Hydroconversion of lignin-monomer over alumina-supported Pd and Ni catalysts

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www.ttk.hu/palyazatok/bioeconomy
Lignocellulose as source of carbon and energy

Current carbon and energy resources

- Petroleum 34%
- Natural gas 24%
- Coal 28%
- Renewable 10%
- Nuclear 4%
- Wind 18%
- Geothermal and Biomass 9%
- Solar 7%

Distribution of energy sources (BP Statistical Review of World Energy)

Structure of lignocellulose

Lignin utilization

Biomass → FRACTIONATION → Isolated lignin → BIO-BASED MATERIALS

Carbon fiber

High MW Lignin

Chemical/Thermal Depolymerization

Low MW Lignin

Asphalt binder

BIO-oxygenates

http://biomassmagazine.com/articles/14388/researchers-use-waste-lignin-to-make-carbon-fiber
Products from GUA could replace the materials of fossil origin.
Objectives:

- to convert GUA to value-added materials
- to elucidate the pathways of product formation
- optimization of HDO catalysts
## Catalyst preparation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursor</th>
<th>Support</th>
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</thead>
<tbody>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>Pd(NH$_3$)$_4$(NO$_3$)$_2$</td>
<td>γ–Al$_2$O$_3$ (Alfa Aesar)</td>
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<td>Ni(NO$_3$)$_2$·6H$_2$O</td>
<td></td>
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<tr>
<td>Pd/Al$_2$O$_3$ (P)</td>
<td>Pd(NH$_3$)$_4$(NO$_3$)$_2$</td>
<td>γ–Al$_2$O$_3$ (Alfa Aesar) impregnated with H$_3$PO$_4$ solution, dried and calcined (550 °C, 4h)</td>
</tr>
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- **Impregnation**: metal salt solution
- **Calcination**: 350 °C (Pd), 450 °C (Ni), 4h → PdO NiO
- **In situ reduction**: 350 °C (Pd), 450 °C, 550 °C (Ni), 2h, H$_2$ → Pd$^0$ Ni$^0$

- Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor
Metal impregnation has no influence on SSA

Impregnation of Al₂O₃ support with H₃PO₄ solution reduces SSA

Al₂O₃ is the only detectable phase

NiO and PdO crystallites are well dispersed on the Al₂O₃ surface
Surface structure of phosphated $\gamma$-alumina

**FT-IR spectra in the vOH region**
(ev. 450 °C, 1 h)

Phosphoric acid reacts with the hydroxyls of alumina $\rightarrow$ monomeric and polymeric phosphate species are formed

**OH groups** (G. Busca, Cat. Today 226 (2014) 2.)

$\gamma$-Al$_2$O$_3$
- 3770 cm$^{-1}$, $\square$-O-$\text{Al}^{IV}$-OH, (terminal)$_{tetra}$ with vacancy
- 3728 cm$^{-1}$, Al$^{VI}$-OH, (terminal)$_{octa}$ without and with vacancy
- 3673 cm$^{-1}$, Al-O(H)-Al, bridged
- 3588 cm$^{-1}$, triple-bridged

$\gamma$-Al$_2$O$_3$(P)
- 3791 cm$^{-1}$, Al$^{IV}$-OH, (terminal)$_{tetra}$
- 3676 cm$^{-1}$, P-OH on phosphates

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On the Al$_2$O$_3$ (P) support the intensity of bands at 1450, 1455 cm$^{-1}$ and 1615, 1624 cm$^{-1}$ is lower than on lower Lewis acidity.

Phosphorus modification reduces the Lewis acidity of the alumina support.

Pd can be easily reduced around 100 °C (not shown in the figure).

The degree of reduction at 450 °C:
- Ni/Al$_2$O$_3$ ~ 4.5 % of Ni (H/Ni=0.09)
- Ni/Al$_2$O$_3$ (P) ~ 0.5% (H/Ni=0.01)
* Ni/Al$_2$O$_3$ (P) (550) ~ 3.5% (H/Ni=0.07)
Activity of Al₂O₃ and Al₂O₃ (P) supports

300 °C, 10 bar, 1 g_{cat}/g_{GUA} * h, H₂/GUA=20

- Demethylation (DME) and transalkylation (AL) are the main reactions
- CAT derivatives are the main products
- Demethoxylation (DMO) and dehydroxylation (DHO) also takes place
- PHE derivatives were also formed

CH₄, Others, CHL derivatives, CAT derivatives, PHE derivatives, BEN derivatives, CHN derivatives, Cycloalkanes
Comparison of catalysts activity

$300 \, ^\circ C, \, 10 \, \text{bar}, \, 1 \, \text{g}_{\text{cat}}/\text{g}_{\text{GUA}} \ast \text{h}$

$\text{H}_2/\text{GUA}=20$, time-on-stream $= 2 \, \text{h}$

$\text{H}_2/\text{GUA}=20$, time-on-stream $= 38 \, \text{h}$ ($\ast = 4 \, \text{h}$)

- Cyclohexanones and cycloalkanes are the main products on $\text{Pd/Al}_2\text{O}_3$
- O-free compounds were mainly formed on $\text{Ni/Al}_2\text{O}_3$
- Aromatics (phenols, catechols) were formed on $\text{Ni/Al}_2\text{O}_3 \,(\text{P})$ and $\text{Ni/Al}_2\text{O}_3 \,(\text{P})(550)$
Effect of temperature

Pd/Al₂O₃

10 bar, 1 g_cat/g_GUA *h, H₂/GUA=20

Pd/Al₂O₃ (P)

The yield of phenols increases with temperature

1-Methoxycyclohexane and 2-methoxy-cyclohexanone were also formed (not shown)

The yield of aromatics (phenols, catechols) increases with temperature

1,2-Dimethoxybenzene was also formed at lower temperature (not shown)
Effect of temperature

At 225 °C cyclohexanols were the main products
At 250 °C high yield and selectivity to CHA
With temperature the yield of benzenes increased as dehydrogenation is accelerated

The yield of phenols increases with temperature
Effect of space time and total pressure on Ni/Al₂O₃

225 °C, 10 bar, H₂/GUA=20

- At lower space time phenol and benzol intermediates appear in the product mixture
- GUA hydrodeoxygenation to CHL and CHA proceeds through PHE and BEN intermediates

300 °C, 1 gₐₙ/cat/g₂₀₆*ₐₙ , H₂/GUA=20

- At lower pressure the hydrogenation activity is lower
- With total pressure more hydrogenated products were formed
The sequential steps of GUA hydroconversion can be controlled by using noble and non-noble metal and modifying the alumina support.

Pd/Al₂O₃ catalyst shows high activity and selectivity in GUA hydrodeoxygenation to cyclohexanones.

Ni/Al₂O₃ catalyzed hydroconversion of GUA to O-free compounds like cyclohexane.

Pd and Ni supported on phosphorus-modified alumina behave similarly, they are selective to aromatics.

Pd/Al₂O₃(P) and Ni/Al₂O₃(P) catalysts remain active in demethylation and demethoxylation, but lose their ability to hydrogenate the aromatic ring. (low hydrogenation activity, and/or weaker interaction between substrate molecules and phosphated support)
Thank you for your kind attention!

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