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Advances in PMO (Periodic Mesoporous Organosilica) and OMP (Ordered Mesoporous Polymers)

A new generation of catalytic supports

i-SUP – BRUGGE - 2008

Prof. dr. P. Van Der Voort
COMOC – University of Ghent

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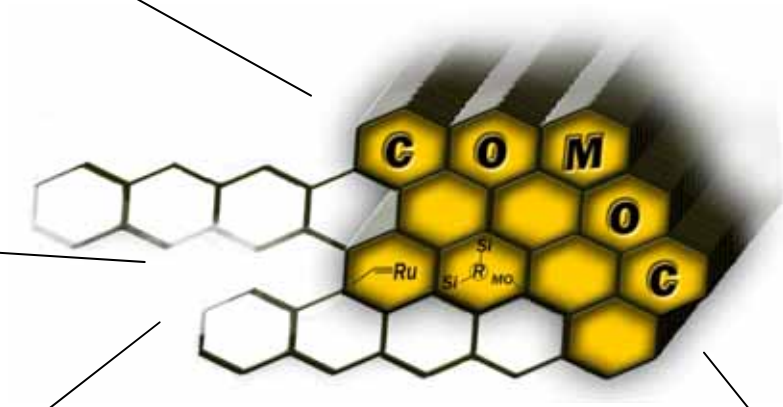
Activities overview

Hybrid nanoporous materials for the selective removal of heavy metals from aqueous solutions.

Thin mesoporous organosilica films for low-k applications (micro-electronics).

New packing materials for HPLC chromatography.



Ordered mesoporous phenol/formal-dehyde polymers as a ‘zero-leaching’ support material heterogeneous catalysts.

OMP

Development of PMOs with controllable properties as catalytic supports -- boomerang catalysts (metathesis); acid catalysts (biodiesel) PMO

Introduction

- Support Materials for heterogeneous catalysis
  - Silanol not always the best anchoring group
  - Dangling groups → effects on stability and porosity
  - PMO Materials as an alternative

  - Silica materials have weak interactions with some metal oxides (leaching)
  - Silica materials are often structurally unstable in aqueous or liquid media
  - OMP Materials as an alternative

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PMO

Carl Vercaemst

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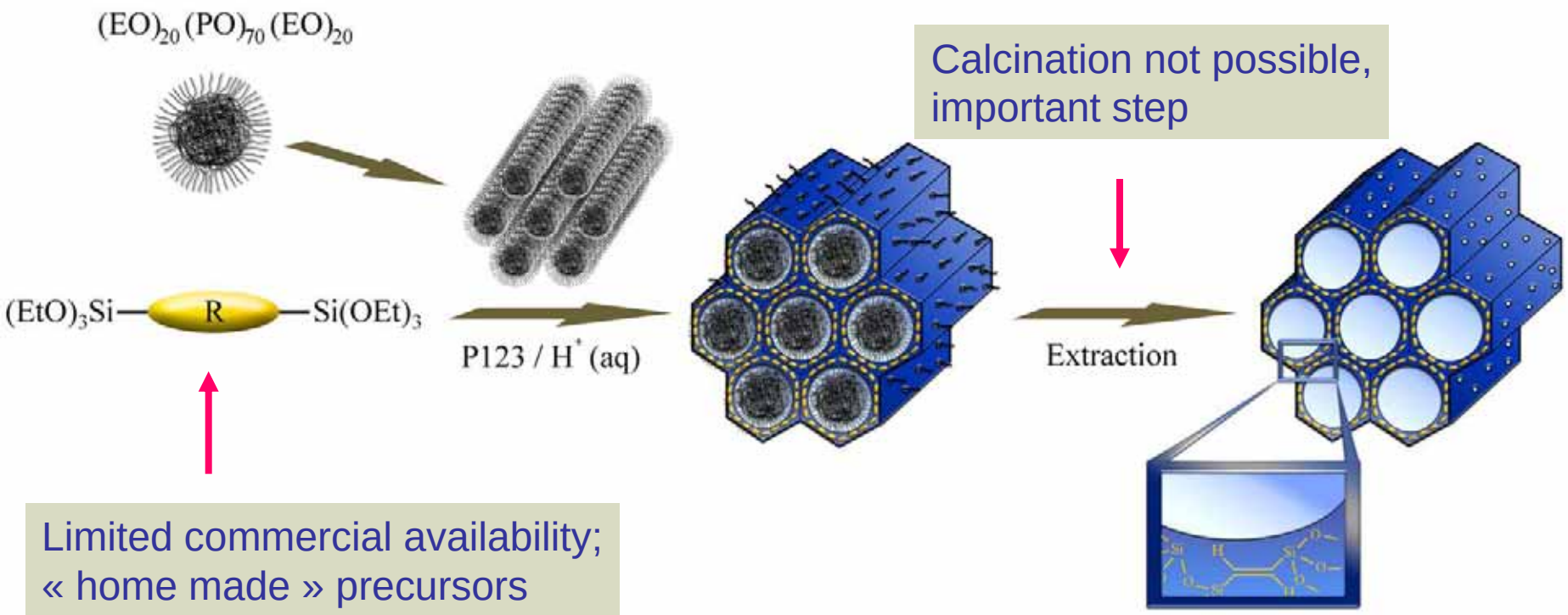
PMO -- What is a PMO ?



Calcination not possible, important step

Limited commercial availability; « home made » precursors

Functional groups in ENTIRE WALL

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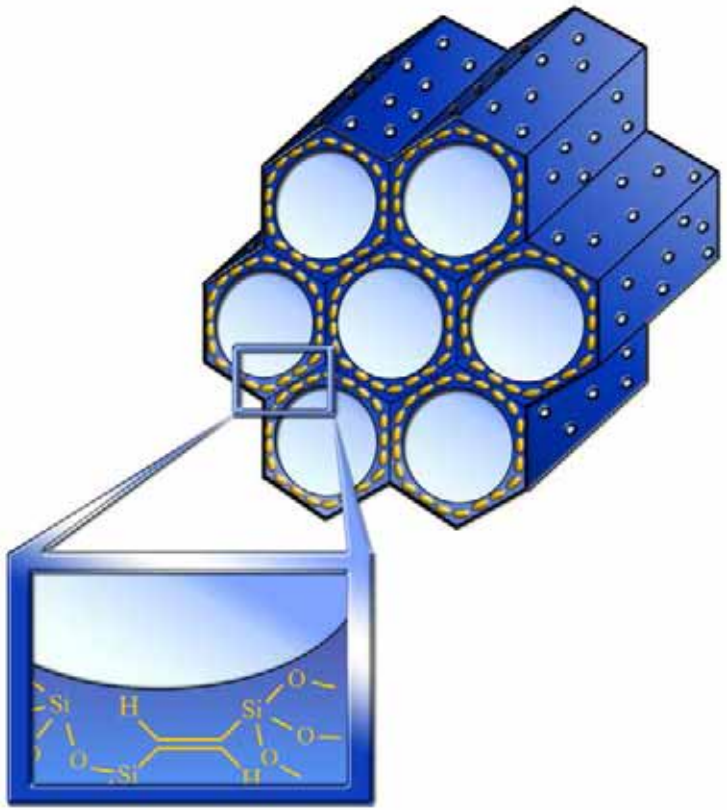
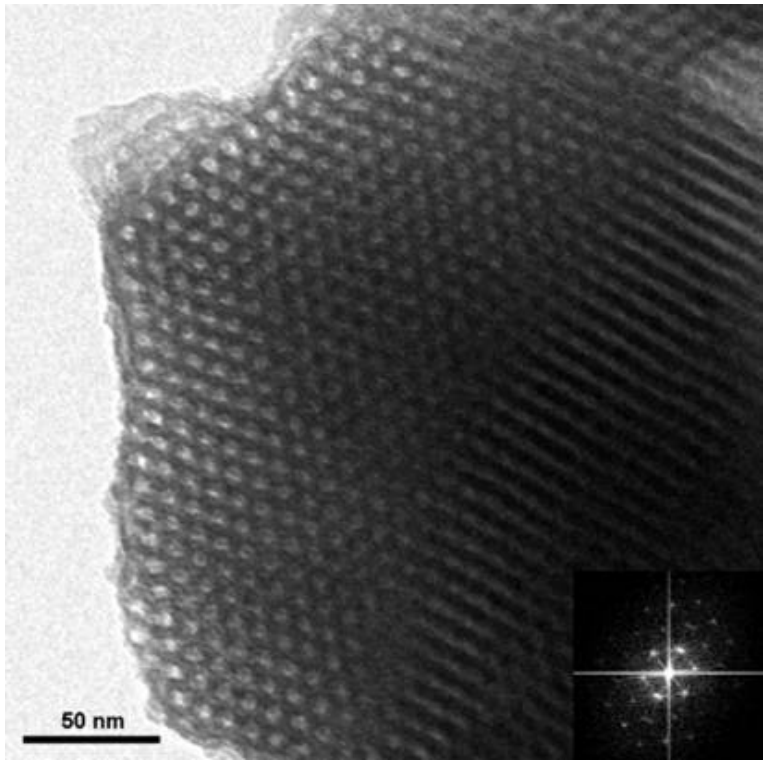
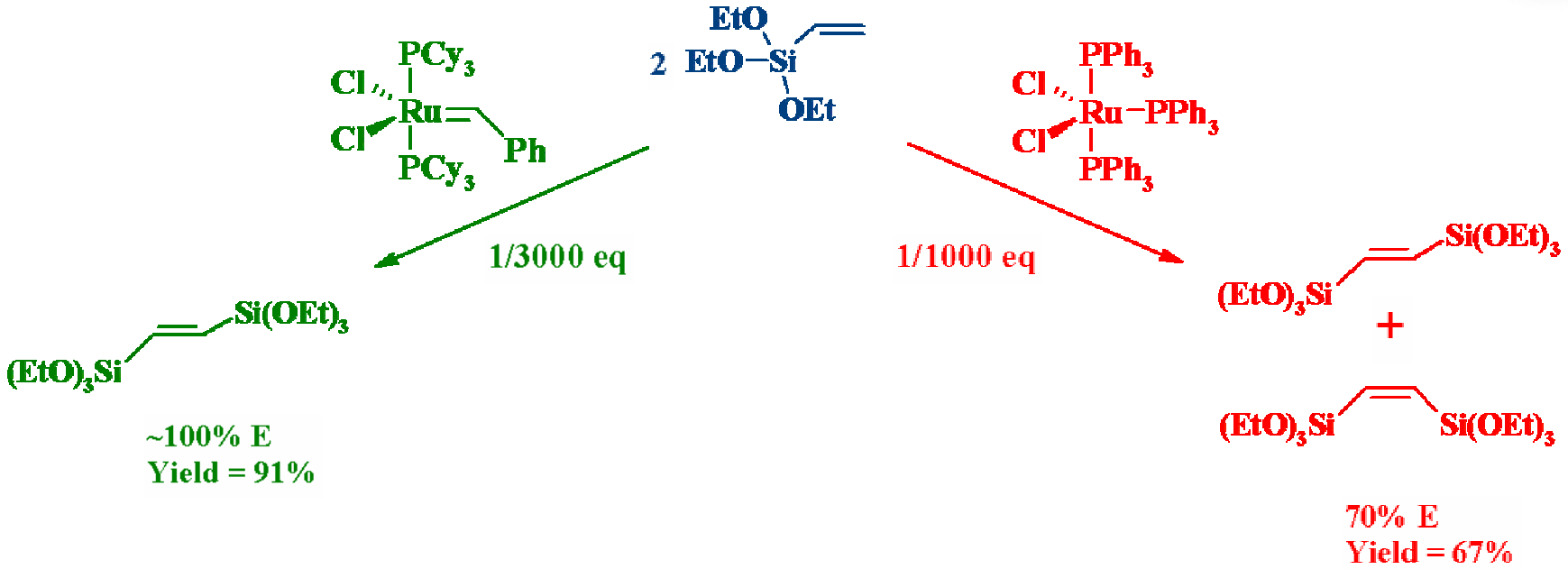
PMO -- Ethene PMO





