Study on the synthesis and stability of hybrid organic-inorganic membranes for solvent filtration

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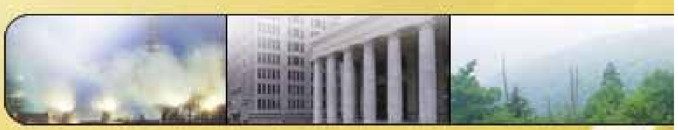

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Outline

- INTRODUCTION
- OBJECTIVES AND METHODS
- ORGANOSILANE MODIFICATION ON DIFFERENT METAL OXIDES
- STABILITY OF THE MODIFICATION
- ALTERNATIVE HYDROPHOBISATION METHOD
- CONCLUSIONS

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Introduction

Polymeric membranes:

- Cheap
- Versatile
- Limited chemical and thermal stability
- Loss of separation properties due to swelling and cracking

Ceramic membranes:

- higher cost
- High thermal stability, chemical inertness
- Resistance to decomposition in acid and alkaline medium
- Easy cleaning
- Long lifetimes
- Low pressures
- Intrinsic hydrophilic → low fluxes for apolar solvents

Overcome disadvantages of both polymeric and ceramic membranes by formation of hybrid organic-inorganic composites

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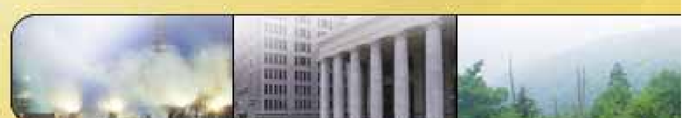
Surface modification on ceramic membranes



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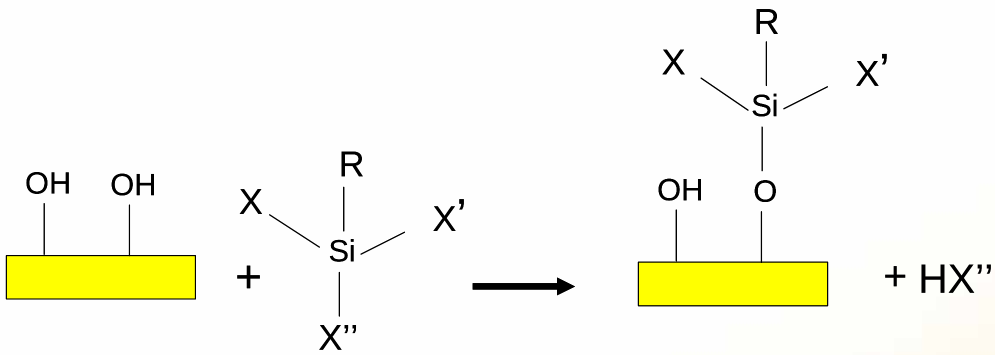
Objectives and methods

Reasons for surface modification

- Polarity (hydropobic/hydrophilic) → better fluxes for apolar solvents
- Pore sizes → decreasing cut-off
- Functionality/affinity of the surface → increasing selectivity, selective adsorption, ….

Surface reaction of TiO_2-membranes with organosilane reagents



X ,X', X'' = Cl, alkoxy, alkyl,R'

R = desired functional group: alkyl chains, amines, fluorocarbons etc.

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Chain length and functional groups will determine flux behaviour and selectivity

