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

Gyula Novodárszki, József Valyon, Alexander Kaszonyi, Dhanapati Deka, Magdolna R. Mihályi

Renewable Energy Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, Budapest H-1117, Hungary

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**

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

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

**Structure of lignocellulose**

- **Cellulose**
- **Lignin**
- **Hemicellulose**

**Chemical/Thermal depolymerization**

- Lignin
- Bio-oxygenates

Guaiacol-based chemicals

- Lignin

- Products from GUA could replace the materials of fossil origin

- OH

- GUA

- OH

- CHL

- CHN

- PHE

- BEN

- TOL (BTX)

- XIL

- CHA

- Me-CHA

- Nylon

- Biofuel

- Drugs, cosmetics, pharmaceuticals

- Rubber, plastic

- H₂ production, storage, transport
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></td>
</tr>
<tr>
<td>Pd/Al₂O₃ (P)</td>
<td>Pd(NH₃)₄(NO₃)₂</td>
<td>γ-Al₂O₃ (Alfa Aesar) 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
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 γ-alumina

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

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

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

γ-Al₂O₃
- 3770 cm⁻¹, □-O-AlIV-OH, (terminal)₄ with vacancy
- 3728 cm⁻¹, AlVI-OH, (terminal)₈ without and with vacancy
- 3673 cm⁻¹, Al-O(H)-Al, bridged
- 3588 cm⁻¹, triple-bridged

γ-Al₂O₃(P)
- 3791 cm⁻¹, AlIV-OH, (terminal)₄
- 3676 cm⁻¹, P-OH on phosphates

γ-Al₂O₃

^aStanislaus et al., Appl. Cat. 39 (1988) 239; A. Vikár et al., manuscript under preparation
On the Al$_2$O$_3$ (P) support the intensity of bands at 1450, 1455 cm$^{-1}$ and 1615, 1624 cm$^{-1}$ is lower. 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/Al$_2$O$_3$ ~ 4.5 % of Ni (H/Ni=0.09)
- Ni/Al$_2$O$_3$ (P) ~ 0.5% (H/Ni=0.01)
Activity of Al$_2$O$_3$ and Al$_2$O$_3$ (P) supports

Al$_2$O$_3$

300 °C, 10 bar, 1 g$_{\text{cat}}$/g$_{\text{GUA}}$ *h, H$_2$/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

CH$_4$

Others

CHL derivatives

CAT derivatives

PHE derivatives

BEN derivatives

CHN derivatives

Cycloalkanes
Cyclohexanones and cycloalkanes are the main products on Pd/Al$_2$O$_3$.

- 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
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

European Regional Development Fund (Interreg, SKHU/1902/4.1/001/Bioeconomy) www.skhu.eu