I Synthesis of diastereoisomeric pure precursor via a cross metathesis reaction:



Carl Vercaemst et al., *Chem. Commun.*, 2007, 2261

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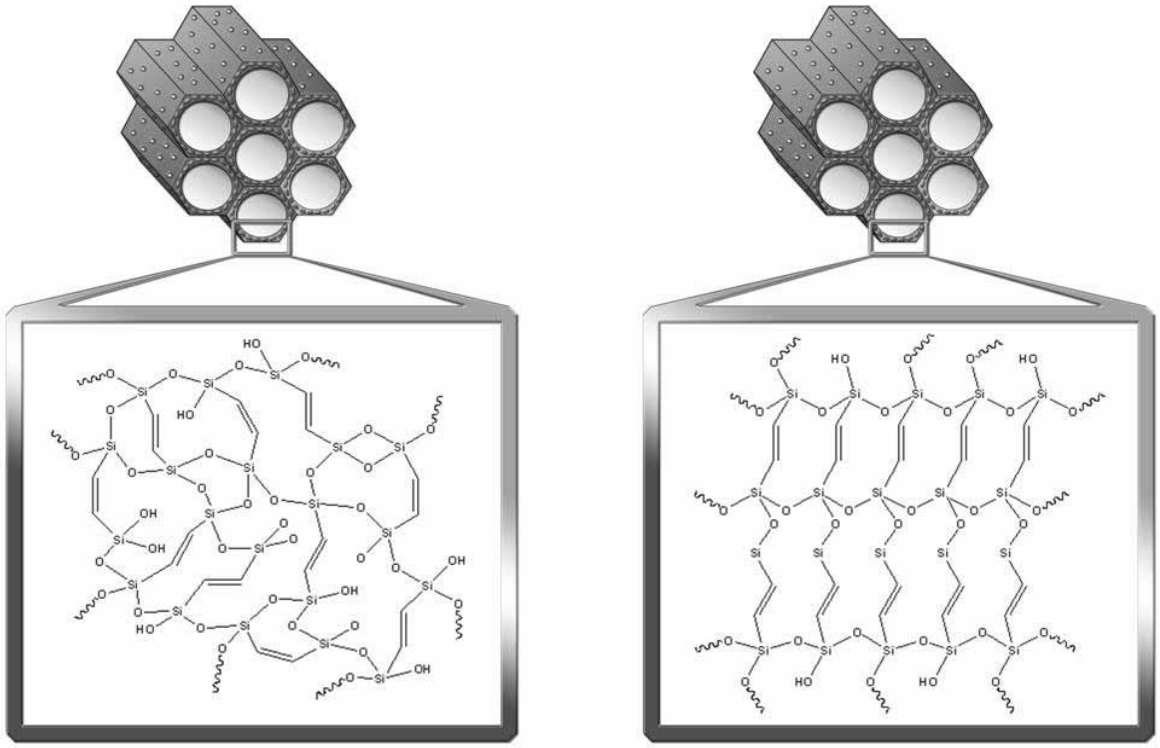
Influence diastereoisomeric purity on PMO properties



(*E*,*Z*)-PMO

E-PMO

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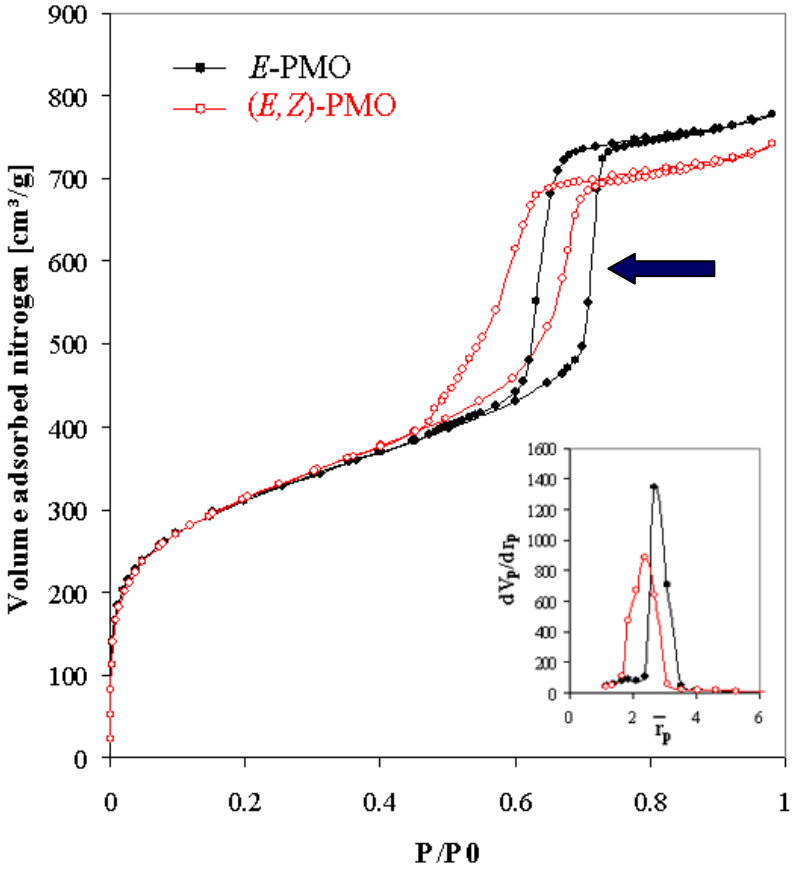
Nitrogen physisorption