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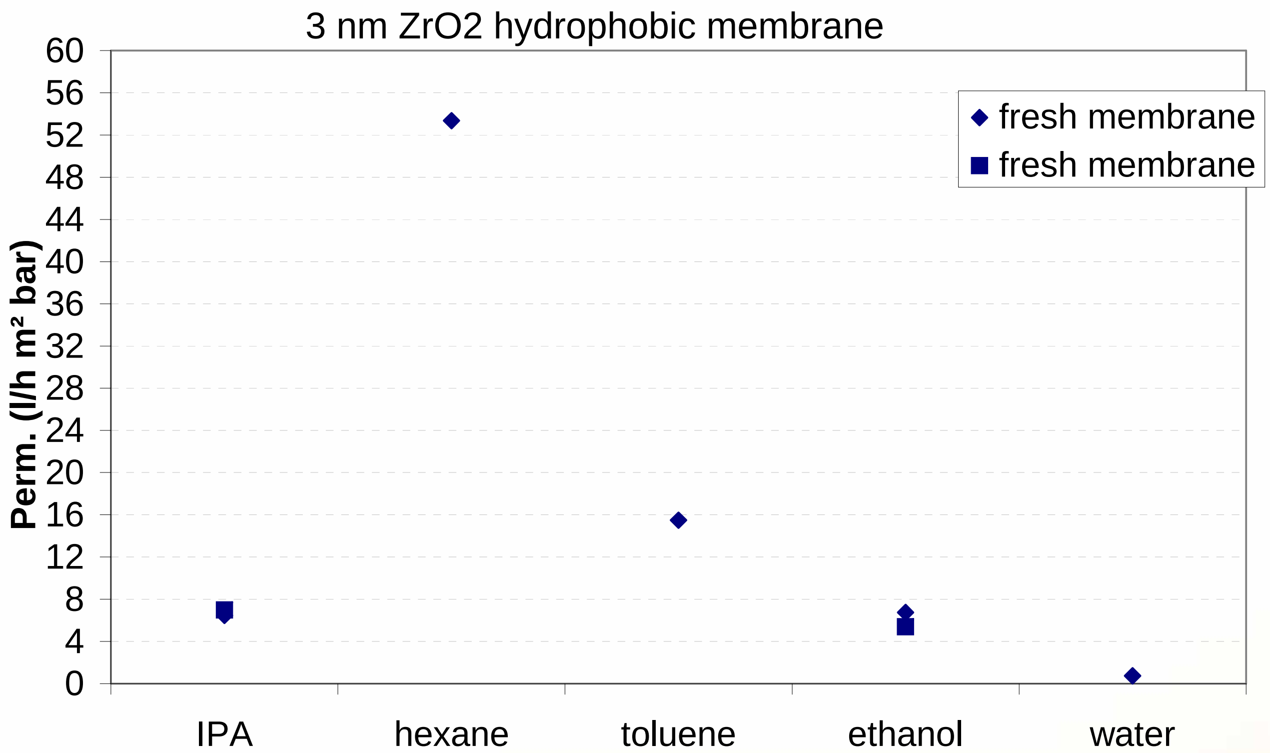
Flux behaviour organosilane modified hydrophobic membrane



Perfectly hydrophobic behaviour

High fluxes for hexane
Low fluxes for water

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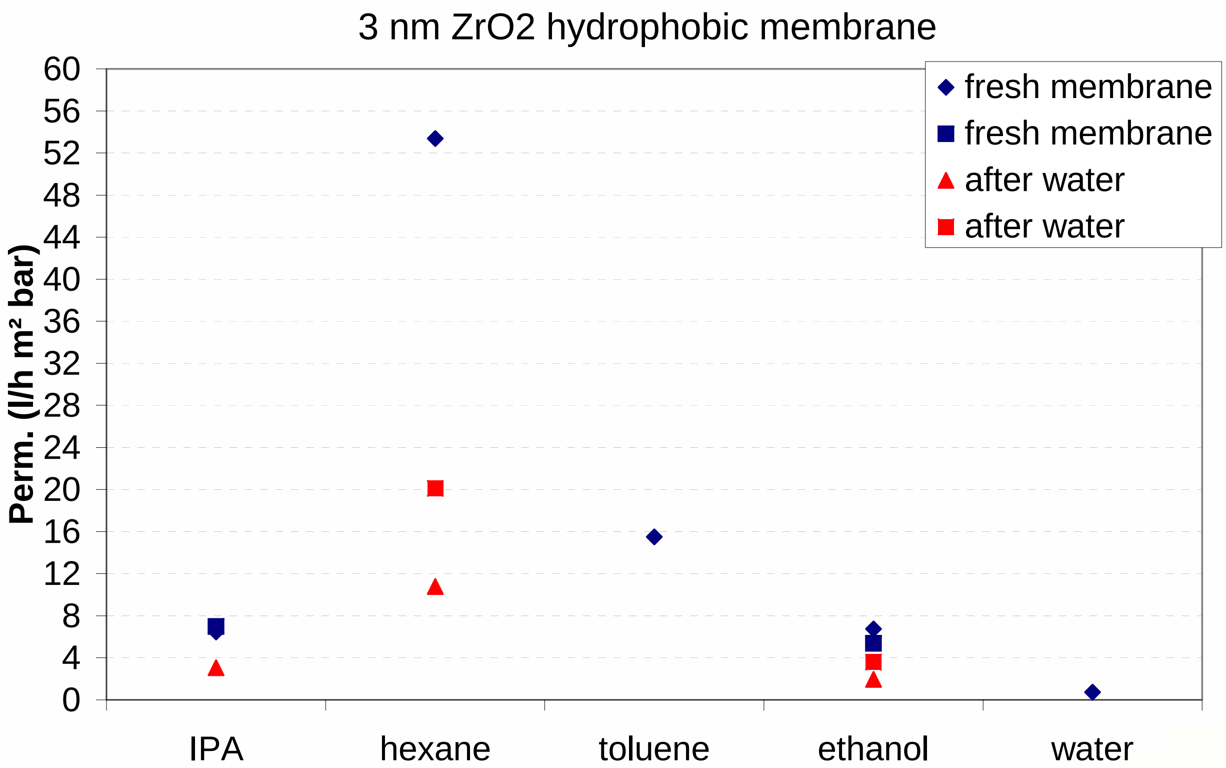
Flux behaviour organosilane modified hydrophobic membrane



