Recycling of homogeneous metathesis catalysts via nanofiltration or membrane reactor: how to achieve a sustainable production?

✓ Coordinator: Professor Murielle RABILLER-BAUDRY, Université Rennes 1

✓ Call for proposals ANR-CP2D 2009
✓ project: NanoRemCat2 – n° ANR-09-CP2D-11-01
✓ Duration: 1 october 2009 – 31 march 2013

✓ This project is labeled by 2 competitive clusters: IAR and AXELERA
Main goal of the Project

✓ To contribute to develop a route for a sustainable production in fine chemistry
  ❑ Particular case of olefin metathesis

✓ Thanks to the integration of nanofiltration in organic solvent (OSN) in the overall process scheme

❑ OSN = Separation process ➔ efficient at molecular scale
  ▪ Performed in liquid media
  ▪ without state change ➔ favorable to maintain the integrity of fragile molecules
  ▪ Eco-friendly process
    ▪ low energy consumption
    ▪ possible low solvent consumption, depending on
      ▪ diafiltration steps (product extraction step + purification)
      ▪ solvent recycling (can be achieved by membrane process)

❑ OSN= Based on selective transfer of target molecules through a membrane
  ▪ Composite media, a layer of which is
    ▪ generally made of « dense polymer » ➔ main choice of this study
    ▪ Can be « porous inorganic structure » ➔ lower retentions (nowadays)
Olefin metathesis

✓ Route to obtain new double carbon= carbon bound
  □ Obtained by *intra* or *inter* molecular rearrangements
    ▪ Often in toluene or dichloromethane…

✓ Provides access to many chemical intermediates
  □ Chemistry Nobel Prize in 2005: Chauvin, Grubbs, Schrock
  □ Many possible substrates:
    ▪ the origin of which can be either petrochemical or bio-resources

✓ An identified route to prefer
  □ for a green and sustainable fine chemistry

✓ Needs the use of organo-metallic catalysts, can be either
  □ Heterogeneous (solid)
  □ Homogeneous (soluble)
    ▪ Preferred in this study ➔ more favourable on a kinetic point of view
      ▪ (energy saving)
General questions of the project

✓ How to develop a sustainable production

- Involving the use of a olefin metathesis reaction
  - With an homogeneous organo-metallic catalysts

- One main limitation identified at the project start
  - is the optimisation of the catalyst use / life cycle

✓ Catalyst recycling is the most popular approach

- our initial proposal matches with: originality ➔ use of OSN

- Among alternative routes (sometimes efficient) proposed by chemists
  - Use of immobilized catalysts
    - For instance in non-conventional media as ionic Liquids (iL)
      - Is it really green chemistry ? (see debates about iL toxicity)
    - Extraction of catalyst from the reaction media by the use of precipitation
      - leading to frequent inactivation
      - Need of solvent for purification steps (chromatography…)
General questions of the project

✓ Catalyst recycling
  ➔ the most popular approach
  ❌ Our initial proposal: use of OSN

✓ To rationalise the catalyst loss
  ➔ Complementary approach added after 1 year
  ❌ Could be interesting if catalyst is very active and/or used at homeopathic dose

✓ In both cases integration of organic solvent nanofiltration could be efficient
  ❌ On an experimental point of view ➔ Similar approach to match different goals
    ▪ catalyst recycling
    ▪ limitation of metal residues in final target product
      ▪ due to pre-catalyst / active catalyst / deactivated catalyst
Scientific and Technical Objectives

- To separate components of the olefin metathesis reaction medium
- To enhance retention of catalyst in the medium for recycling purpose
- To limit the solvent additions
  ➔ By the mean of Organic Solvent Nanofiltration

**Route A: 2 steps in cascade**

- Synthesis performed in batch mode
- OSN on final medium, containing
  - solvent,
  - target products
  - residual catalyst, if any…
  - deactivated catalyst (several forms)

**Route B: 1 step**

- Process intensification

- Synthesis performed in a membrane reactor
  - continuous or semi-continuous

- OSN on reaction medium, containing
  - solvent,
  - substrate
  - target products
  - catalyst
  - deactivated catalyst (several forms)
Choice of olefin metathesis catalyst

- Grubbs-Hoveyda II type
  - Choice guided by the high stability of this catalyst type
  - Catalyst commercially available in a pre-catalyst form

Active catalyst

The molecular weight of (pre)-catalyst
- is a priori compatible with a high retention by OSN membranes
Objective initially defined according to the olefin metathesis mechanism

Active catalyst combined with substrate/product

+ Substrate

(1) “release of ligand” quick step

Product

Pre-catalyst

(2) “return of ligand” quick step

Free ligand

Assumption commonly admitted at project start invalidated after the first year!