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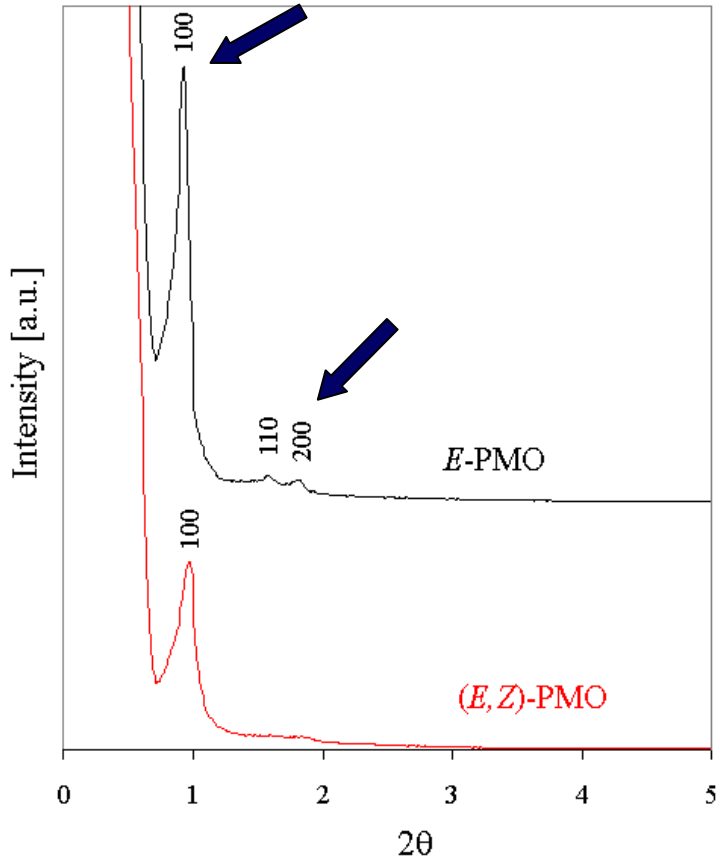
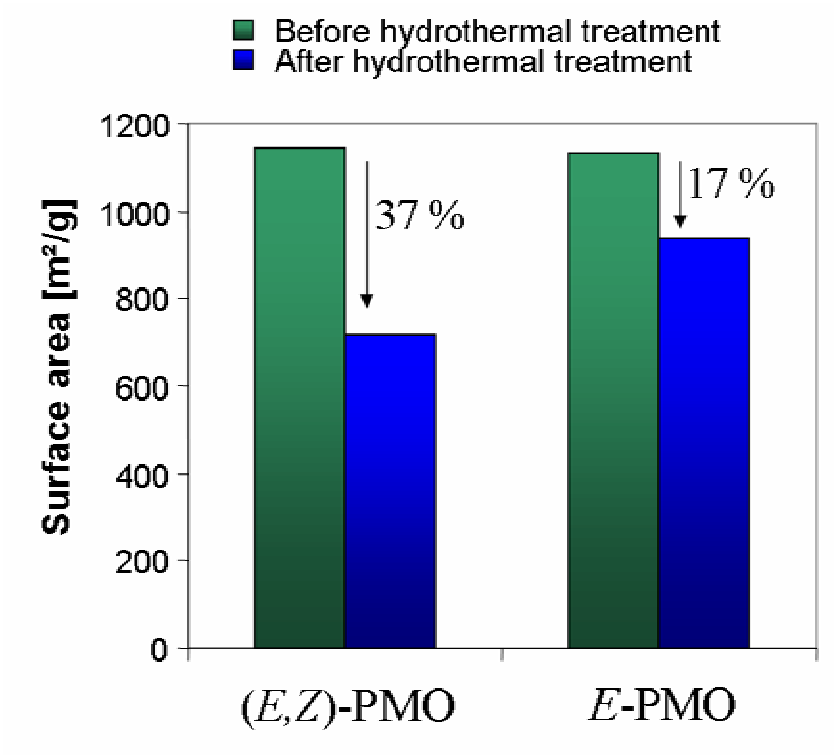
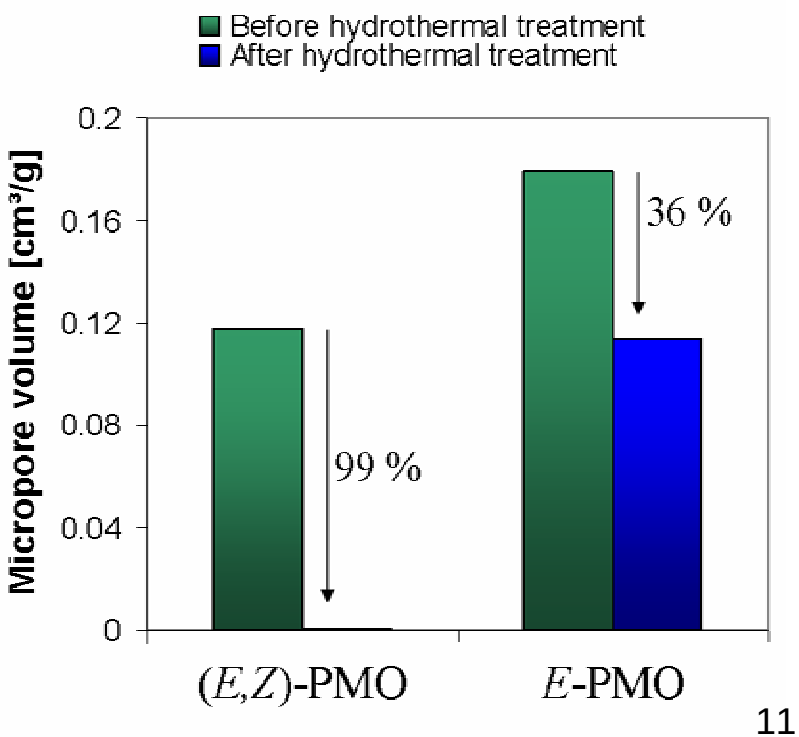
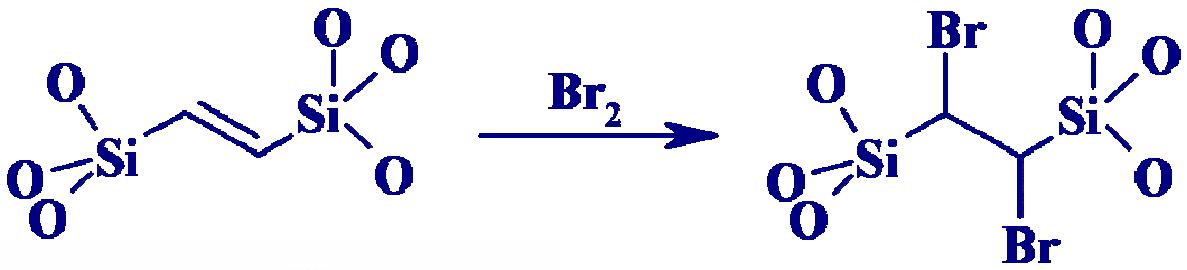
XRD