Fluxbehaviour changes after measurement with water

Hexane flux
Ethanol flux } Decreases proportional to their apolarity

Contact angles decrease

Stability of the modification?

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Methods and characterisation

1) Synthesis of flakes representative for the top layers of the membranes

2) Modification of the flakes with attention for different parameters (liquid phase):

- Type of organosilane
- Pre-treatment of the flakes
- Reaction time
- Reaction atmosphere
- Curing
- …

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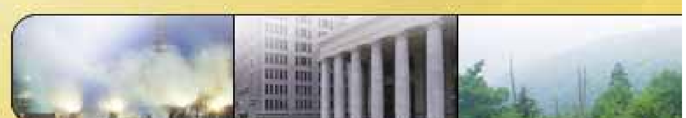
3) Characterisation of the obtained organic-inorganic hybrid materials

- DRIFT, PAS, Raman
- XRD
- TGA
- N_2-sortpion
- ……..

4) Testing of the stability of the material in different solvents and temperature



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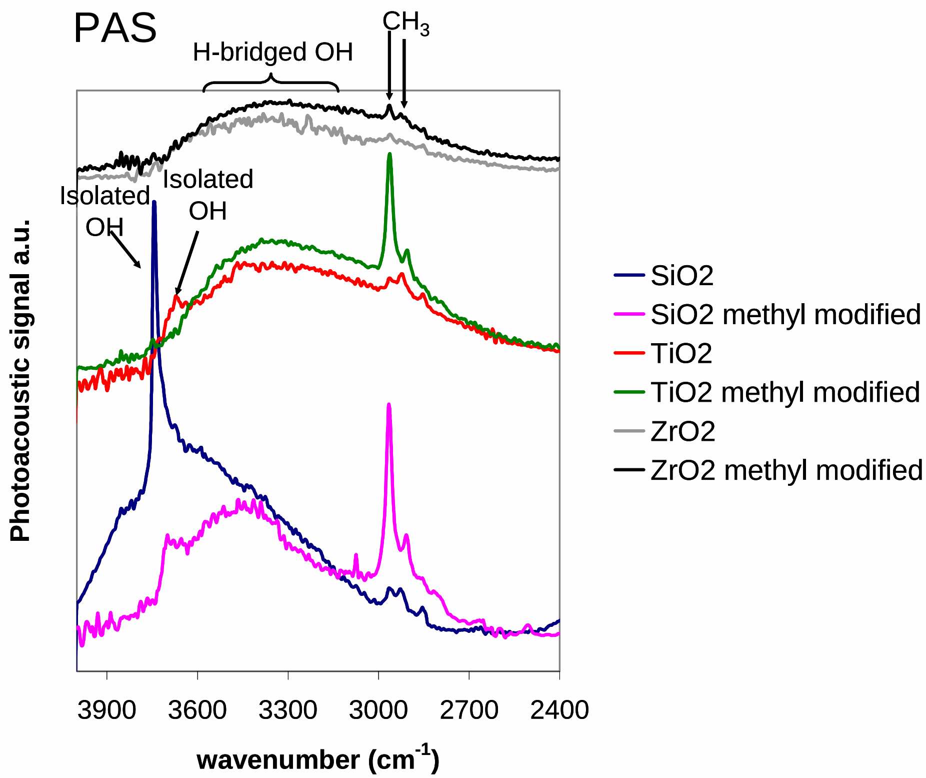
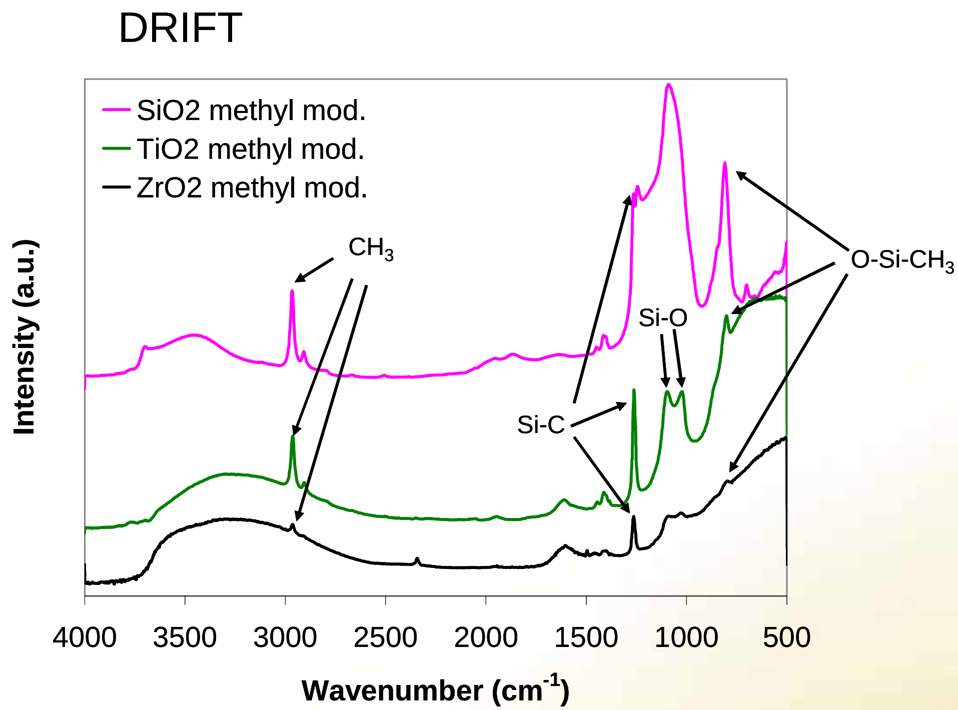
Organosilane modification on different metal oxides





		C-value
SiO_2		97
SiO_2	dichlorodimethyl modified	43
TiO_2		70
TiO_2	dichlorodimethyl modified	19
ZrO_2		63
ZrO_2	dichlorodimethyl modified	24

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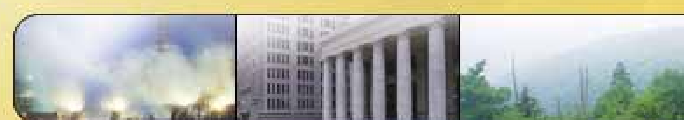

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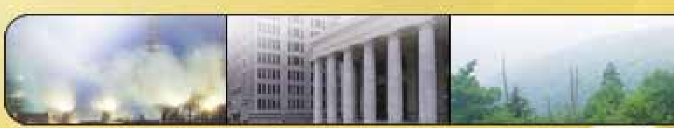
Organosilane modification on different metal oxides

- Decrease in OH after modification
- amount of isolated OH is very important for the degree of modification
- Number of functional groups strongly depends on the OH number
- Strongly hydrophobic in all cases

Degree of surface modification strongly depends on the surface properties of the metal oxide

→ Why decreasing fluxes? Stability?



