FASTCARD (2014 – 2017)
Fast industrialization by Catalyst R&D

Catalytic HDO of phenolics in the gas and liquid phase over supported MoO$_3$ and its pre-carburized analogues

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PhD candidate Chanakya Ranga and Prof. Joris Thybaut (UGent)

CALL NMP.2013.1.1-1
"Exploration, optimisation and control of nano-catalytic processes for energy applications"

Cascatbel workshop
18 – 20 May, Porto Carras, Greece 2016
Biofuels in Norway

Norway;
- "A laboratory for electric cars"
- Share of new cars sold spring 2016; 20% hybrid cars, 18% electrical cars

Do we need biofuels?
- October 2015: Tax on bio-fuels was lowered as part of a campaign to increase biofuel share towards 5.5% (assist market development)
- February 2016: Surprise when it was discovered that 60% of biofuel on market ("HVO100") is based on palm oil (NOT sustainable was politicians opinion)
- Other sustainable options still not easily available with relevant capacity
- Discussion then triggered in media about to what degree use of wood etc is climate friendly and sustainable, or if it just contributes to increased levels of CO₂ in the atmosphere (waste wood ok, whole trees not?), politicians remains confused

FASTCARD is based on lignocellulose as raw material
Norway is committed to the EU-30-30-30 targets
A national research centre for renewable energy is planned
Fastcard global objectives

- To speed up catalyst industrialisation in Europe
  - Compatible with existing refinery infrastructure in Europe
  - Or breaking investment costs for new units
  - By a systematic demonstration at pilot scale

- To speed up catalyst development
  - Decreasing failure risks
    - Down and upscaling solutions to enable unbiased catalyst design and R&D
  - Increasing success rates
    - Parallel testing on long runs to monitor deactivation

- Scale integration of knowledge-based design approaches
  - Miniaturisation: by reactor simulations laboratory $\leftrightarrow$ pilot scales
  - Rational design: by µkinetics supported by DFT & in-situ tech.
Structure, strategy, deliverables

Diversified Biomass Sources

Gasification

(Cat)Pyrolysis

Integrated modelling including O, S containing compounds

Down-Up scaling methods for syngas & biooils

Conditioning "Hydrocarbon reforming"

"CO₂" FTS

Conditioning "Hydro-stabilisation"

Co-FCC

Rational design of catalyts for biomass conversion

Reliable catalyst development process

Diesel

Transportation biofuel

Gasoline

High energy efficiency
Low capital costs

EU project, FP7-NMP: FAST industrialisation by CATalysts Research and Development
Coordinator: SINTEF
FAST implementation strategy

Figure 2: FASTCARD knowledge-based approach to decrease risk, cost and time for catalyst development

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Coordinator: SINTEF
**Liquid value-chain / Partners**

- **FAST PYROLYSIS**
  - BTG, WP3 lead R. Venderbosch
  - Boreskov (BIC)
  - STABILIZATION
  - NiCu/SiO₂
  - Piquula

- **Deep HDO (Phenolics)**
  - SINTEF, UGent
  - MoOₓ/ZrO₂ + carburized analogues
  - SoA: CoMoOₓ/ZrO₂ and Al₂O₃

- **Co-FCC**
  - Repsol, Grace, CNRS, SINTEF

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**Key words:** Next generation catalysts for producing high quality co-feed to FCC plants

**Challenges:** Robustness of performance, hydrogen consumption and pressure, improved durability, and selectivity at varying depth of O removal

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Catalyst materials

MoO$_3$/ZrO$_2$
- 7 wt.% Mo (oxide + two levels of carburization severity)
- 15 wt.% Mo (- - -)
- 25 wt.% Mo (- - -)

"CoMo" reference materials (SoA)
- 15 wt.% Mo 3.68 wt.% Co/Al$_2$O$_3$
- 15 wt.% Mo 3.68 wt.% Co/ZrO$_2$

Supports
- ZrO$_2$-A (ca. 51 m$^2$/g, 160/600 Å bimodal pores, 0.3 cm$^3$/g)
- ZrO$_2$-B (ca. 90 m$^2$/g, 80/400 Å bimodal pores, 0.31 cm$^3$/g)
- Al$_2$O$_3$ ((ca. 100 m$^2$/g, 100Å, 0.49 cm$^3$/g V$_p$)

Carburization
Gas: CH$_4$/H$_2$ = 4/1
Severity: 550 ºC and 700 ºC

Preparation inspired by:
ICP / Elemental analysis

<table>
<thead>
<tr>
<th></th>
<th>Mo loading [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nominal</strong></td>
<td>7</td>
</tr>
<tr>
<td><strong>Analysed</strong></td>
<td>7</td>
</tr>
</tbody>
</table>

*) Data from UGent
Temperature Programmed Reduction (TPR)

Mo-oxide & carburized analogues

SoA; Mo-oxide & (Co) metal

- 15 MoO$_3$/ZrO$_2$
- 15 MoOC/ZrO$_2$ ("550 oC")
- 15 Mo$_2$C/ZrO$_2$ ("700 oC")

