Ordered porous materials in liquid phase catalytic reactions
Towards zero leaching supports
Multi-scale modeling and design of chemical reactions and reactors

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<th>subprogram</th>
<th>MC member</th>
</tr>
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<td>P1 Single event microkinetics (SEMK) in complex reaction mixtures</td>
<td>Joris Thybaut Marie-Françoise Reyniers</td>
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<td>P2 Catalyst design based on catalyst descriptors</td>
<td>Joris Thybaut Marie-Françoise Reyniers Pascal Van der Voort</td>
</tr>
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<td>P3 Adsorption by nanoporous materials</td>
<td>Joris Thybaut Marie-Françoise Reyniers</td>
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<td>P4 Polymer design accounting for diffusion and mixing</td>
<td>Geraldine Heynderickx Marie-Françoise Reyniers</td>
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<td>Geraldine Heynderickx Chris Stevens</td>
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<td>P6 From fossil to renewable feedstocks</td>
<td>Chris Stevens Joris Thybaut Marie-Françoise Reyniers</td>
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</table>
Evolving from Performance analysis To Kinetics Based Design...
Methusalem – formal and informal

- **Formal**: 1 PhD student (+ benchfee)
  - Working on catalytic activity of MOFs
- **Informal**
  - Collaboration on acid catalysis (transesterification reactions, modelling)
  - Use of infrastructure (GC-GC/MS, ammonia ads)
  - Preparing joint research projects (JT @ FWO; possibly @IWT)
  - Copromotorships in PhDs & mastertheses (starting 2010)
COMOC - Center for Ordered Materials, Organometallics and Catalysis

- Development of ordered porous materials
  - Synthesis and characterization
  - Applications in versatile fields

- Adsorbents for heavy metals
- Low k-materials; Thin films
- Packing materials for HPLC
- Zero leaching catalysts in liquid phase reactions
Spray drying mesoporous particles
Spray drying is robust

Varying spray dryer

Buchi B290, two-fluid nebulizer

GEA Niro A/S Mobil Minor, rotary nozzle
Spray drying is robust

**Results - Morphology**

H$_2$O concentration is the main factor
HPLC evaluation

**Results** - Stability vs Packing and evaluation

Packing conditions:
30 minutes at 900 bar
Measurement after 170 chromatographic runs
HPLC evaluation

**Results - Chromatographic performance**

A, B: Analysis of a mixture containing uracil (1), 1-phenyl-1-ethanone (2), 1-phenyl-1-butanoine (3), 1-phenyl-1-pentanone (4), 1-phenyl-1-hexanone (5), 1-phenyl-1-heptanone (6), 1-phenyl-1-octanone (7), 1-phenyl-1-decanone (8) and 1-phenyl-1-dodecanone (9) (50 µg/mL each); C: Analysis of a mixture of uracil (1, 50 µg/mL), benzene (2, 80 µg/mL), naphthalene (3, 50 µg/mL), antracene (4, 300 µg/mL), fluoranthene (5, 50 µg/mL), benzo[k]fluoranthene (6, 300 µg/mL); D: Analysis of a mixture containing uracil (1), methyl-4-hydroxybenzoate (2), ethyl-4-hydroxybenzoate (3), propyl-4-hydroxybenzoate (4) and butyl-4-hydroxybenzoate (5) (50 µg/mL each). The flow rate was 0.2 ml/min in A and 0.3 mL/min in B, C and D.
Action points

• Back pressure is not reduced to the expected level
• Shift attention to
  ▫ CEC (Capillary Electro Chromatography) - Excellent preliminary results by coating open tubular columns with mesoporous layer;
  ▫ Spraydrying of hybrid materials (PMOs)
  ▫ Lab on a chip – Collaboration VUB – Work in Progress.
Low-k materials: 

Low relative dielectric constant compared to SiO₂ (k<4)

In microelectronics industry: Low-k materials are used as insulators of interconnect wiring in computerchips


• Frederik Goethals, Carl Vercaemst, Veerle Cloet, Serge Hoste, Pascal Van Der Voort and Isabel Van Driessche, “Comparative study of ethylene and ethylene-bridged periodic mesoporous organosilicas”, Microporous and Mesoporous Materials, 2010, 131 (1-3), 68-74. DOI
New low-k materials:

- Low-k value (current value 2.3)
  - Thin Films
    - Porous
    - Low polarisable
    - Hydrophobic
    - Mechanical stable
PMO -- What is a PMO?