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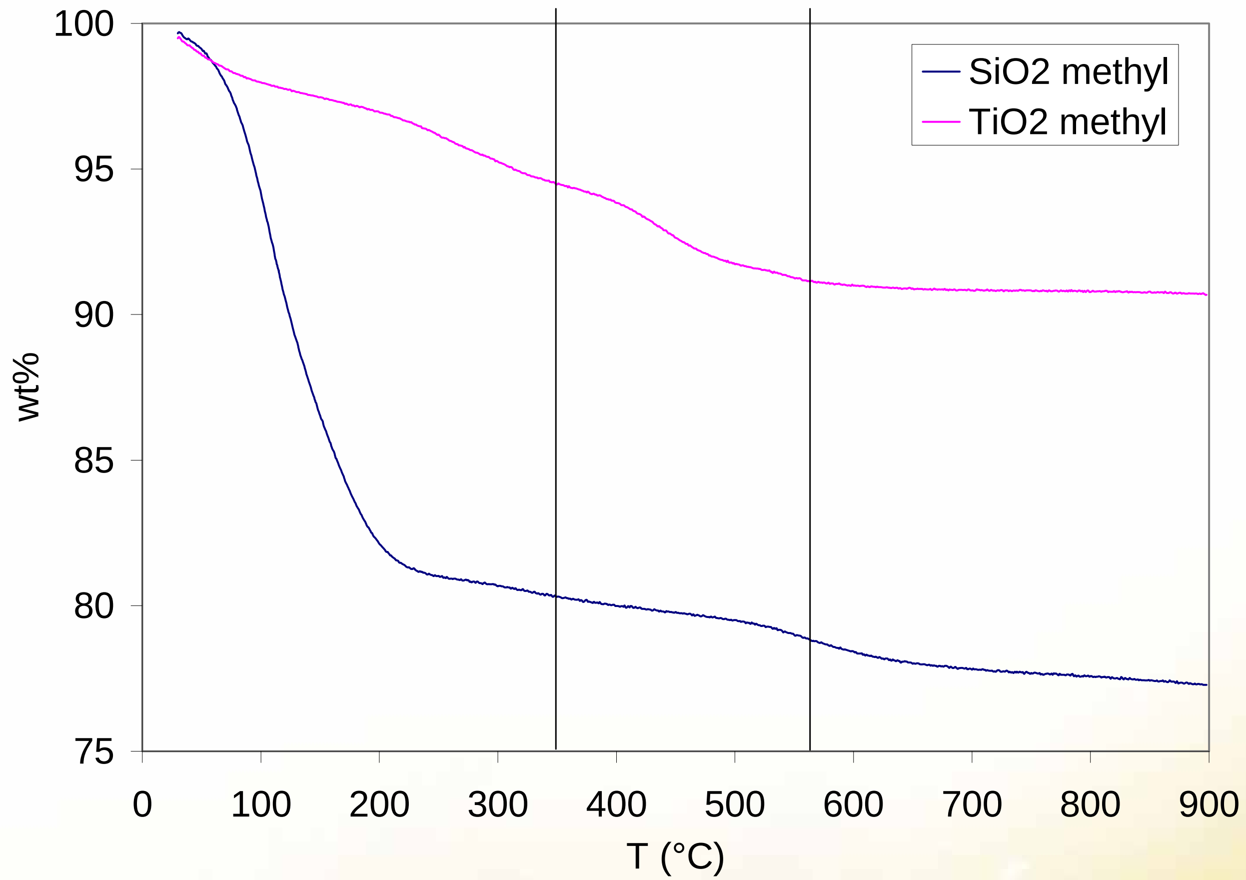
Results and discussion