Support; ZrO$_2$-A (ca. 51 m$^2$/g, 160/600 Å bimodal pores, 0.3 cm$^3$/g)

- Carburization decreases the reducible phase of the "MoO$_3$/ZrO$_2" system
- SoA more complex reduction, Al$_2$O$_3$ supported is the least reducible
The high temperature treatment appears to be associated with:

- reduction of MoO$_3$ to MoO$_2$
- formation of molybdenum carbide
- possible formation of carbon

X-ray diffraction spectrometry (XRD)

MoO$_3$/ZrO$_2$ and carburized analogues
Dispersion (D) by CO chemisorption

<table>
<thead>
<tr>
<th>Mo loading [wt.%]</th>
<th>15 MoO₃/ZrO₂</th>
<th>15 Mo - carburized 550 °C</th>
<th>15 Mo - carburized 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1.6</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>19</td>
<td>1.1</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Support; ZrO₂-B (ca. 90 m²/g, 80/400 Å bimodal pores, 0.31 cm³/g)

- Rather low D values
- D decreases with Mo loading
- D decreases with carburization severity
X-ray photoelectron spectroscopy (XPS)

Relative atomic Mo/Zr ratios in surface layers

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo/Zr ratio [atomic]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 MoO₃/ZrO₂ A</td>
<td>0.16</td>
</tr>
<tr>
<td>7 MoO₃/ZrO₂ B</td>
<td>0.17</td>
</tr>
<tr>
<td>12 MoO₃/ZrO₂ A</td>
<td>0.22</td>
</tr>
<tr>
<td>19 MoO₃/ZrO₂ A</td>
<td>0.23</td>
</tr>
<tr>
<td>19 MoO₃/ZrO₂ B</td>
<td>0.28</td>
</tr>
</tbody>
</table>

• Low loading gives better Mo distribution
• Particle size on "7 Mo" and "25 Mo" smallest on high SA support

Spectra of Mo 3d core level shows
• Dominant MoO₃
• Growing peak of Mo₂O₅ (beam sensitive samples)
• Carbon is located on surface
TEM; 7 MoO$_3$/ZrO$_2$ (A) catalyst

- The crystallite typical size is around 20 nm. Crystallites tended to aggregate so that it is only possible to observe individual crystallites at the edges of the aggregates clearly.

For the 25 wt.% catalyst crystal particle size distribution from 20nm to larger aggregates.
STEM/EDS analysis of $7 \text{ MoO}_3/\text{ZrO}_2$ (A) catalyst

- Figures shows EDS analysis of an other aggregate of the 7Mo/ZrO2 (A) catalyst. This indicated compositional homogeneity of the sample

For the 25 wt.% catalyst it was some visible coarse scale inhomogeneity within the aggregates of the materials
## Combustion IR / Carbon content

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon content [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 MoO3/ZrO2</td>
<td>0.024</td>
</tr>
<tr>
<td>15 MoOC/ZrO2</td>
<td>0.024</td>
</tr>
<tr>
<td>15 Mo2C/ZrO2</td>
<td>0.097</td>
</tr>
<tr>
<td>7 Mo2C/ZrO2</td>
<td>0.074</td>
</tr>
<tr>
<td>25 Mo2C/ZrO2</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Support; ZrO$_2$-B (ca. 90 m$^2$/g, 80/400 Å bimodal pores, 0.31 cm$^3$/g)

Higher C content in the 15 and 25wt% samples than "base level"

Amounts are large enough to make a difference, if on surface
The document describes a Trickle-bed reactor with the following specifications:

- **1/8" ¼" o.d. stainless steel tube**
- **I.d. = ca. 4 mm**
- **200 mm**
- **115 mm**
- **SiC inert Catalyst bed**
- **Thermo-couple / aligned at inner wall**
- **Positioned at bed inlet**
- **T < 550 °C, < 100 bars**

The reactor is designed for downflow mode and operates within specified temperature and pressure limits.
Single (model) feed components

Phenol

Anisole

Guaiacol

Strategy: Target kinetics of simple feeds and models with different functionality
**Typical test conditions (liquid and gas phase)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SINTEF Liquid phase</th>
<th>SINTEF Gas phase</th>
<th>Univ. Gent Liquid phase</th>
<th>Univ. Gent Gas phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space time [Kg(_{\text{cat}}).s.mol(^{-1})]</td>
<td>100 - 1500</td>
<td>120 - 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)/phenolic ratio</td>
<td>ca. 100</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>30 - 70</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature [(\degree)C]</td>
<td>300 - 375</td>
<td>300 - 360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inert oil</td>
<td>n-decane</td>
<td>n-hexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenolic conc. [wt.%]</td>
<td>0.75 - 1.5</td>
<td>ca. 10 - 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle size [mm]</td>
<td>0.1 - 0.3</td>
<td>0.1 - 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Standard pretreatment = reduction in H\(_2\)

No effect of reduction observed at 350 \(\degree\)C (1.5 to 19 hours)
Phenolics and O removal potential

