Hydrodeoxygenation of lignin-derived guaiacol on supported Pd and Ni catalysts using neat and phosphorus-modified $\gamma$-alumina supports

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2nd International Conference on Reaction Kinetics, Mechanisms and Catalysis, 20–22 May 2021 Budapest, Hungary
Lignocellulose as source of carbon and energy

Current carbon and energy resources

- Petroleum 34%
- Natural gas 24%
- Nuclear 4%
- Renewable 10%
- Coal 28%

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

Structure of lignocellulose


Lignin depolymerization

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>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃</td>
<td>Pd(NH₃)₄(NO₃)₂</td>
<td>γ–Al₂O₃ (Alfa Aesar)</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>γ–Al₂O₃ (Alfa Aesar)</td>
</tr>
<tr>
<td>Pd/Al₂O₃ (P)</td>
<td>Pd(NH₃)₄(NO₃)₂</td>
<td>impregnated with H₃PO₄ solution, dried and calcined (550 °C, 4h)</td>
</tr>
<tr>
<td>Ni/Al₂O₃ (P)</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td></td>
</tr>
</tbody>
</table>

- **Impregnation:** metal salt solution
- **Calcination:** 350 °C (Pd), 450 °C (Ni), 4h → PdO, NiO
- **In situ reduction:** 350 °C (Pd), 450 °C (Ni), 2h, H₂ → Pd⁰, Ni⁰

Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor.
### Catalyst characterization

#### Metal and P content; Specific surface area (SSA)

<table>
<thead>
<tr>
<th>Supports and catalysts</th>
<th>Metal content wt%</th>
<th>P content wt%</th>
<th>SSA m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>196</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>0.47</td>
<td>-</td>
<td>194</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>5.21</td>
<td>-</td>
<td>192</td>
</tr>
<tr>
<td>Al₂O₃ (P)</td>
<td>-</td>
<td>-</td>
<td>167</td>
</tr>
<tr>
<td>Pd/Al₂O₃ (P)</td>
<td>0.49</td>
<td>4.87</td>
<td>163</td>
</tr>
<tr>
<td>Ni/Al₂O₃ (P)</td>
<td>5.06</td>
<td>4.82</td>
<td>165</td>
</tr>
</tbody>
</table>

- Metal impregnation has no influence on SSA
- Impregnation of Al₂O₃ support with H₃PO₄ solution reduces SSA

#### X-ray diffraction (XRD)

- Al₂O₃ is the only detectable phase
- NiO and PdO crystallites are well dispersed on the Al₂O₃ surface
Surface structure of phosphated γ-alumina

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

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

$$\gamma-\text{Al}_2\text{O}_3(\text{P})$$

- 3791 cm\(^{-1}\), \(\square\)-O-Al\(^{IV}\)-OH, (terminal)\(_{tetr}\) with vacancy
- 3728 cm\(^{-1}\), Al\(^{VI}\)-OH, (terminal)\(_{oct}\) without and with vacancy
- 3673 cm\(^{-1}\), Al-O(H)-Al, bridged
- 3588 cm\(^{-1}\), triple-bridged

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

- 3770 cm\(^{-1}\), \(\square\)-O-Al\(^{IV}\)-OH, (terminal)\(_{tetr}\) with vacancy
- 3728 cm\(^{-1}\), Al\(^{VI}\)-OH, (terminal)\(_{oct}\) without and with vacancy
- 3673 cm\(^{-1}\), Al-O(H)-Al, bridged
- 3588 cm\(^{-1}\), triple-bridged

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

\(^{a}\)Stanislaus et al., Appl. Cat. 39 (1988) 239; A. Vikár et al., manuscript under preparation
On the Al₂O₃ (P) support the intensity of bands at 1450, 1455 cm⁻¹ and 1615, 1624 cm⁻¹ is lower lower Lewis acidity

Phosphorus modification reduces the Lewis acidity of the alumina support

Pd can be reduced at room temperature (not shown in the figure)

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

$\text{Al}_2\text{O}_3$

$300 \degree \text{C}, 10 \text{ bar, } 1 \text{ g}_{\text{cat}}/\text{g}_{\text{GUA}} \ast \text{h, } \text{H}_2/\text{GUA}=20$

$\text{Al}_2\text{O}_3$ (P)

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
Comparison of catalysts activity

300 °C, 10 bar, 1 g_{cat}/g_{GUA} * h, 
H_{2}/GUA=20, time-on-stream = 4 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>GUA conversion, Products, TIC %</th>
</tr>
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<tr>
<td>Al_{2}O_{3}</td>
<td>[Diagram]</td>
</tr>
<tr>
<td>Pd/Al_{2}O_{3}</td>
<td>[Diagram]</td>
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<td>Ni/Al_{2}O_{3}</td>
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- Cyclohexanones and cycloalkanes are the main products on Pd/Al_{2}O_{3}
- O-free compounds were mainly formed on Ni/Al_{2}O_{3}
- Aromatics (phenols, catechols) were formed on Pd/Al_{2}O_{3} (P) and Ni/Al_{2}O_{3} (P)
The yield of CHN derivatives is high at 250 °C and does not change 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)
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 aromatics (phenols, catechols) increases with temperature
**Effect of space time and total pressure on Ni/Al₂O₃**

- **225 °C, 10 bar, H₂/GUA=20**
  - Bar charts show GUA conversion, Products, TIC % over space time (0.25 to 1 h).
  - Space time, h: 0.25, 0.5, 0.75, 1.
  - Products and TIC % are visually represented.

- **300 °C, 1 g cat/g GUA * h, H₂/GUA=20**
  - Bar charts show GUA conversion, Products, TIC % over total pressure (1 to 10 bar).
  - Total pressure, bar: 1, 5, 10.
  - Products and TIC % are visually represented.

- **Chemical Reactions and Products**
  - GUA to Me-PHE (alkylation).
  - Me-PHE to CAT (hydrodeoxygenation).
  - CAT to DHO (dehydroxylation).
  - DHO to DME (dimerization).
  - DME to PHE (alkylation).
  - PHE to OH (hydrodeoxygenation).
  - OH to CHL (hydrogenation).
  - CHL to Me-CHA (alkylation).

- **Key Observations**
  - At lower space time, phenol intermediates appear in the product mixture.
  - GUA hydrodeoxygenation to CHL and CHA proceeds through PHE intermediates.
  - At lower pressure, the hydrogenation activity is lower.
  - With total pressure, more hydrogenated products were formed.
Conclusions

✓ The sequential steps of GUA hydrodeoxygenation can be controlled by using noble and non-noble metal and modifying the alumina support.

✓ Both neat and phosphorus-modified Al$_2$O$_3$ supports are active in demethylation of GUA to form catechol.

✓ Pd/Al$_2$O$_3$ catalyst shows high activity and selectivity in GUA hydrodeoxygenation to cyclohexanones.

✓ Ni/Al$_2$O$_3$ catalyzed hydrodeoxygenation of GUA to O-free compounds like cyclohexane.

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

✓ Pd/Al$_2$O$_3$(P) and Ni/Al$_2$O$_3$(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!

Acknowledgement