TiO_2-O-Si-C bonds are much less stable compared to SiO_2-O-Si-C bonds

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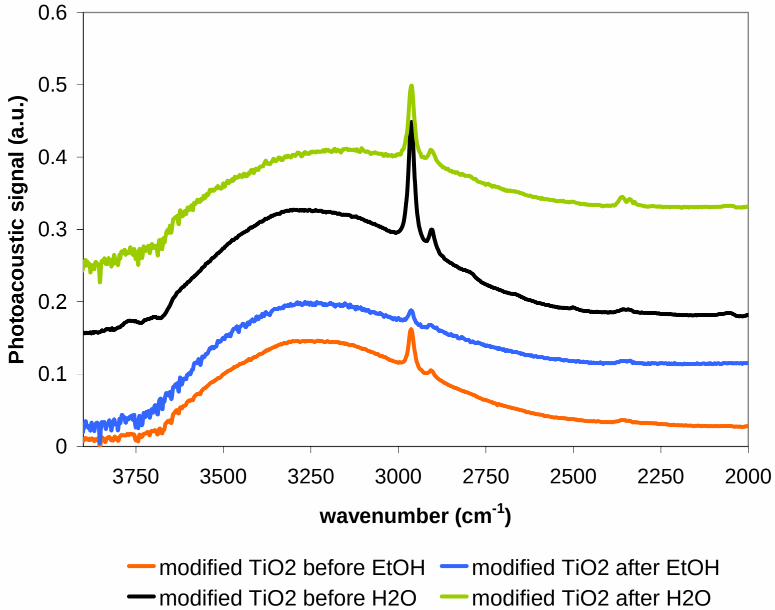
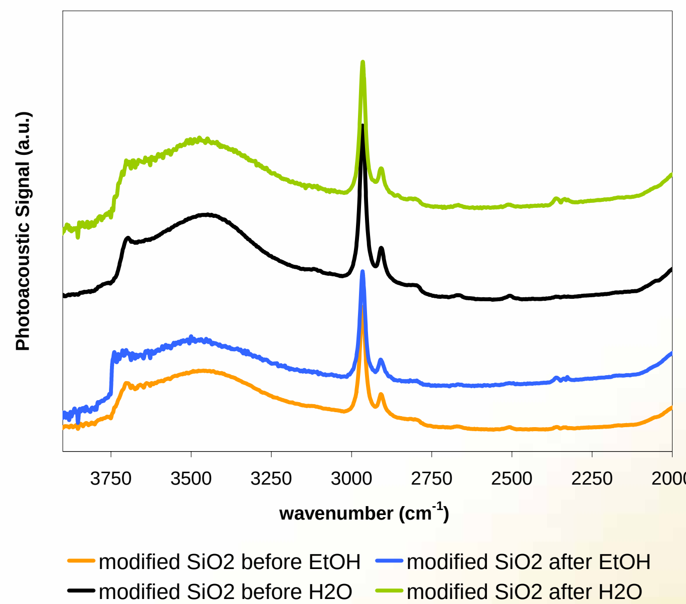
Results and discussion

TiO_2



SiO_2



TiO_2-O-Si-C bonds are much less stable compared to SiO_2-O-Si-C bonds

Bond breaking due to weaker bondings can explain decreasing, instable fluxes

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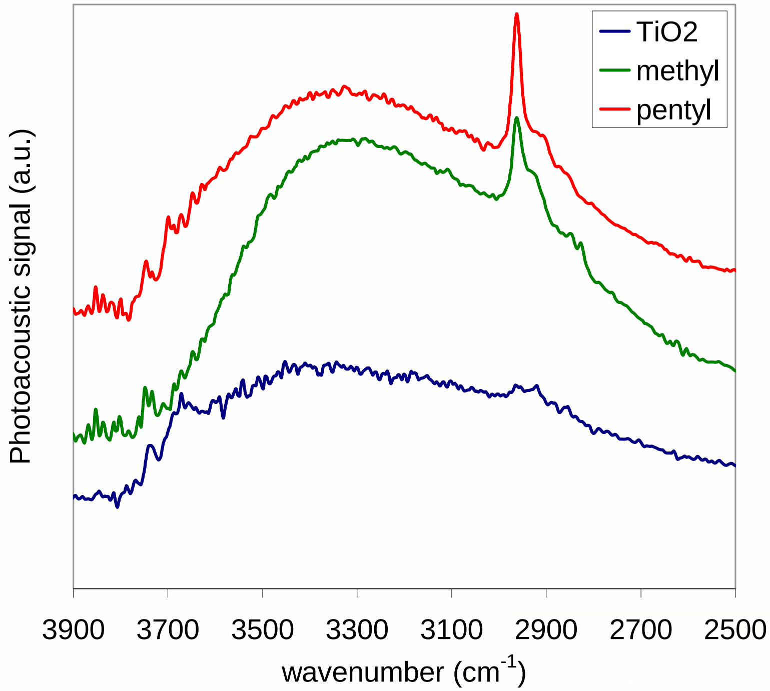
Alternative hydrophobisation method