The main objective is the retention by OSN of pre-catalyst for recycling purpose (the most stable form)
**Scientific Context…/3**

- **Active catalyst**
- **Pre-catalyst**
- **Substrate**
- **Product**
- **Deactivated catalyst**
- **Free ligand**

(1) “release of ligand” quick step

- **The main objective evolves**
  - Full retention of pre-catalyst
    - now considered as stable reservoir of active catalyst
  - High retention of active catalyst
    - to enhance its turn over number
  - High retention of deactivated catalyst
    - to limit Ru amount in final product
Program structured in 5 Work Packages

- **At start the scientific and technical challenges are focus on pre-catalyst retention**
  - Regardless of organic reaction, up to now, the preferred approach in literature concerns:
    - catalyst retention
    - substrate conversion rate
    - nothing about product recovery…

- **WP1: to master the nanofiltration of single pre-catalyst in toluene**
  - Choice of commercial membrane, pressure, hydrodynamic…
  - WP2: adaptation of pre-catalyst structure ➔ to enhance the retention of all Ru forms
  - WP3: adaptation of membrane materials ➔ few commercially available membranes

- **WP4: to realise nanofiltration membrane reactors: discontinuous (continuous)**
  - on a model reaction
  - then on a medium issued from bio-resource

- **WP5: to make an assessment**
  - Discussion of the sustainability of the different studied processes
NanoRemCat2  Partners

CIP team
Murielle Rabiller-Baudry  
Thierry Renouard  
Anthony Szymczyk  
Lydie Paugam  

Ghassan Nasser  
(PhD student, ANR)  
David Delaunay  
(post-doc, ANR, 12 months)  
Adel Keraani  
(PhD student, MENRT, 8 months)  

COM team
Cédric Fischmeister  
Christian Bruneau  
Saurabh Shahane  
(PhD student, ANR)  

+ 1 sub-contractor: Novasep Process  
Didier Dhaler  
Membrane manufacturer / equipment supplier

Denis Roizard  
Eric Favre  
Haifa Ben Soltane  
(PhD, ANR)  

Jean Luc Couturier  
Jean Luc Dubois
Some selected results…

1. Membrane materials
2. Optimisation of single pre-catalyst OSN in toluene
3. Modification of pre-catalysts
4. Membrane reactors
1. Membrane materials…

WP 3- leader: Denis Roizard, LRG-P-Nancy (P3)

✓ OSN: needs membrane materials that are resistant to solvent
  - especially toluene
  - A main bottleneck of the process
  - Very few materials are commercially available
  - Those allowing the higher retentions are dense organic membranes
    - MWCO 200-400 g.mol⁻¹
    - Some industrial applications already exist, mainly for solvent recycling

✓ A need of new membrane material is nevertheless identified
  - The load specification is (by order of importance)
    1. Stability in toluene
    2. Full retention of pre-catalyst
    3. Full retention of all metal components

  ➔ 2 Tasks
  Route of dense membrane based on polyurethane (Partner 3)
  Route of modified inorganic membrane (Partner 1)
**Original Membrane Material ➔ block co-polymers/ WP3**

- Flexible block
- Rigid block

- **First: Validation of formulation of self supported dense membranes in the polyurethane series**
  - Diisocyanate (2') + a,w -oligomer diol (P) (1) + Triol \( \rightarrow \text{membrane} \)

  
  - MDI
  - PEG 400
  - Glycerol
  - MW= 400 ± 20 g.mol\(^{-1}\)
  - MW= 92 g.mol\(^{-1}\)