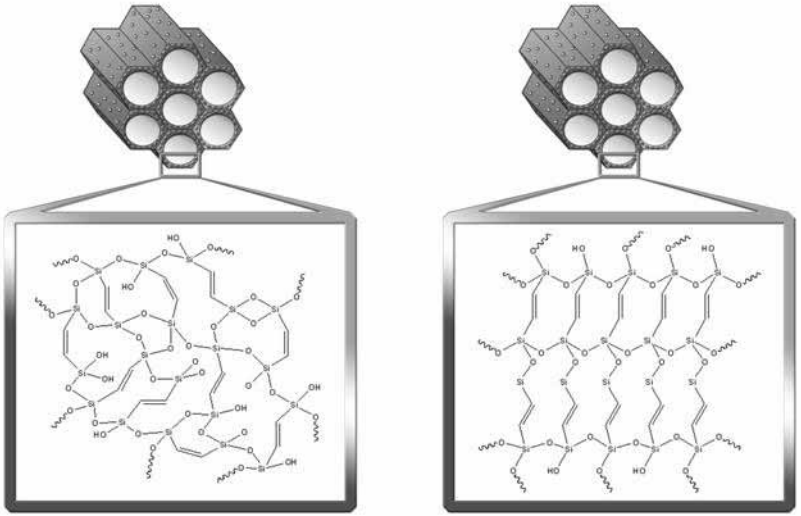


- Autoclave
- Steamed for 24 h
- Autogenous pressure





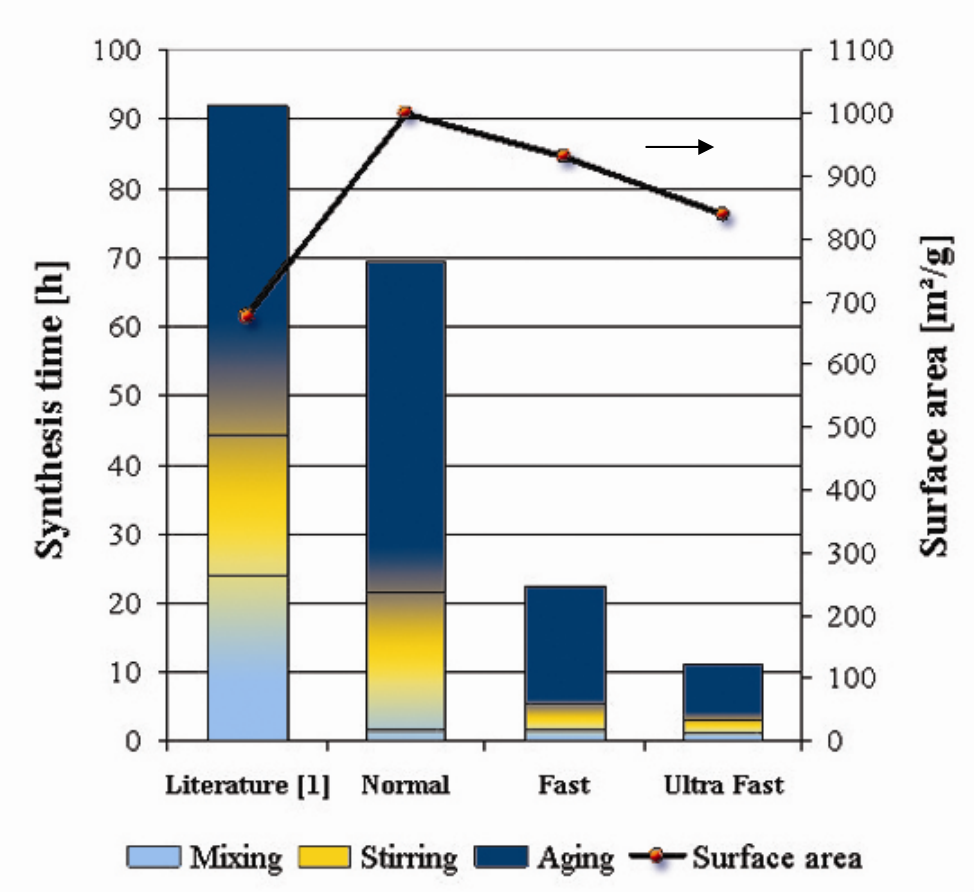




Accessibility ↑
Δ 31 %

1.9 C=C per nm² brominated
(app. 30% of total C=C in structure)

II Ultra-fast synthesis of ethene-PMOs with exceptional properties



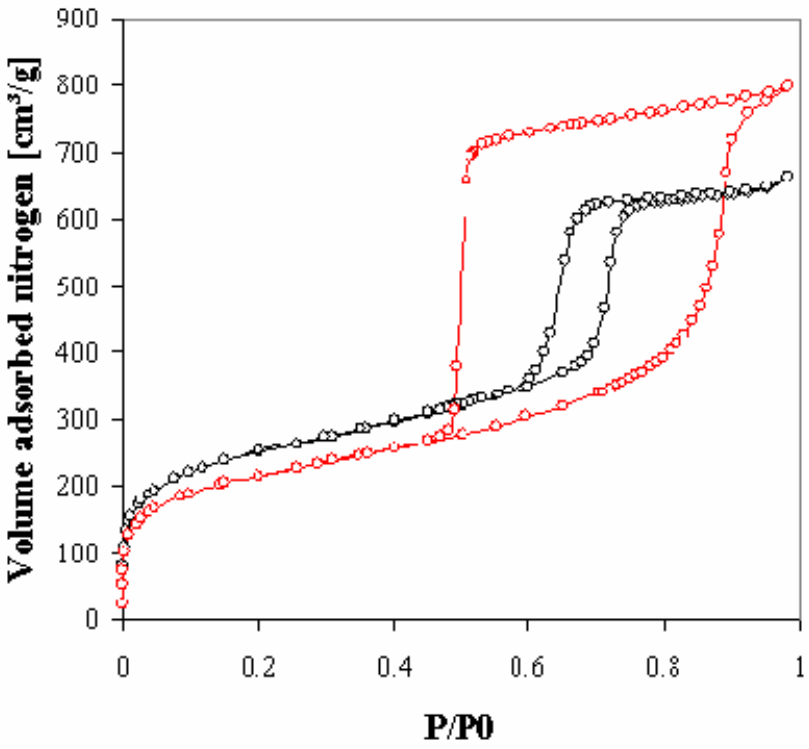
- Pure precursor
- Optimized reaction conditions:
  - pH
  - Additives
- Improved extraction

