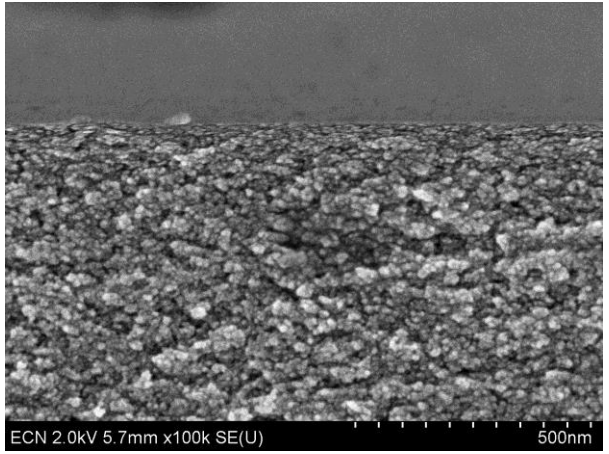
67%



50%



40%



Thinner membrane layer

Membrane	Thickness (nm)	Water permeance (kg/bar.m^2.h)	MWCO for PEG in water (Dalton)
1	1220	0.006	190
2	375	0.009	180
3	14	0.010	180
4	< 5	0.015	180

A thickness reduce by two orders of magnitude
→ a flux increase by a factor of 3,
→ MWCO remains low and constant

Infiltration into the support?

Sol Modification

- CTAB concentration trends:

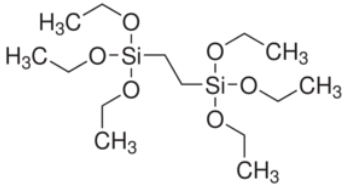
- Low → Pervaporation quality
- Medium → Nanofiltration quality
- High → unstable sol, flocculation not suitable for membrane preparation

- Not surprisingly, micelle formation require a critical minimum concentration (CMC).
  For CTAB in EtOH[1]: 0.24 mol/L, in our sol ~ 0.2 mol/L

[1]Frontiers of Chemistry in China, 2006, Volume 1, 438

Hydrolysis ratio

- Hr: Ratio water : ethoxy on the original precursor

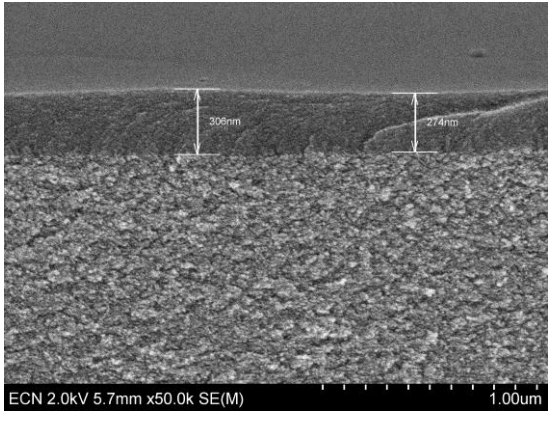


- Small → Nanofiltration quality
- Medium → Pervaporation quality
- High → Unstable sol, flocculation

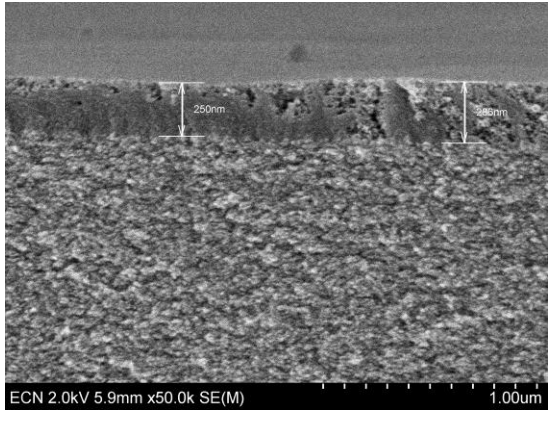
- Trend: a higher water content results in larger sol ‘particles’, as measured with Dynamic Light Scattering