Temperature = 350 °C
Pressure = 60 bars

1.5wt.% Phenol
1.5wt.% Anisole

Conversion [%]

Contact time \( [g_{\text{cat}}, \, h/g_{\text{liq}}] \)

Initial data, \( t_0 \)

Gua / O - removal

= %O removal
Effect of Mo-oxide loading / Phenol HDO

Conversion of Phenol [%]

Time on stream [h]

LHSV = ca. 1 gPh/gcat·h

R14 7MoO₃/ZrO₂-A
R13 15MoO₃/ZrO₂-A
R33 25MoO₃/ZrO₂-A

Support ZrO₂ - A:
SSA = 50 m²/g
Pores = 160/600Å

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Performance comparison MoO$_3$ catalysts

**Operating conditions**

- Temperature (K): 613
- Pressure (MPa): 0.5
- Space time (kg$_{\text{cat}}$·s/mol$_{\text{anisole}}$): 124
- H$_2$/anisole (mol/mol) : 50

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**Conversion vs. Temperature**

- 7MoO$_3$/B-ZrO$_2$
- 15MoO$_3$/B-ZrO$_2$
- 25MoO$_3$/B-ZrO$_2$

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**Conversion vs. TOS**

- 7MoO$_3$
- 15MoO$_3$
- 25MoO$_3$

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**Additional Operating conditions**

- Pressure (MPa): 0.5
- Space time (kg$_{\text{cat}}$·s/mol$_{\text{anisole}}$): 156
- H$_2$/anisole (mol/mol) : 50
Effect of carburizing severity

Temperature = 350 °C
Pressure = 60 bars
1.5wt% phenol
LHSV = ca. 1.07 h⁻¹

R13 15MoO₃/ZrO₂ - A
R20 15MoOC/ZrO₂ - A
R23 15 Mo₂C/ZrO₂ - A

Fingerprint of product composition is also basically similar
Effect of carburization severity

Support; ZrO$_2$-B (ca. 90 m$^2$/g, 80/400 Å bimodal pores, 0.31 cm$^3$/g)

Operating conditions

- Temperature (K): 613
- Pressure (MPa): 0.5
- Space time (kg$_{\text{cat}.}$/s/mol$_{\text{anisole}}$): 124
- H$_2$/anisole (mol.mol$^{-1}$): 50

Temperature: 340 °C
Pressure: 5 bars
Anisole HDO, conversion and products

Green = O-free product

Temperature = 350 °C
Pressure = 60 bars
LHSV (anisole) = 0.24 g/gcat,h

Conversion

- Benzene
- Toluene
- Cresol
- Phenol

Conv - feed basis
Conv - product basis

- Benzene
- Cyclohexene
- Toluene
- Phenol
- Cresol

Time on stream [hours]

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Coordinator: SINTEF
Typical product selectivity distribution
MoO$_3$/ZrO$_2$ and carburized analogues

Operating conditions
- Temperature (K): 613
- Pressure (MPa): 0.5
- Space time ($\text{kg}_{\text{cat}}\cdot\text{s}/\text{mol}_{\text{anisole}}$): 124
- $\text{H}_2$/anisole (mol.mol$^{-1}$): 50
- $40 - 50\%$ oxygen removal efficiency

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Main Pathways Phenol HDO
(Systems; MoO$_3$ and carburized analogues)

Carbonaceous, coverage and/or polymerization

"Pre-stage of gum?"

Same basic fingerprint with very high hydrogenolysis to hydrogenation ratio.
Main pathways Phenol HDO

(SoA system: CoMo/ZrO₂)

Cyclohexanol not observed (350 °C)

Co introduces higher hydrogenation activity and poorer stability

EU project, FP7-NMP: FAST industrialisation by CATalysts Research and Development Coordinator: SINTEF
Main Pathways Anisole HDO Liquid Phase

(MoO$_3$ on ZrO$_2$)

Anisole $\xrightarrow{H_2} \text{Phenol} \xrightarrow{H_2} \text{Cyclohexenes}$

- Anisole $\quad \text{OCH}_3$
- Phenol $\quad \text{OH}$
- Cyclohexenes
- Cresol $\quad \text{CH}_3\text{OH}$
- Toluene $\quad \text{CH}_3$

Light prod.: Hydrogenolysis
TA: transalkylation

10% 10% 10%
Conclusions

Catalyst and active phase

- A loading of 12 wt.% Mo more optimal than 7 and 19 wt.%
- The first 7 wt.% Mo has highest activity, though
- Activity is related to Mo oxide in a high oxidation state

Carburization

- Causing reduction
- Some surface carbon formed, but position/state is not clear
- Carburization is not providing positive effects on performance

Liquid phase versus gas phase HDO

Similar order of activity

- **Loading;** 7, 12, 19 wt.% MoO₃/ZrO₂
- **Carburization severity;** MoO₃/ZrO₂ and its carburized analogues

Differences in O removal efficiency

- Transalkylation and isomerization reactions more prominent at gas phase conditions, i.e. at higher reactant concentrations and lower H₂ pressures
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