Modification of TiO_2 flakes



	porediameter (nm)	C value
TiO_2	5.6	70
TiO_2 (methyl-organosilane)	5	19
TiO_2	5.6	58
TiO_2 (methyl)	5	22
TiO_2	6.5	53
TiO_2 (penthyl)	5.5	6.2

Similar hydrophobicity (C values decrease to strongly)
Different chain lengths and functional groups possible

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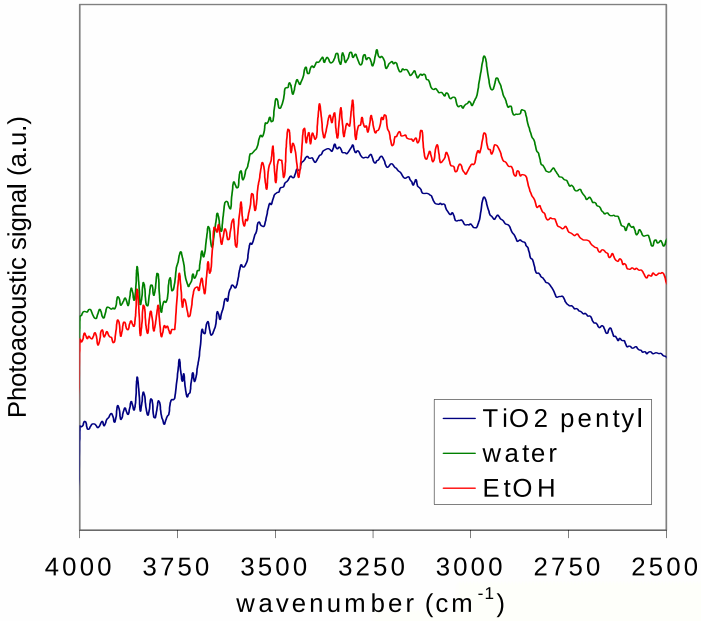
Alternative hydrophobisation method

PAS on flakes



Flux behaviour of the modified membrane

	cut off
hydrophilic TiO2	5880
hydropobic TiO2 (pentyl)	4535

Solvent	Flux (l/h m²) [5 bar]
Water	260
Ethanol	125
Hexane	350

TGA, IR, Flux indicate a good stability of the modification

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Conclusions

Organosilane modification

- Modification depends on the OH-number
- Number of functional groups strongly depends on the metal oxide
- Different chain lengths and organic groups possible
- Physical and chemical bonded groups

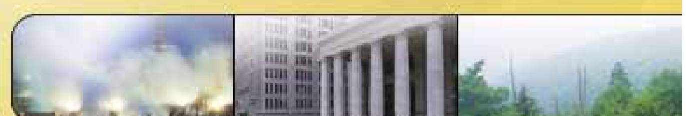
→ Instability of the organosilane layer towards water and alcohol

Weak TiO_2-O-Si-C bonds compared to SiO_2-O-Si-C

Alternative modification

- Different chain lengths and organic groups possible
- Similar characteristics after modification compared to organosilane

→ Stable modification layer towards water and alcohol



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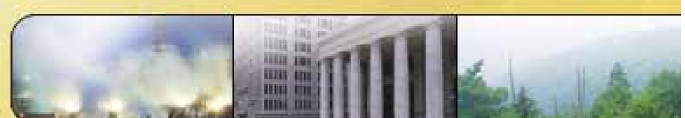
Future

Organosilane modification

- In depth study on instability (mechanism of bond breaking)
- Increasing stability of the organosilane layer
- Flux behaviour

Alternative method

- Optimalisation of the modification (deposited amount, mixed functional groups and chain lengths, surface charcteristics, important parameters, ….)
- Transfer of the method on various membranes (TiO_2, ZrO_2, ….)
- Study on the long term stability
- Flux behaviour



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Acknowledgements

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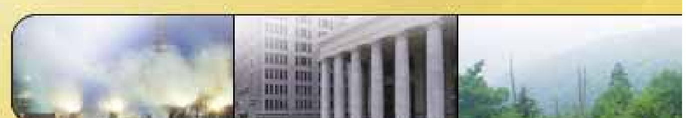
You for your attention!



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