Limited commercial availability; « home made » precursors

Calcination not possible, important step

Functional groups in ENTIRE WALL
Precursors
Low k-materials;
Thin films

(1) MeO-Si-OMe

(2) OEt-Si-Si-OEt

(3) OEt-Si-Si-OEt

(4) EtO-Si-Si-OEt

(5) EtO-Si-Si-OEt

(6) EtO-Si-Si-OEt
Formation of porous material = surfactant removal
Influence of porogen loading on porosity

Toluene adsorption/desorption isotherm

Influence of porosity on dielectric constant

Pore size distribution
<table>
<thead>
<tr>
<th>Precursor</th>
<th>Porosity</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure 1" /></td>
<td>58</td>
<td>1.96</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure 2" /></td>
<td>55</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Low $k$-materials; Thin films
PMOs still have silanol groups -> high affinity to water
=> Removal of silanol groups:
=> Grafting with HMDS: $2\text{SiOH} + (\text{CH}_3)_3\text{SiNHSi(CH}_3)_3 \rightarrow 2\text{SiOSi(CH}_3)_3 + \text{NH}_3$
Low k-materials; Thin films

<table>
<thead>
<tr>
<th>Porosity</th>
<th>$k_{\text{RMPMO}}$</th>
<th>$k_{\text{EPMO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32%</td>
<td>2.28</td>
<td>2.45</td>
</tr>
<tr>
<td>45%</td>
<td>1.95</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Top contact: silver dots
Bottom: Si sputtered with Pt/Ti
Finding optimum between $k$ value and Young Modulus is crucial:

$\Rightarrow$ HMDS treated PMOs have a high young modulus and low-$k$ value

Close collaboration with IMEC for further implementation
PMOs as adsorbents and as catalysts

Thiol containing PMOs

- Bromination with Br₂ (g)
- Substitution with Cl-Mg-(CH₂)₃-SH

• Other mesoporous silica adsorbents
  ▫ One-pot-synthesis with \(-(CH_2)_3\)-SH functionalities

• Using this material as an adsorbent results into:
  ▫ Complete loss of mesoporous structure

=> Hydrolysis of Si-O-Si bond
• Other mesoporous silica adsorbents
  ▫ SBA-15 functionalized with −(CH₂)₃-SH (post-synthesis)

• Using this material as an adsorbent results into:
  ▫ Loss of thiol functionalities

=> Hydrolysis of Si-O-Si bond
• Structural stability: XRD and nitrogen adsorption measurement
• Chemical stability: No loss of thiol groups
  => Stable C-C bond
• Experiments show a 1:1 ratio $\text{Hg}^{2+}/\text{SH}$
Sulfonic functionalized periodic mesoporous organosilicas

\[(EO)_{20}(PO)_{70}(EO)_{20}\] + \[(\text{EtO})_3\text{Si} - R - \text{Si(OEt)}_3\]

P123 / H⁺ (aq)

Extraction

Sulfonation
Sulfonation

Acidity 1.19 mmol H⁺/g
Acidic (trans)esterification

Homogeneous versus heterogeneous catalyst

- Propanol and acetic acid
- 90°C
- 3 hours

=> Conversion of propanol ~ 93%
Pore size and pore structure engineering

N$_2$-Physisorption

Swelling agent

Carl Vercaemst, Bart Goderis, Petra E. de Jongh, Johannes D. Meeldijk, Francis Verpoort and Pascal Van Der Voort, Ethenylene-bridged periodic mesoporous organosilica foams with ultra-large mesopores, Chemical Communication, 2009, 4052-4054
II Controlling the pore channel length and pore connectivity