- **Second: Synthesis of supported dense membranes**
  - Commercial support = PET-PAN
  - MDI \( \_2 \) + PEG-400 \( \_1 \) + Polyglycerol
  - \( n=3 \)
  - MW=250g.mol\(^{-1}\) \( \_2/3 \)
« Best » Supported PU membrane / WP3

criterion = retention of pre-catalyst

- Polymer layer
- PET-PAN support

OSN of Grubbs-Hoveyda II pre-catalyst
0.5 x 10^{-3} mol.L^{-1} / toluene / cross-flow
20 bar, 30 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>« Best » Membrane</th>
<th>Starmem 122 Membrane (polyimide)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Image" /></td>
<td>MDI-PEG400_{1-3}</td>
<td>(polyimide)</td>
</tr>
<tr>
<td>Lp L.h-1.m^{-2}.bar^{-1}</td>
<td>0.07</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>48 ± 2</td>
<td>98.4</td>
</tr>
</tbody>
</table>

• homogeneous dense film
• Good adhesion on support
• No penetration of polymer in support pores

Scientific point of view
This membrane allows to propose a first model of transfer taking into account the swelling gradient on both sides of membrane as driving force

- too low retention
- Low flux
**Evolution of PU membrane / WP3**

- In progress…
- slight modifications of polymer structure
  - polarity, polymer size…
- Hybrid membranes by incorporation of silica nanoparticles in PU structure

<table>
<thead>
<tr>
<th>Membrane</th>
<th>MDI.2</th>
<th>MDI.2</th>
<th>MDI.2</th>
<th>MDI.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEG.1</td>
<td>PEG400.1</td>
<td>PEG400.1</td>
<td>PEG1000.1</td>
<td>PEG1000.1</td>
</tr>
<tr>
<td>PG3.2/3</td>
<td>PG3.2/3</td>
<td>PG3.2/3</td>
<td>PG3.2/3</td>
<td>PG3.2/3</td>
</tr>
<tr>
<td>hydrophilic SiO₂</td>
<td>« best »</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lp (L.h⁻¹.m⁻².bar⁻¹)</th>
<th>0.07</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swelling in toluene (%)</td>
<td>0.18</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Mastering of single pre-catalyst retention...

**WP 1- leader : Thierry Renouard ISCR-CIP Rennes (P1)**

✓ Objectives

- To obtain the higher possible retention
  - Membrane choice
  - Impact of hydrodynamic parameters…
  - Dead-end *versus* cross-flow filtration

Retention increases from 67 % to 99.5 %

"Best" membrane ➔ Starmem 122 (dead-end)

Best OSN mode ➔ cross-flow (starmem 122)
**Pre-catalyst modification…**

**WP 2- leader : Cedric Fischmeister , ISCR-COM- Rennes (P2)**

- At program start: pre-catalyst retention was only 67 %
  - dead-end mode, 25 bar, Starmem 228 membrane (Met-Evonik, UK)

- Task: to modify pre-catalyst structure
  - To enhance retention by the « best available » commercial membrane (to identify)
  - Following a molecular engineering approach
    - Catalysis in synergy with Nanofiltration

- The load specification is (by order of importance)
  1. active in metathesis
  2. full retention of pre-catalyst
  3. full retention of catalyst, regardless of its form

→ 2 routes

**Route 2**
Modification of amino-carbene part preferred after 1 year

**Route 1**
Modification of ligand part
Aborted after 1 year
(« release/return mechanism »)
Pre-catalyst modification…/WP2

Route 1
Modification of ligand

OSN in dead-end mode
Starmem 228 (Met-Evonik)
25 bar

1: MW = 627 g.mol⁻¹
Retention = 67%

Retention not only based on size…!