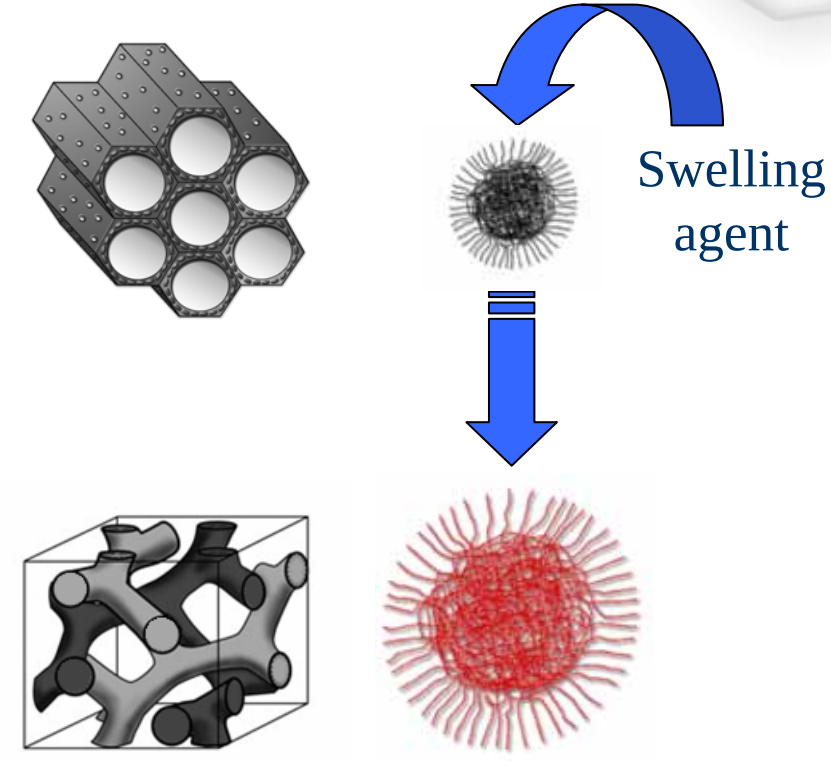
Carl Vercaemst et al., *Chem. Commun.*, 2007, 2261

Controlling the material properties

I Pore size and pore structure engineering

N_2-Physisorption





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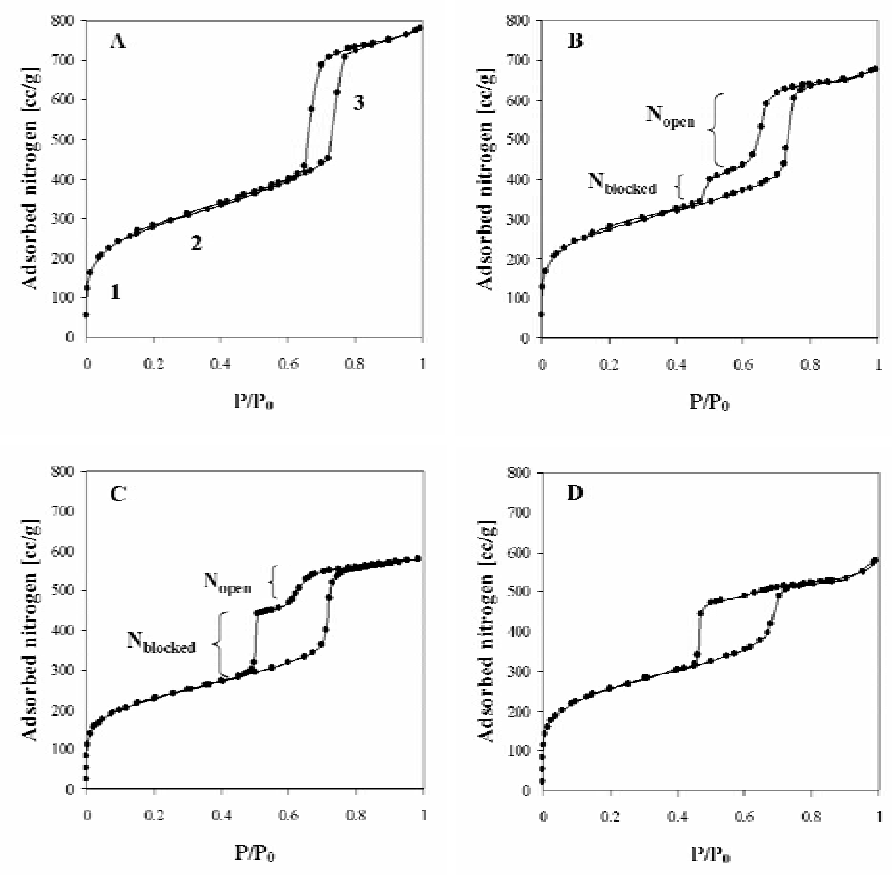
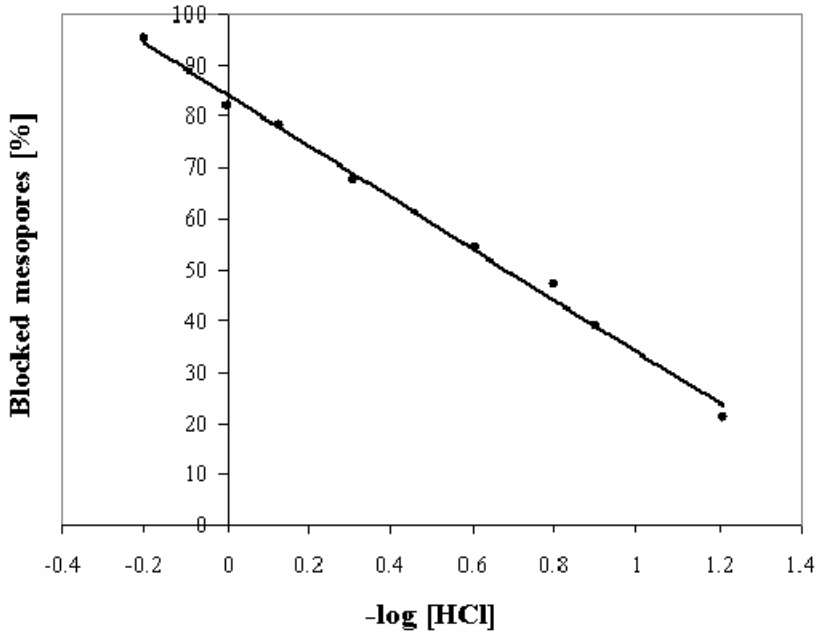
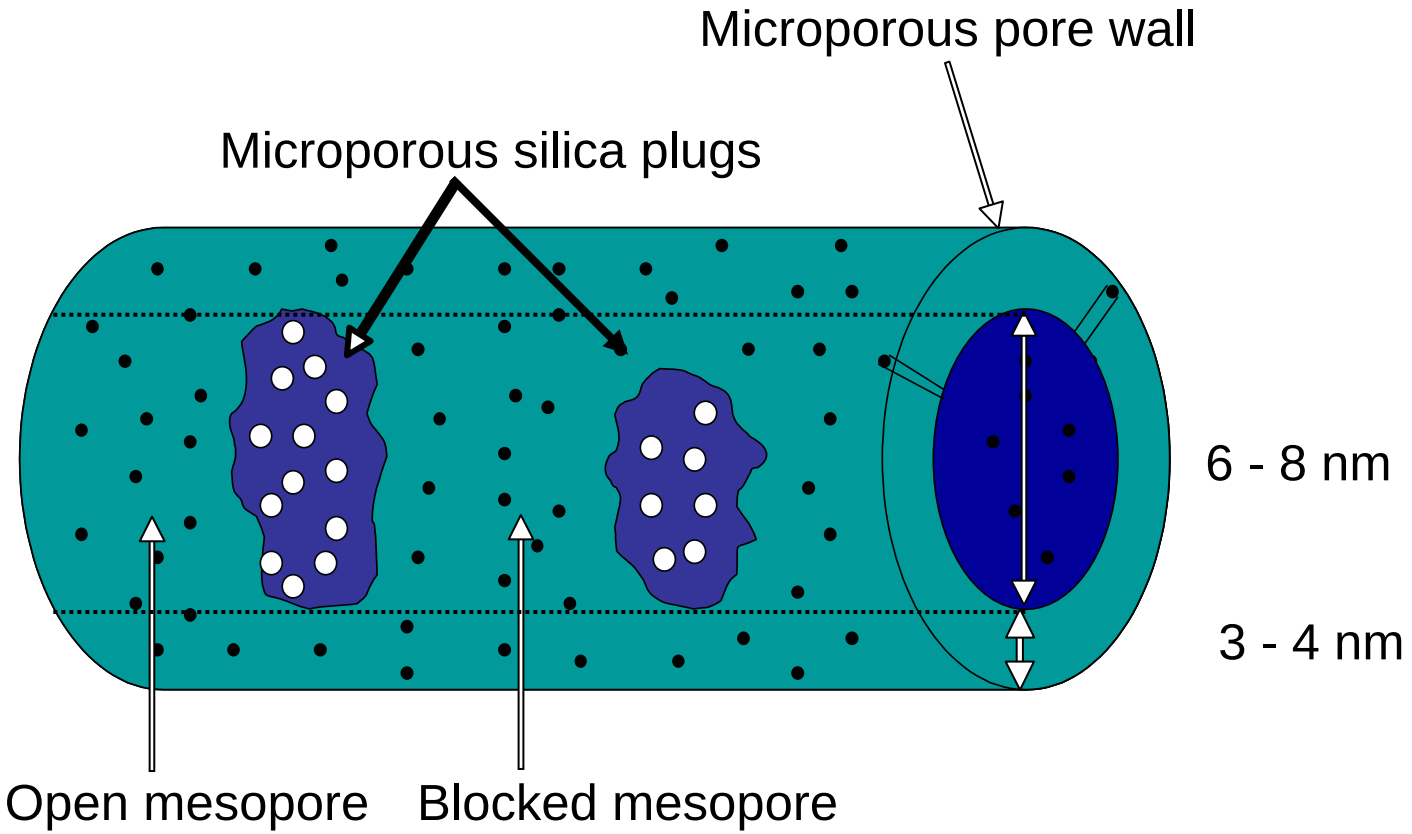
II Controlling the pore channel length and pore connectivity