Hydrolysis ratio

Hr = 2.0



Hr = 0.75



- Smaller hydrolysis ratio:
  - Smaller particles
  - less viscous sol
  - Increased infiltration
  - more open layer

Sol modification

Hydrolyses ratio	Layer thickness (nm)	H_2O perm (kg/bar.m^2.h)	Retention PEG 200	Retention PEG 1000
2.0	275	0.003-0.008	57%	84%
0.75	~ 250 infiltrated	0.02-0.06	65%	93%

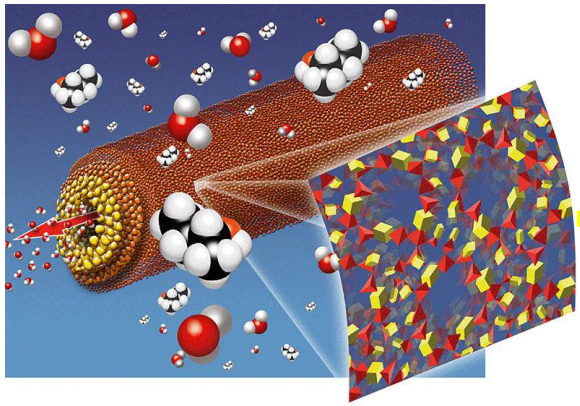
A lower Hr leads to an:

→ Increased permeance

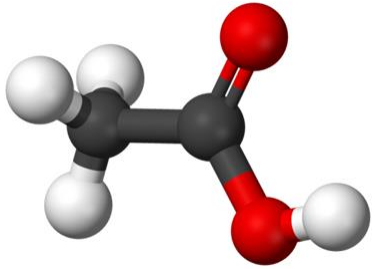
→ Improved retention

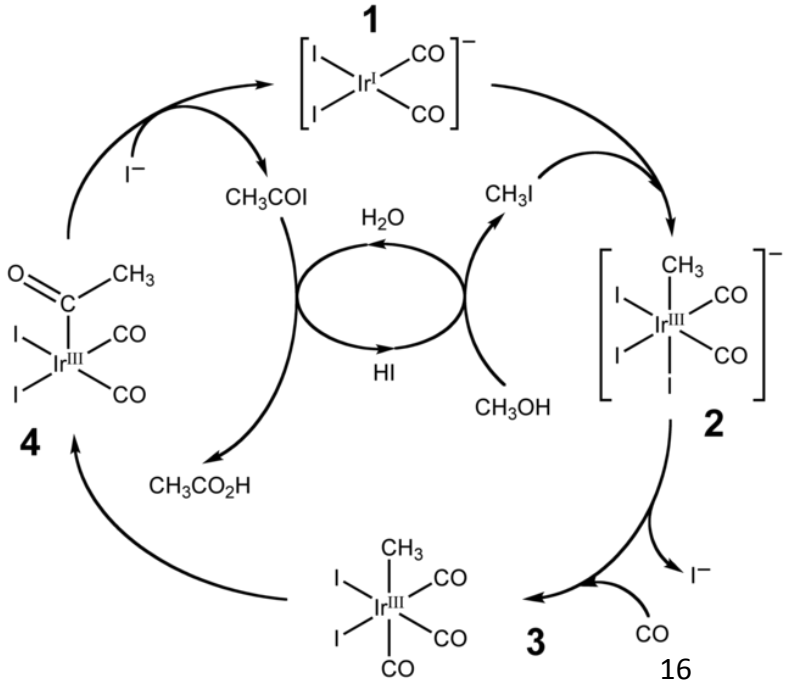
Conclusions

- Organic – inorganic hybrid materials can be tailored towards NF membranes
  - By applying pore formers (CTAB)
  - By modifying the sol – gel recipes and procedures
- The layer thickness has a limited influence on the permeance
  - Infiltration?
- Indication for infiltration of the sol in the support layer
- Performance
  - Retention of ~200 Dalton is possible
  - Fluxes/permeances are still lower than an industrial application would require



- More on HybSi
- 2 PM in this same hall!
- Revealing high acid resistance





Thank you for your attention

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