Best retention: 92%
**Pre-catalyst modification and OSN …/WP2 + WP1**

**Route 2**
Modification of amino-carbene

1: MW = 627 g.mol⁻¹
Retention = 99.8 %

2: “C8” : MW = 739 g.mol⁻¹

3: “adamantyl” : MW = 927 g.mol⁻¹

4: “PEG” : MW = 834 g.mol⁻¹

**OSN in cross-flow mode (0.1 m.s⁻¹)**
Starmem 122 (Met-Evonik)
40 bar
0.5 x 10⁻³ mol.L⁻¹

**Similar retentions!**

<table>
<thead>
<tr>
<th>Pre-catalyst</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ret (%)</td>
<td>99.6</td>
<td>98.4</td>
<td>99.3</td>
<td>99.6</td>
</tr>
</tbody>
</table>

**But different behaviours in discontinuous membrane reactor**
Nanofiltration membrane reactor...

WP 4- leader: Murielle Rabiller-Baudry ISCR-CIP Rennes (P1)

✓ 2 Nanofiltration membrane reactors working in cross-flow mode
- semi-continuous
- continuous

✓ The general trends shown here are obtained for a model reaction
- without any industrial application
- but allowing
  - establishment of the proof of concept
  - identification of limitations in the use of OSN

- Ring Closing metathesis of DEDAM (RCM)

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{CO}_2\text{Et} \\
\longrightarrow & \quad \text{pre-catalyst: 0.5 mM} \\
\text{toluene, } & \quad \text{-C}_2\text{H}_4 \\
\text{DEDAM} & \quad \text{MW} = 240 \text{ g.mol}^{-1} \\
\text{c-DEDAM} & \quad \text{MW} = 212 \text{ g.mol}^{-1}
\end{align*}
\]
Semi-continuous membrane reactor

Substrate Conversion varied with pre-catalyst structure

3 consecutives RCM + OSN
DEDAM load: 3 x 0.032 mol

[Diagram showing the semi-continuous membrane reactor setup and substrate conversion graphs]
Continuous membrane reactor

Permeate quality

<table>
<thead>
<tr>
<th>TMP bar</th>
<th>Pre-catalyst load mol</th>
<th>DEDAM mol</th>
<th>formed c-DEDAM mol</th>
<th>conversion rate %</th>
<th>apparent TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.6 x 10^{-4}</td>
<td>0.032</td>
<td>0.015</td>
<td>47</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>1.6 x 10^{-4}</td>
<td>0.032</td>
<td>0.028</td>
<td>88</td>
<td>172</td>
</tr>
</tbody>
</table>

Better conversion at lower pressure
Comparison
semi-continuous / continuous membrane reactors

<table>
<thead>
<tr>
<th>membrane reactor</th>
<th>TMP bar</th>
<th>Pre-catalyst load mol</th>
<th>DEDAM mol</th>
<th>formed c-DEDAM mol</th>
<th>conversion rate apparent TON %</th>
<th>c-DEDAM recovery before diaf. mol</th>
<th>toluene mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>continuous</td>
<td>40</td>
<td>1.6 x 10^-4</td>
<td>0.032</td>
<td>0.015</td>
<td>47</td>
<td>94</td>
<td>0.0077</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.6 x 10^-4</td>
<td>0.032</td>
<td>0.028</td>
<td>88</td>
<td>172</td>
<td>0.0086</td>
</tr>
<tr>
<td>semi-continuous</td>
<td>40</td>
<td>1.6 x 10^-4</td>
<td>0.032</td>
<td>0.031</td>
<td>97</td>
<td>194</td>
<td>0.0051</td>
</tr>
</tbody>
</table>

- Close performances can be achieved with the 2 configurations
- Continuous mode favoured less solvent consumption (before diafiltration)
- Diafiltration to extract product from the reaction medium is the main encountered limitation
- Need: to found a compromise between pre-catalyst retention/ product extraction
- Transposition to a substrate of industrial interest is in progress…
Main program for the six last months

✓ To achieve olefin metathesis on media issued from bio-resources
  - Cascade: batch synthesis + OSN step
  - Semi-continuous membrane reactor
  - Continuous membrane reactor
    - Change of membrane to enhance the product recovery ➔ if needed

✓ Assessment

✓ Valorisation
  - Proceedings + several oral and poster communications in international congresses
    - Sustainable chemistry 2011, WFC 2011, Euromembrane 2012…
  - Writing of publications
    - several submitted papers…

✓ 3 theses to be defended before december 2012
  - Ghassan NASSER, P1
  - Saurabh SHAHANE, P2
  - Haifa BEN SOLTANE, P3
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