CatchBio
Catalysis for Sustainable Chemicals from Biomass

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• CatchBio focuses on **chemocatalytic** conversion routes

**Chemocatalysis:**
Use of hetero- and homogeneous catalysts

**Biocatalysis:**
Use of enzymes and micro-organisms
**Feedstock:** lignocellulose, oils and proteins

**Biorefinery**
- Chemo- & Bio-Catalysis
- Hybrid Conversion Processes
- clean
- selective
efficiënt

**Products**
- Energy, chemicals & materials for everyone
Our partners

Academic partners:
- Universiteit Utrecht
- Wageningen University
- University of Twente
- Universiteit van Amsterdam
- Technische Universiteit Eindhoven
- Universiteit Leiden
- Radboud University Nijmegen
- ECN

Industrial partners:
- Dow
- DSM
- Albemarle
- MSD
- Avantium
- Sabic
- BASF
- Sasol
- Shell Global Solutions
- VibSpec
- Hybrid Catalysis
The grand challenge

Catalytic toolbox should be adapted:

• selective defunctionalisation
• C-C cleavage vs. C-C making
• hydrophobicity/hydrophilicity
• catalysis in aqueous media

apolar, unfunctionalized compounds of carbon and hydrogen

polar, highly functionalized compounds of carbon, hydrogen and oxygen
Research clusters

- Energy
- Bulk chemicals
- Fine pharma
- Socio-economic
**Themes**

- **Sugars**
  - ~65% of biomass
  - Formation of sugar derivatives
    - C-O (deoxygenation)
    - C-C (isomerization)
  - HMF, LA

- **(Hemi)Cellulose**
  - ~25% of biomass
  - Transesterification/esterification/decarboxylation
  - Bulks products
  - Energy products
    - Pyrolysis
    - One-step FTS

- **Lignin & Humins**
  - ~5% of biomass
  - Aromatics
  - Others
  - Hydrogen production

- **Vegetable Oils**
  - ~5% of biomass
  - Transesterification/esterification/decarboxylation

- **Proteins**
  - ~5% of biomass
  - Decarboxylation
Design of novel catalytic systems for the selective dehydration of glucose to HMF; HMF is desirable *platform* molecule (fuels and chemicals)
Two highlights from the bulk cluster

- HMF: a key platform molecule
- glucose isomerisation and dehydration

- Chromium salts give exceptional HMF yields in ionic liquid

- The Eindhoven group elucidated the mechanistic details by a combination of kinetic, spectroscopy, and computational studies

Chromium (II) chloride in ionic liquid

Liquid phase EXAFS and DFT

- **EXAFS**
  - Isolated $\text{CrCl}_4^{2-}$
  - No Cr-C coordination

- **DFT**
  - Multinuclear species are prohibited
  - Isolated square planar $\text{CrCl}_4^{2-}$
  - Perfect match with experiment

Two highlights from the bulk cluster

• Ring opening/closure catalyzed by a single chromium ion

• Hydrogen transfer (rds) catalyzed by transient dimeric chromium species

• Enzyme like chemistry
Two highlights from the bulk cluster

Detailed understanding led to **design of new catalysts**:

- immobilization of chromium salts in an ionic liquid film on a mesoporous support

- Conversion 50%, selectivity 65% (yield 33%) in water

- use of cheaper solvents including water/organics

- current focus: further stabilization of the catalyst

Hensen et al., *ChemCatChem* **2011**, *3*, 969
Proton catalyzed conversion of glucose

O₂ and O₃ activation: selective to LA

O₄ activation: humin formation

O₅ activation: selective to LA via fructose and HMF

α-D-Glucose protonation

Side-reactions
Two highlights from the bulk cluster

Two-stage catalytic depolymerization of lignin to bulk chemicals

Prof. dr. ir. Bert Weckhuysen
Annelie Jongerius MSc
Dr. Joseph Zakzeski
Large lignin streams generated by pulp- and paper industry, future streams available from biorefinery operations

Current use: 98%: low value heating fuel
2%: chemicals and materials

Chemocatalytic lignin valorization reviewed in Chem. Rev. 2010, 110, 3552
Two highlights from the bulk cluster

- An integrated approach to the valorization of lignin is under study

- Different lignins are **nearly 100% soluble** in a mixture of ethanol/water

- No agglomeration of solids

- This allows **further catalytic conversion** of the soluble lignin

Zakzeski, Jongerius, Bruijnincx, Weckhuysen, *to be submitted*
Various catalytic processes tested to convert solubilized lignin feed

Product yield and composition depends on the **process/catalyst combination**
Results
Simultaneous near-zero NO$_x$ and soot with various engines & burners

Patented technology

regular diesel + cyclohexanone
Lignin to Cycloxo fuel (reverse engineering)

Lignin (recalcitrant biomass fraction)

- Depolymerization
- Upgrading

Phenolics

Mixture Oxygenated Aromatics

= Cycloxo

Brabant Development Agency

TU/e
Technische Universiteit Eindhoven
University of Technology
• **First phase** (2008): 19 research projects
  - 37 PhD students
  - 17 Postdoc years
  - WUR/FBR & ECN

• **Second phase** (2009): 17 research projects

• **Third phase** (2012-2015):

  Develop integrated process concepts that will be offered to industry for further development. Based on:
  - Delivered proof-of-principles
  - Socio-economic assessment
  - Interest from industry
CatchBio should function as a catalyst itself as well: generate **new research lines** and **spur collaboration**.
### General
- Chemocatalytic biomass conversion: robust catalysts for liquid phase processes
- Development in-situ spectroscopy & computational modeling (liquid phase processes)
- Hybrid concepts for biomass conversion: bio- & chemocatalysis
- Catalytic pyrolysis/Fischer-Tropsch Synthesis of biosynthesis gas
- Green diesel production (upgrading of triglycerides, O removal with or w/o H₂)

### Cellulose/hemicellulose
- Elementary reaction steps C-O, C-C and O-H bond activation
- Aqueous phase reforming (cheap catalysts, high selectivity to hydrocarbon fuels)
- Catalytic chemistry of sugar valorization (dehydration vs. decarboxylation)
- Catalytic chemistry along the chain: sugars → furfural → levulinic acid → fuels

### Lignin
- Depolymerization lignin to fuels and chemicals
- Lignin upgrading to cyclic oxygenates