II Controlling the pore channel length and pore connectivity

P6/mmm

P6/mm
III Controlling the morphology

Action points

- Leaching stability of sulfonated groups must improve;
- Sulfonation mechanism of ethene functions not clear;
- Other functionalities; great prospects by a recent silyl ester method → this Columbian PhD student comes to COMOC in September:
- @ LCT: Use different porosities, plugs, ... to study diffusion effects in a profound way (proven concept with nanoparticles VS-1 INSIDE SBA-15) & Recent interest in “nanoMOFs” → New PhD project ? FWO project ?
- Study “added value” reaction to compete with acid resins. Introduce chirality, size exclusion.
Supports: inorganic & organic

- Metal organic frameworks
- Macroporous metallic scaffolds
- Phenolic resins
- SBA-15
- Porous carbon (starbons)
- Periodic mesoporous organosilica

Zero leaching catalysts in liquid phase reactions
Mesoporous titania on macroporous titanium scaffolds

1) EISA process
titanium precursor

2) Calcination

Mesoporous titania layer
Titanium scaffolds

PU replica

3DFD

Foaming technique
Synthesis optimization

- Variation of synthesis conditions (solvent, Ti-precursor, template ...)
- e.g. template variation:
  - CTAB : \((C_{16}H_{33})N(CH_3)_3Br\)
  - P123 : \(EO_{20}PO_{70}EO_{20}\)
  - F127 : \(EO_{97}PO_{69}EO_{297}\)

<table>
<thead>
<tr>
<th>Type</th>
<th>Template</th>
<th>(S_{BET}) (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CTAB</td>
<td>185</td>
<td>0,26</td>
<td>2,41</td>
</tr>
<tr>
<td>C</td>
<td>P123</td>
<td>232</td>
<td>0,50</td>
<td>3,55</td>
</tr>
<tr>
<td>D</td>
<td>F127</td>
<td>168</td>
<td>0,35</td>
<td>4,05</td>
</tr>
</tbody>
</table>

Graph showing nitrogen adsorption isotherms with relative pressure (p/p₀) on the x-axis and volume adsorbed (cc/g) on the y-axis.
Action points

- Catalysts do not work well in olefinic epoxidations, basically form peroxide adducts;
- Test catalysts in water phase total oxidation of phenol; they could be very suited for gas phase reactions as well. (@ LCT ?)
- Graft V-complexes on TiO₂ surface, using the silyl ester method.
- Graft Ti-complexes on SiO₂ surfaces.
Metal Organic Frameworks (MOFs)

- Metal ions are linked by organic ligands
- 3 dimensional network
- Microporosity
- High metal content
- Rigid structure
- Ligand coordination influences electronic properties

Zero leaching catalysts in liquid phase reactions

MOF
### MOFs

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Linkers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-BDC, R&lt;sub&gt;2&lt;/sub&gt;-BDC, R&lt;sub&gt;3&lt;/sub&gt;-BDC, R&lt;sub&gt;4&lt;/sub&gt;-BDC</td>
</tr>
<tr>
<td><strong>V</strong>&lt;sup&gt;4+&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>Zn</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>R&lt;sub&gt;5&lt;/sub&gt;-BDC, R&lt;sub&gt;6&lt;/sub&gt;-BDC, R&lt;sub&gt;7&lt;/sub&gt;-BDC</td>
</tr>
<tr>
<td><strong>Co</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>Ni</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>Ag</strong>&lt;sup&gt;+&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>Cd</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>Cr</strong>&lt;sup&gt;3+&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

Zero leaching catalysts in liquid phase reactions

**MOF**
V-MOF: synthesis

- Simple synthesis: $\text{VCl}_3 / \text{terephthalic acid} / \text{H}_2\text{O}$
  4 days, 200°C (autoclave)
  Calcination: 22h30 min, 300°C
- Formula: $\text{V}^{IV}\text{O}\{\text{O}_2\text{C-C}_6\text{H}_4\text{-CO}_2\}$
Catalytic performance (MIL-47)

Oxidants: TBHP in H₂O
Solvent: Chloroform
Temperature: 50°C

Zero leaching catalysts in liquid phase reactions

MOF

Reaction mechanism

Zero leaching catalysts in liquid phase reactions

MOF
Regenerability : V-MOF
Action points

- V-MOF synthesis from vanadium(III)-oxo acetic clusters; avoid decavanadates! (bottom up)
- V-ZIF (zeolitic imidazolate framework) synthesis
- Chiral, enantioselective catalysis: oxidation of sulfides to sulfoxides.