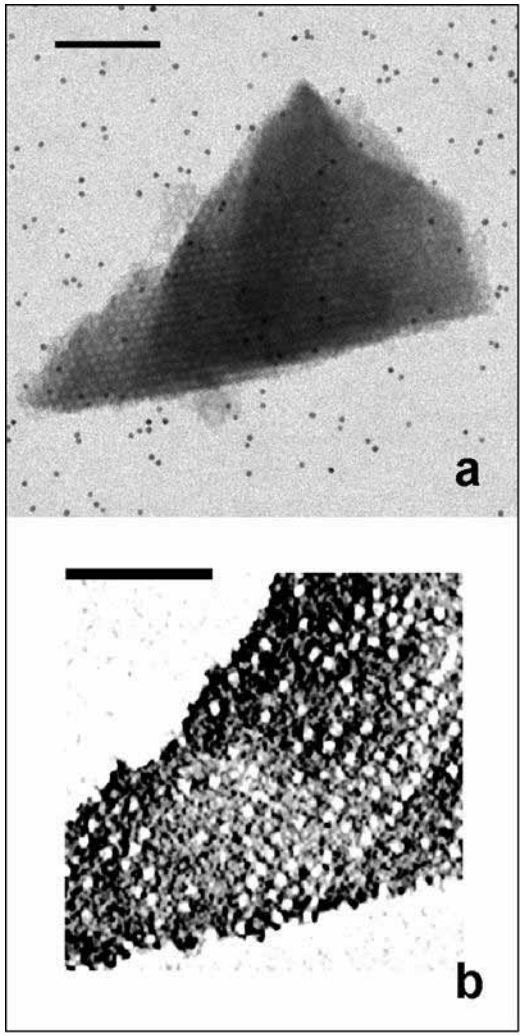


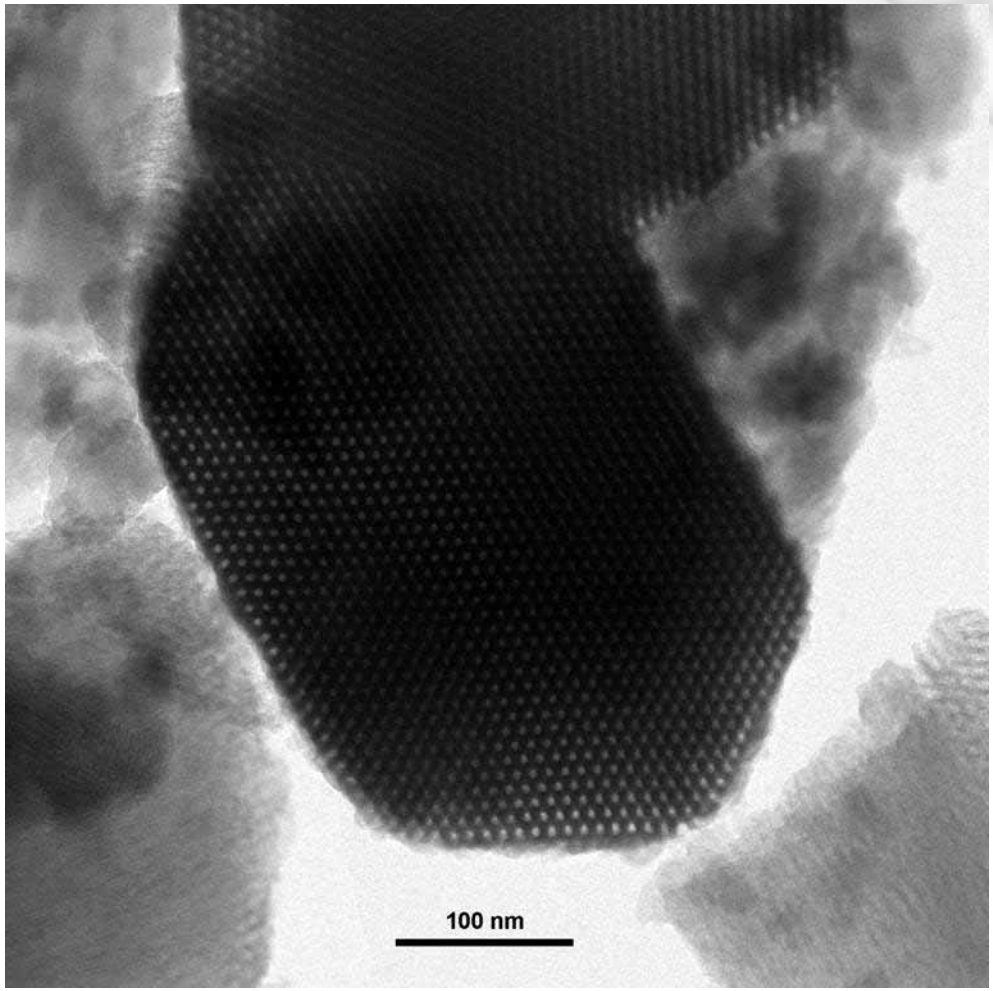


Strong Analogy with PHTS materials…. although…



P. Van Der Voort et al. Journal of Physical Chemistry B, *2002*, **106 (23)**, 5873-5877.


a
b


100 nm

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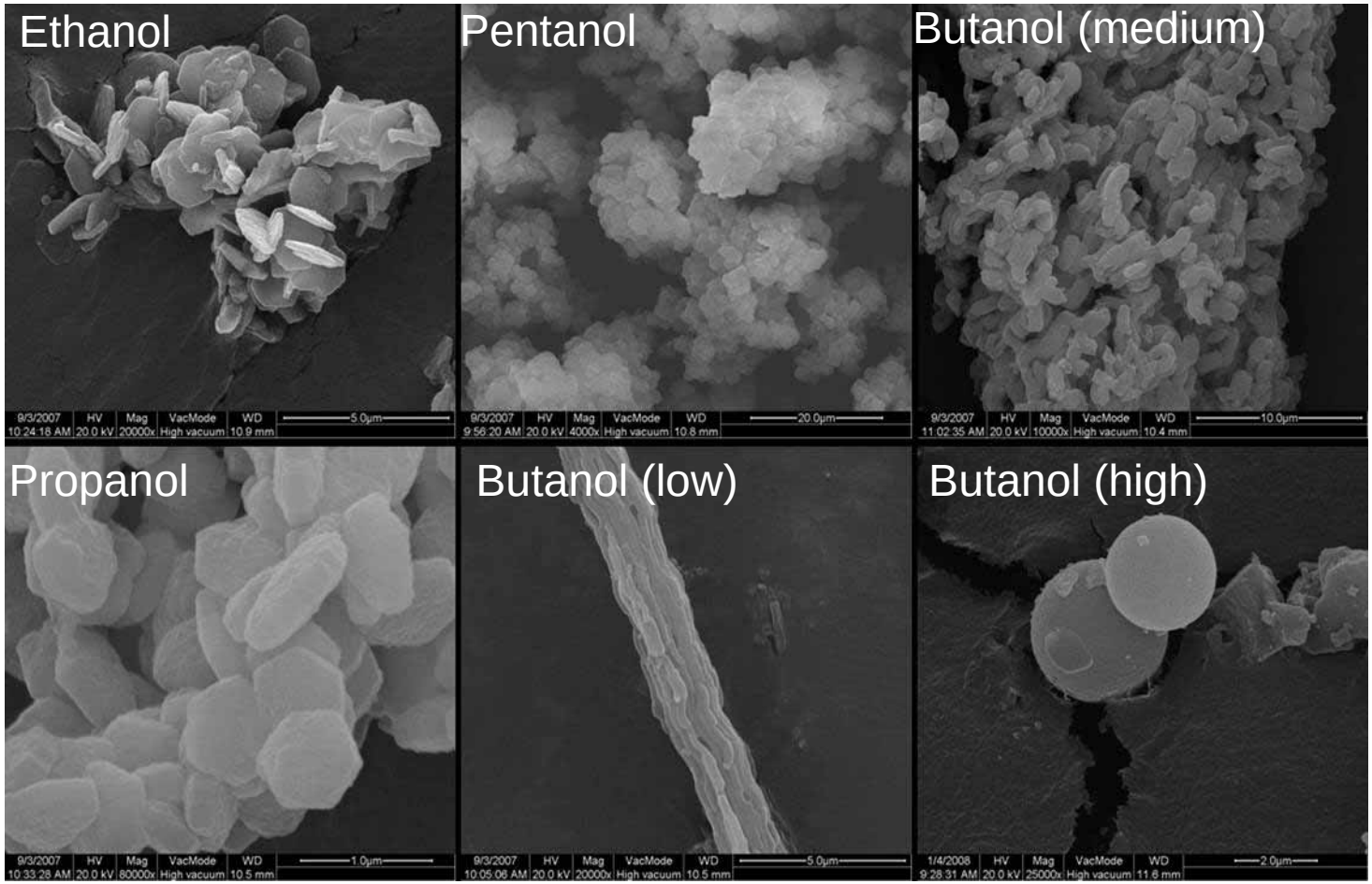
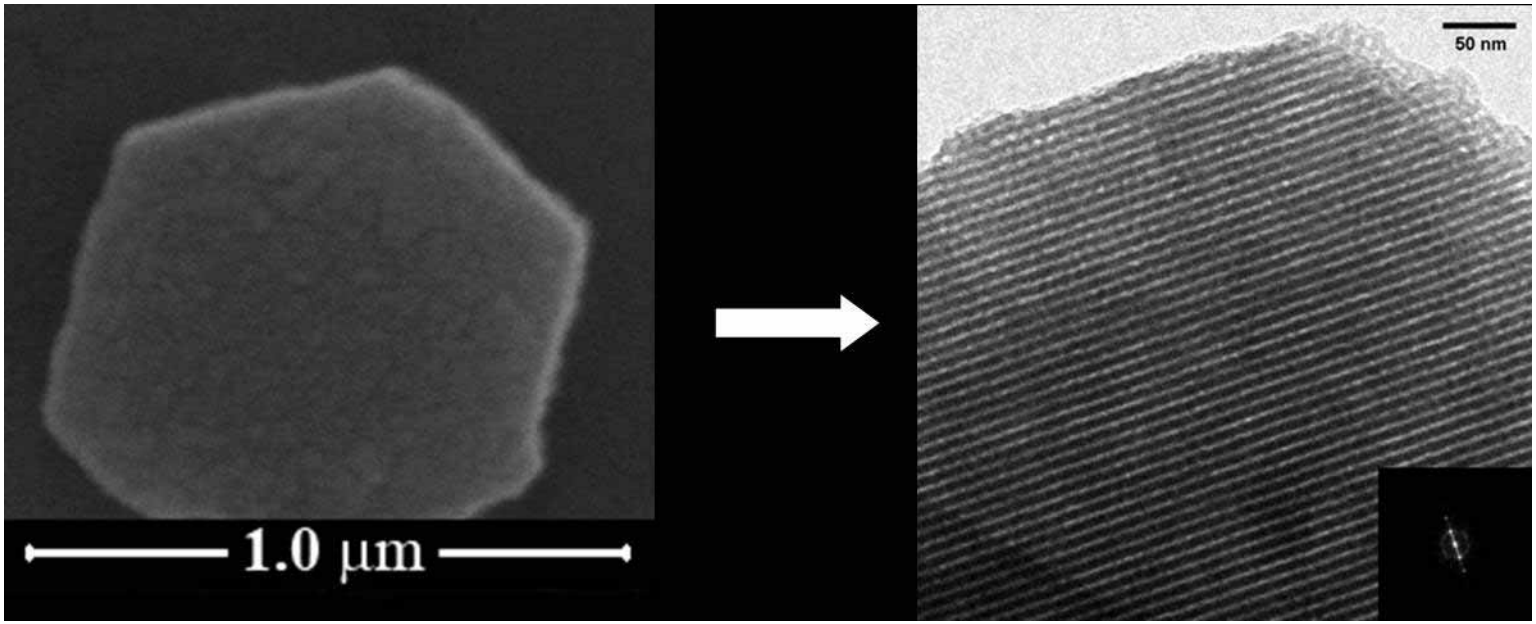
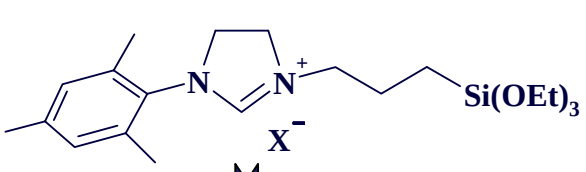
III Controlling the morphology