\[ \beta (\text{T-Imidazole-T}) \approx 147^\circ \]
Mesoporous resins

- Ilke Muylaert, Marijke Borgers, Els Bruneel, Joseph Schauberroek, Francis Verpoort and Pascal Van Der Voort, “Ultra stable ordered mesoporous phenol/formaldehyde polymers as a heterogeneous support for vanadium oxide”, Chemical Communications, 2008, 4475-4477

Mesoporous resins

\[
\text{Phenol} + \text{Formaldehyde} \rightarrow \text{Polymer} \quad \text{NaOH, } 70^\circ C, 1 \text{h}
\]

\[
\text{Carbonization} \quad \text{Functionalization}
\]


Pluronic F127

\[
\text{EO}_{106}\text{PO}_{10}\text{EO}_{106}
\]

\[
\text{Carbonization} \quad \text{Functionalization}
\]

\[
\text{VOCl}_3
\]

Chemical Communications, 2008, 4475-4477

48

P/F resins
ALD depositions
Controlling the porosity

<table>
<thead>
<tr>
<th>Type</th>
<th>Carbon Precursor</th>
<th>Medium</th>
<th>Solvent</th>
<th>Synthesis Temperature [°C]</th>
<th>$S_{\text{BET}}$ [m$^2$/g]</th>
<th>Pore size [nm]</th>
<th>Pore volume [cm$^3$/g]</th>
<th>Pore Size Distribution</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Phenol / formaldehyde</td>
<td>OH$^-$</td>
<td>EtOH</td>
<td>65</td>
<td>402</td>
<td>4.88</td>
<td>0.29</td>
<td>Broad</td>
<td>Membrane</td>
</tr>
<tr>
<td>B</td>
<td>Phenol / formaldehyde</td>
<td>OH$^-$</td>
<td>H$_2$O</td>
<td>65</td>
<td>725$^*$</td>
<td>&lt; 2</td>
<td>0.22</td>
<td>Narrow</td>
<td>Granules</td>
</tr>
<tr>
<td>C</td>
<td>Resorcinol / formaldehyde</td>
<td>H$^+$</td>
<td>EtOH / H$_2$O</td>
<td>Room Temperature</td>
<td>358</td>
<td>8.10</td>
<td>0.46</td>
<td>Very narrow</td>
<td>Granules</td>
</tr>
<tr>
<td>D</td>
<td>Resorcinol / formaldehyde</td>
<td>H$^+$</td>
<td>EtOH / H$_2$O</td>
<td>Room Temperature</td>
<td>626</td>
<td>7.10</td>
<td>0.70</td>
<td>Very narrow</td>
<td>Granules</td>
</tr>
</tbody>
</table>
Leaching behaviour

- Comparison of leaching behaviour of VOx/SiO vs VOx/Resin
- Stirring in water at 80°C
- Stirring in 2.5M H₂SO₄ at 80°C
- VOx/resins are currently under investigation for their catalytic activity
Supported TiO$_2$/SBA-15: synthesis

Atomic layer deposition:
- sequential exposure to a volatile metal precursor and a reactive gas
- self-limitingly
- controlled deposition
- uniform layers
Rotatable powder reactor
Actions points

• Cheap, easy producable, highly stable bakelite resins as catalytic support
• But... Only low to moderate activity of supported TiOx and VOx layers!
• Controlled ALD of resin-V-O-Ti-O-V...
• Alternative activation of the resins:
  ▫ Sulfonation – catalytic tests in progress
  ▫ Metal complexes ?
  ▫ Noble metals ? Reduction reactions.
General remarks

• Some nice materials, generally appreciated and COMOC is starting to become known as center of expertise in synthesis of “new” porous materials (COMOC is founded in 2007)
• Our materials also used in collaboration in
  ▫ Dentistry (University Hospital)
  ▫ Pesticides (bio-engineers – adsorption and controlled release)
• Need to adapt processes to cost and advanced level of the materials themselves
  ▫ High end reactions, selectivity, chirality
  ▫ Sensors, catalysts
  ▫ Stability can compensate for cost
COMOC -- April 2010