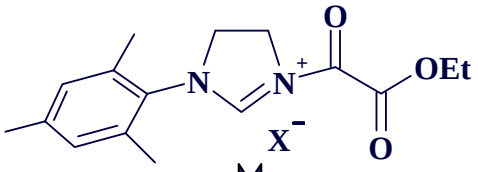

1.0 µm
50 nm

Prospects

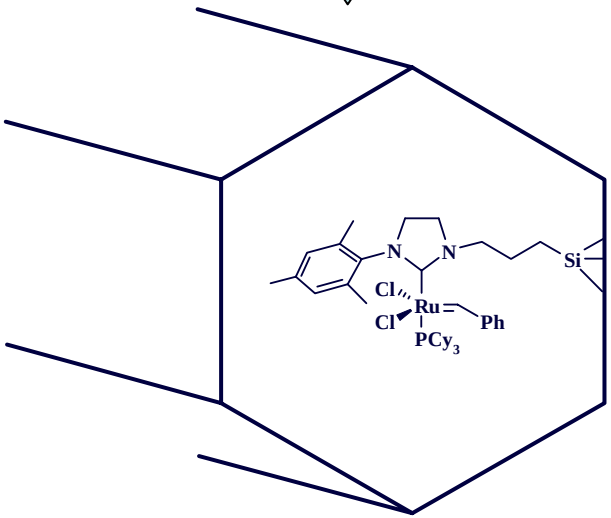
Permanently immobilized catalysts

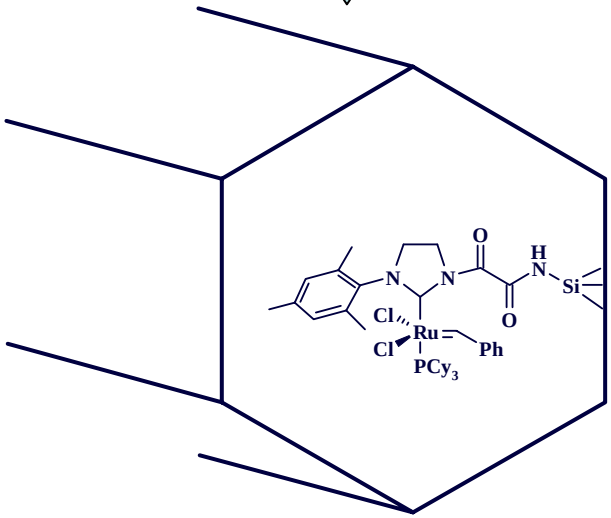


Cocondensation with PMO-precursor

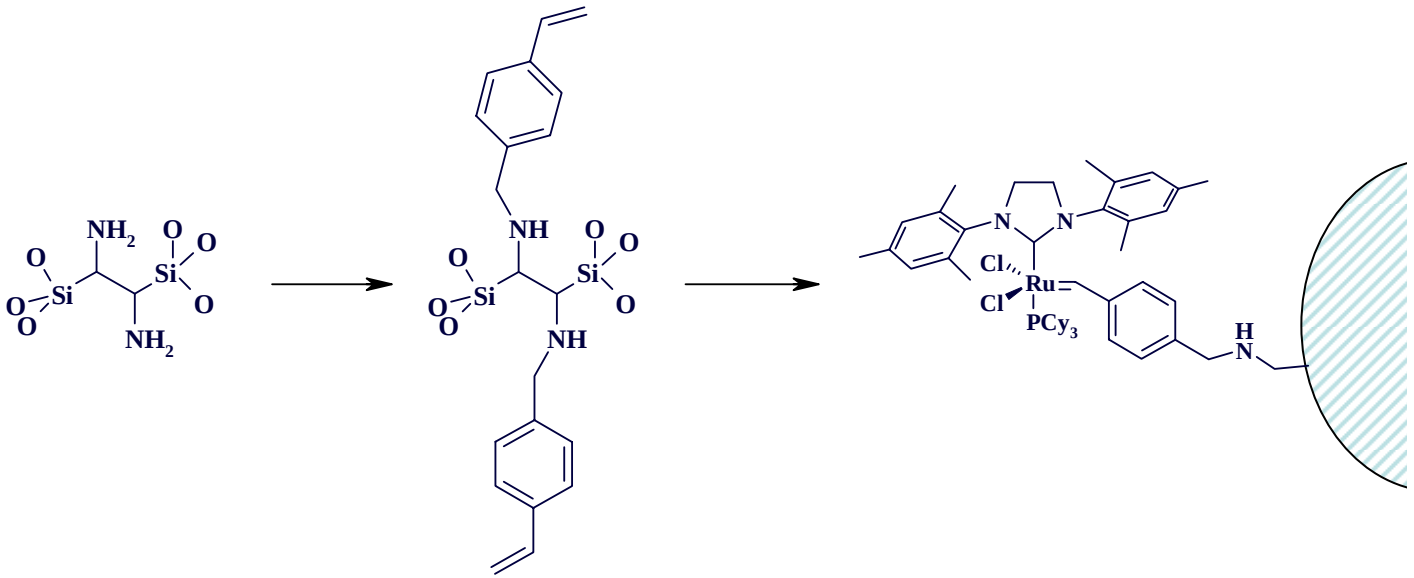


Addition to modified PMO

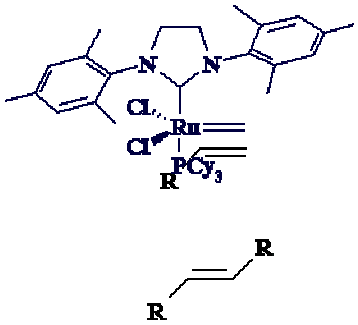


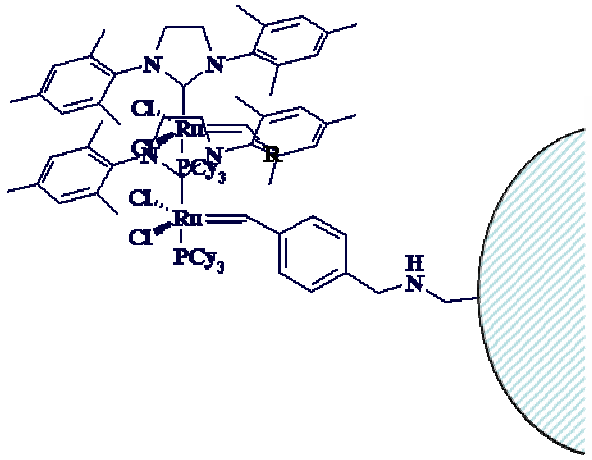


Boomerang catalysts



Boomerang catalysts





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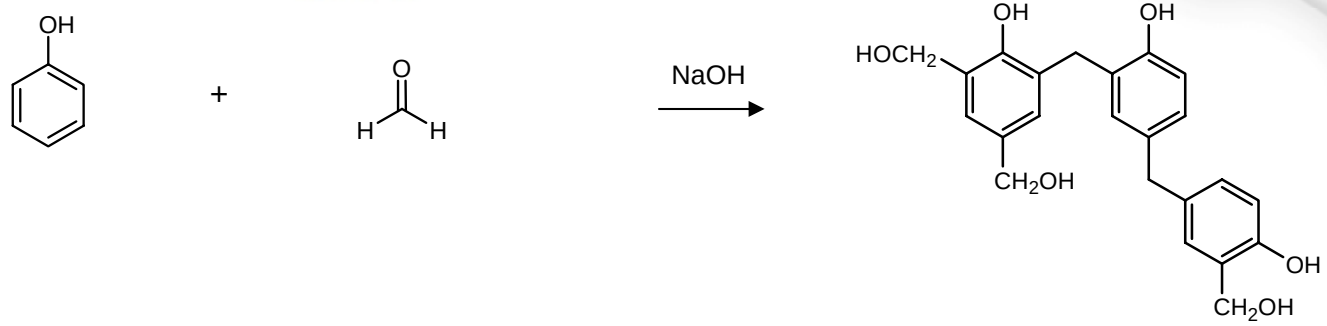
OMP

Ilke Muylaert

Synthesis



Zhao *et al.*, Angew. Chem. Int. Ed. *44* **(2005)** 7053

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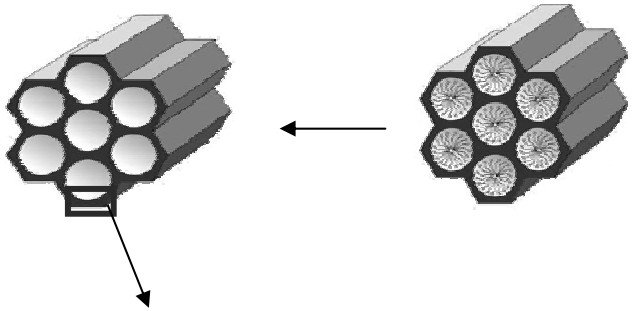
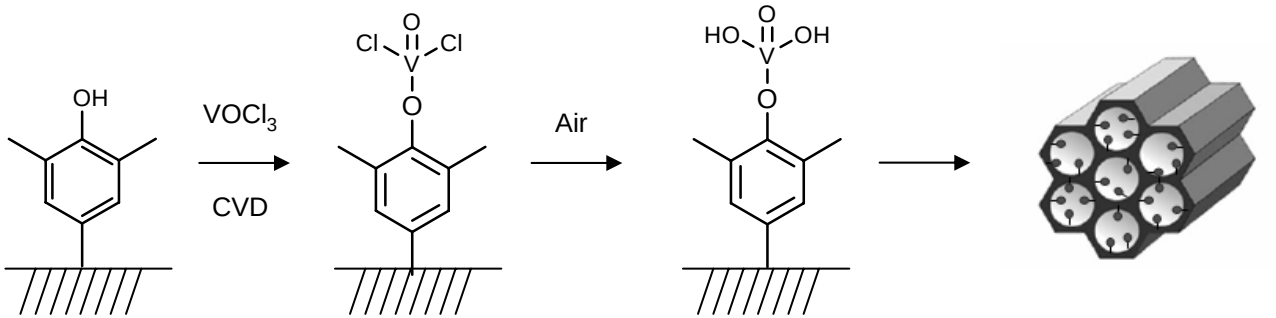


1/ EISA

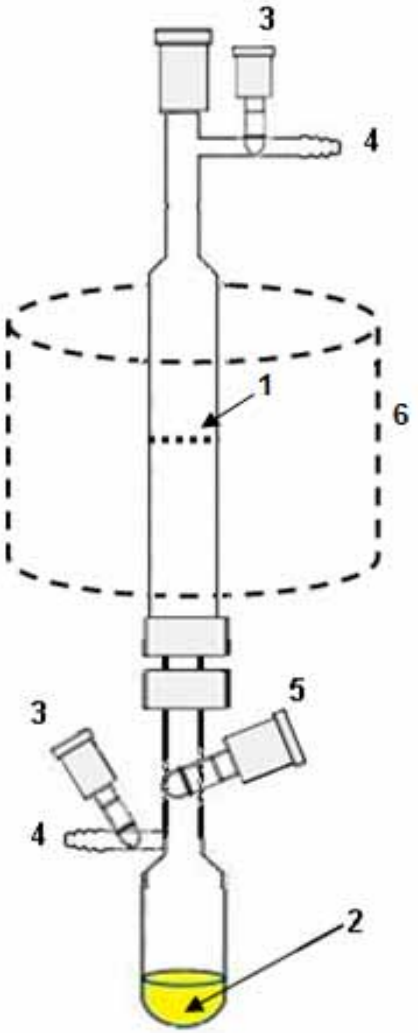
2/ Thermopolymerisation

Pluronic F127

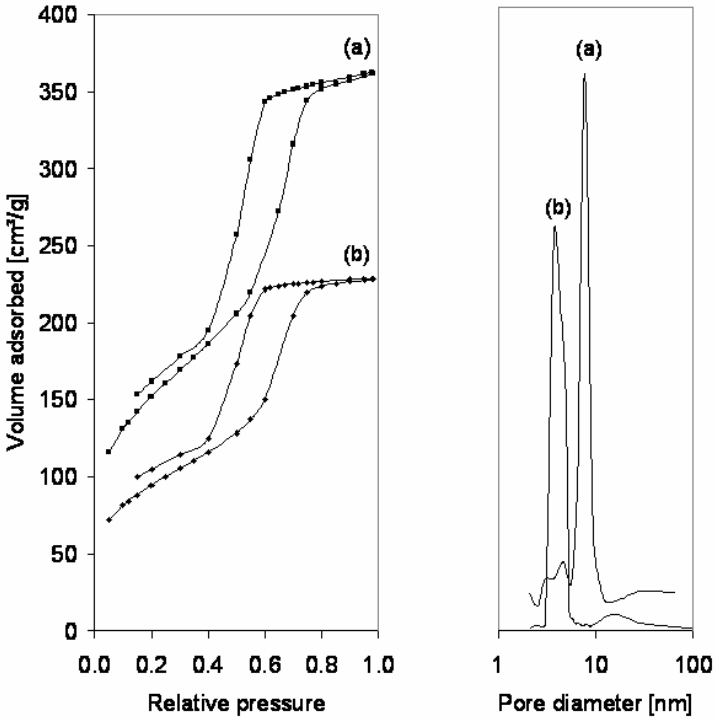
$EO_{106}PO_{70}EO_{106}$



CVD with $VOCl_3$

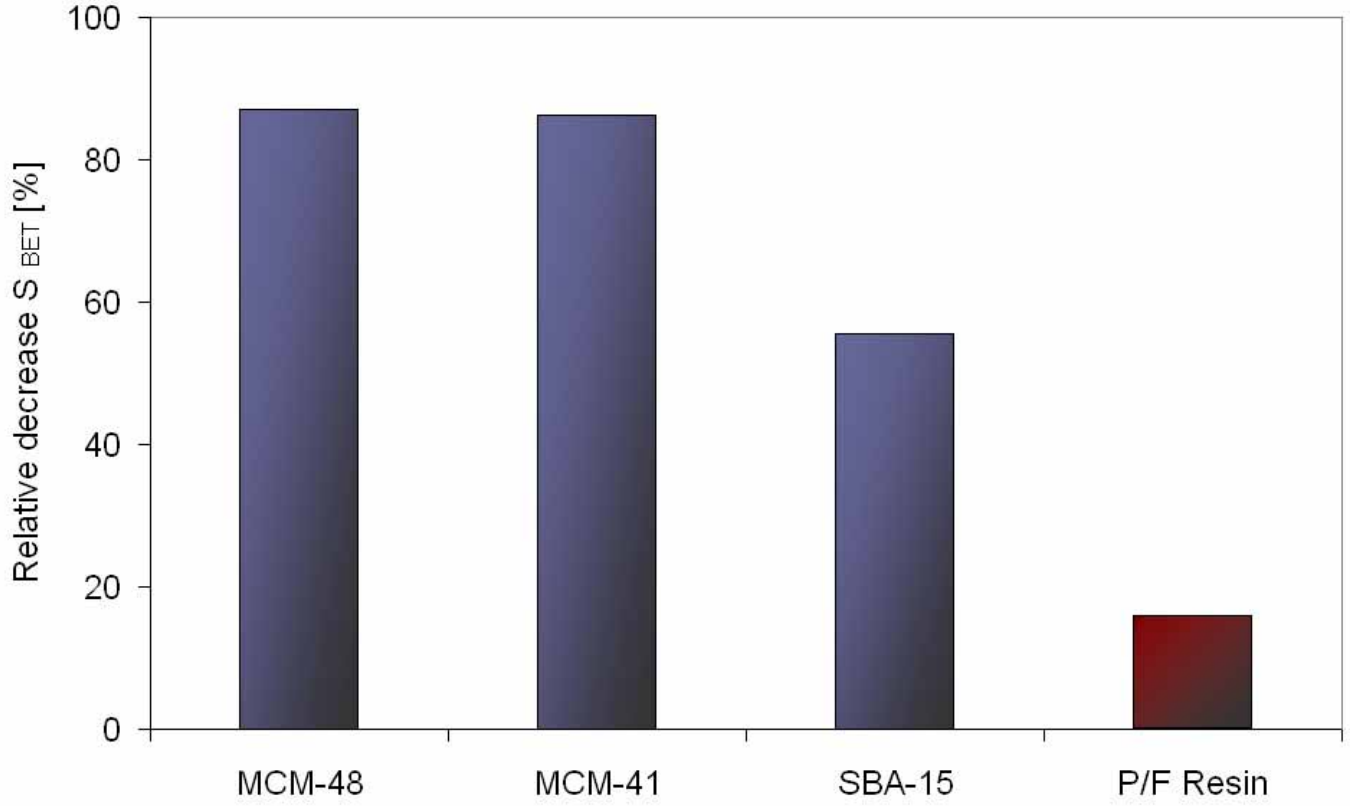


N_2-adsorption / desorption isotherms



		A	B
Specifiek oppervlak	[m²/g]	536	334
Poriegrootte	[nm]	7.7	3.7
Porievolume	[cm³/g]	0.54	0.35

Hydrothermal Stability (100°C, 100% humidity, 24u)



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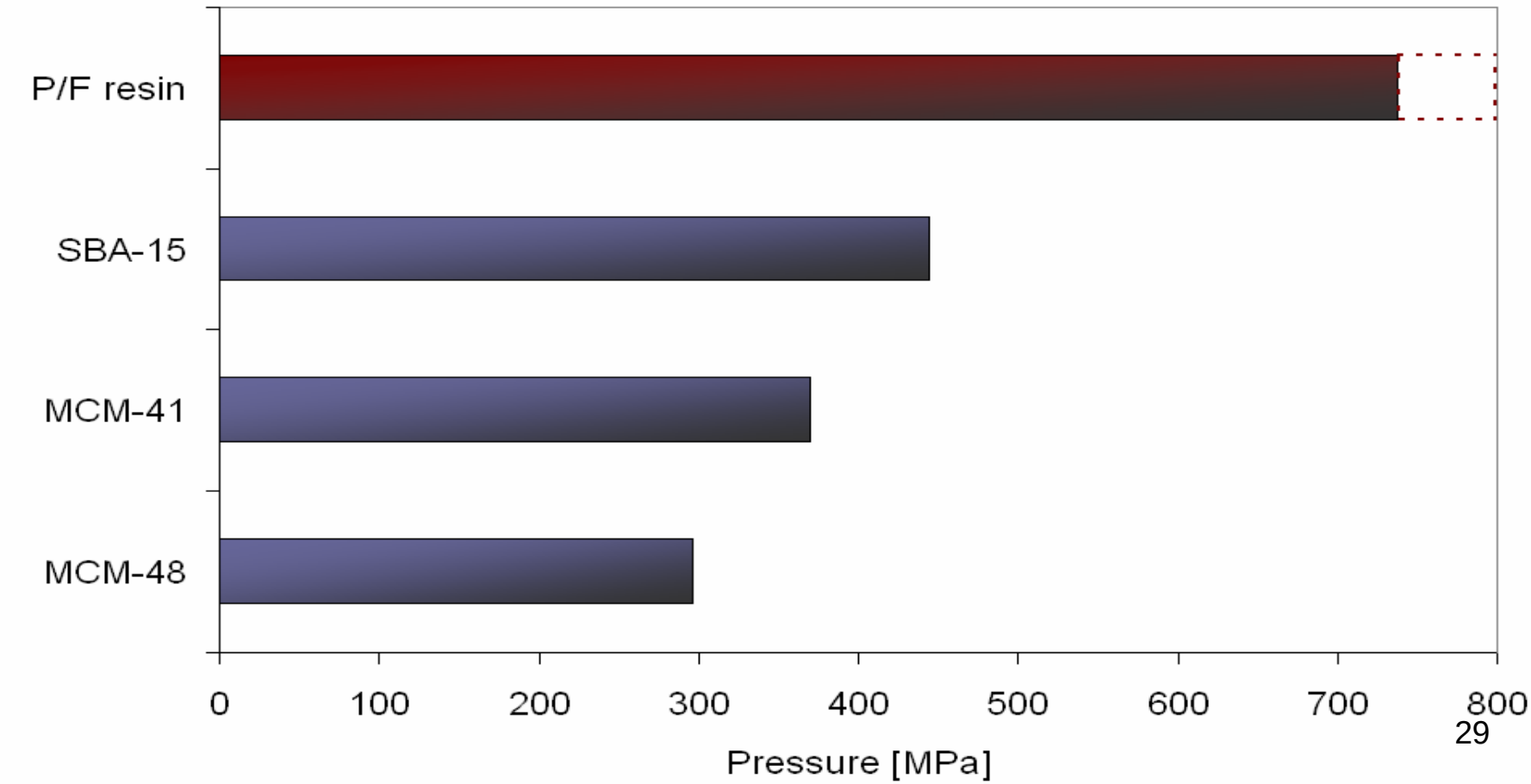
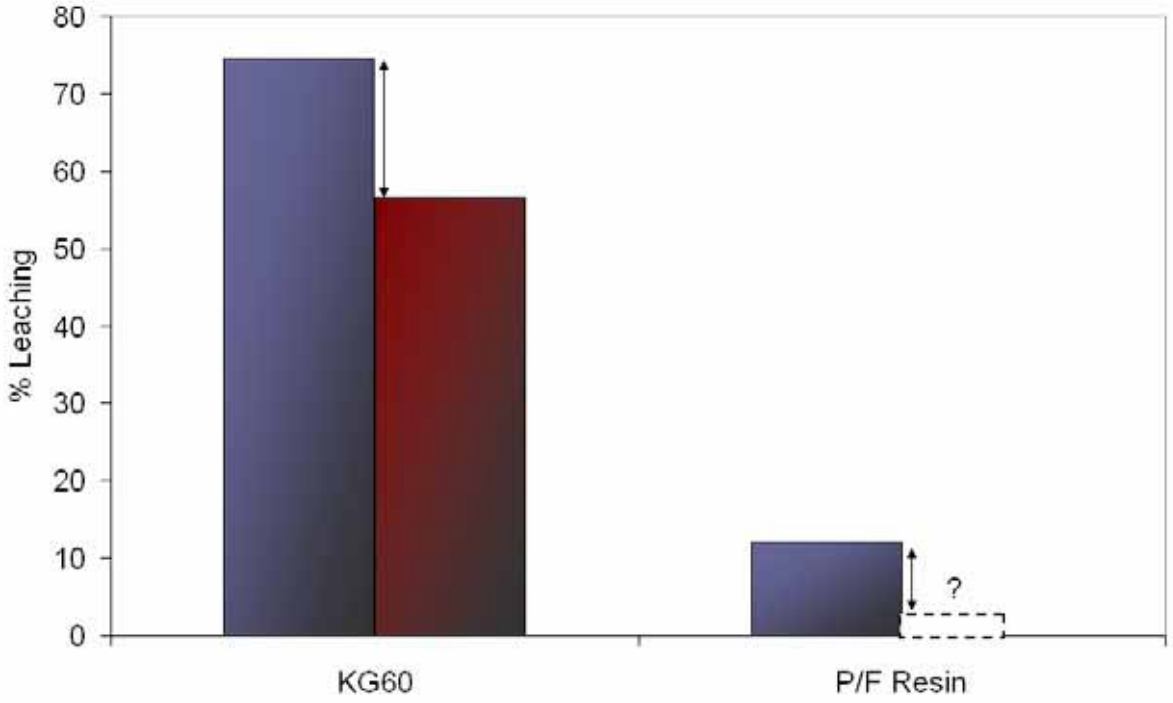
Mechanical Stability



Leaching



	wt% V	#V/nm²	% Leaching
Kieselgel 60	2.14	0.75	56.6
P/F resin	2.80	1.53	?

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Conclusion

- Support Materials for heterogeneous catalysis
  - Silanol not always the best anchoring group
  - Dangling groups → effects on stability and porosity
  - PMO Materials as an alternative
    - Heterogeneous Grubbs catalysts (Ru-complexes)
    - Sulfonic Acid PMOs for biodiesel production
    - But also as selective adsorbents (see Poster 28 – Els De Canck)
  - Silica materials have weak interactions with some metal oxides (leaching)
  - Silica materials are often structurally unstable in aqueous or liquid media
  - OMP Materials as an alternative
    - Mild oxidations in liquid/aqueous phase

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