

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

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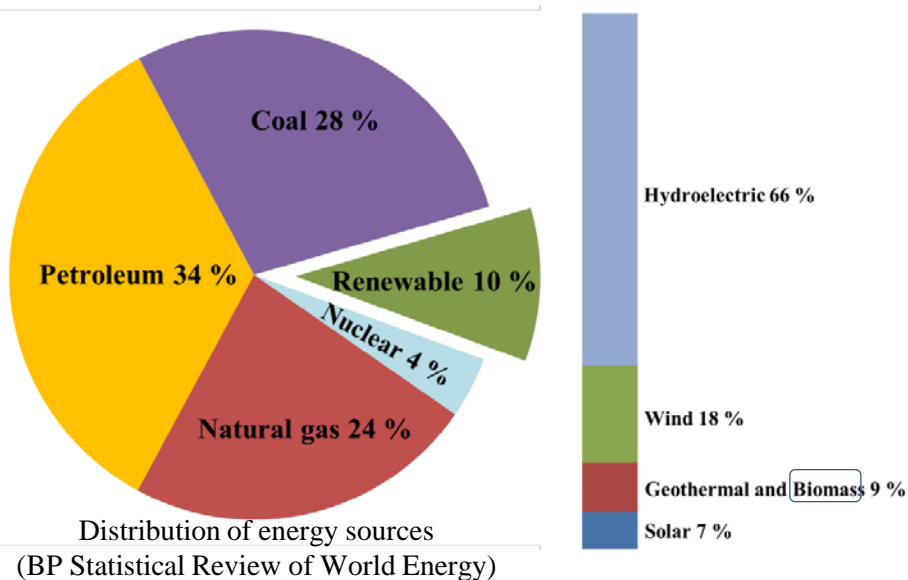


Building Partnership

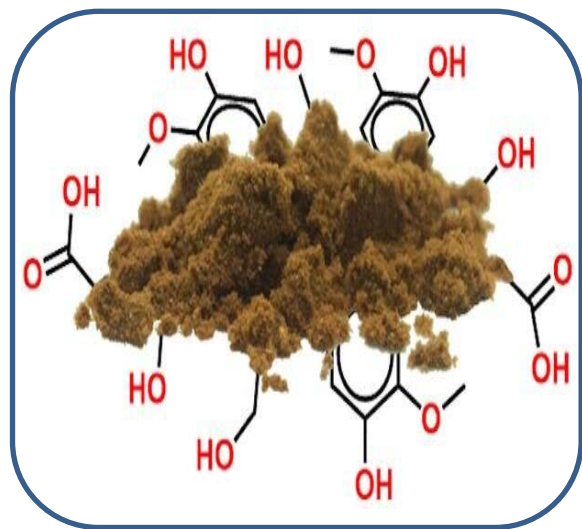
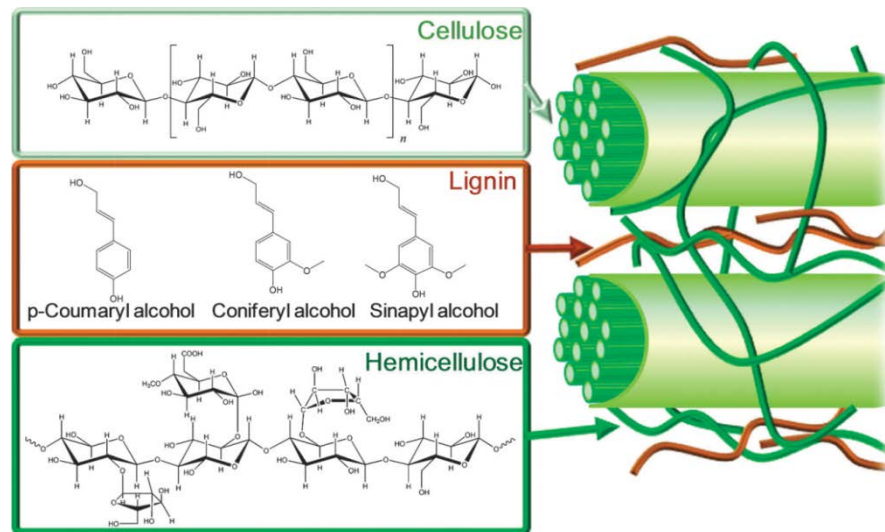


Lignocellulose as source of carbon and energy

Current carbon and energy resources

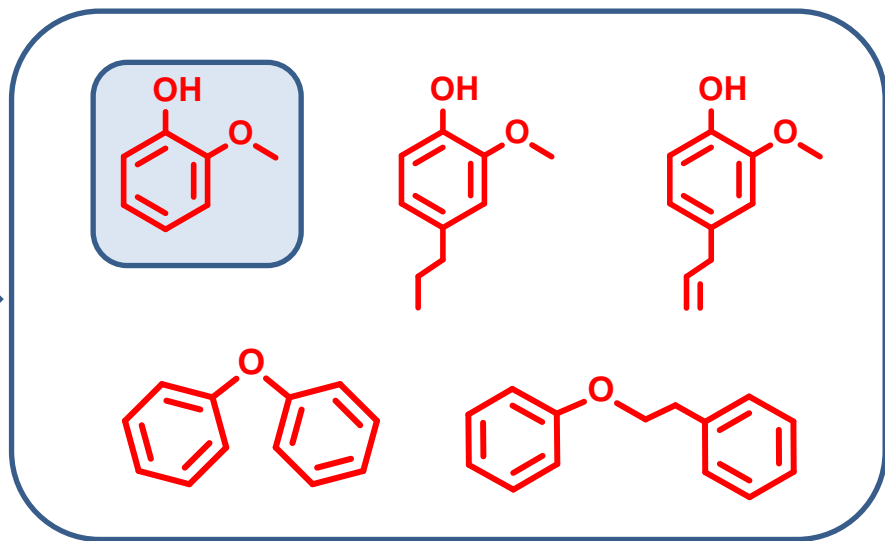


Structure of lignocellulose



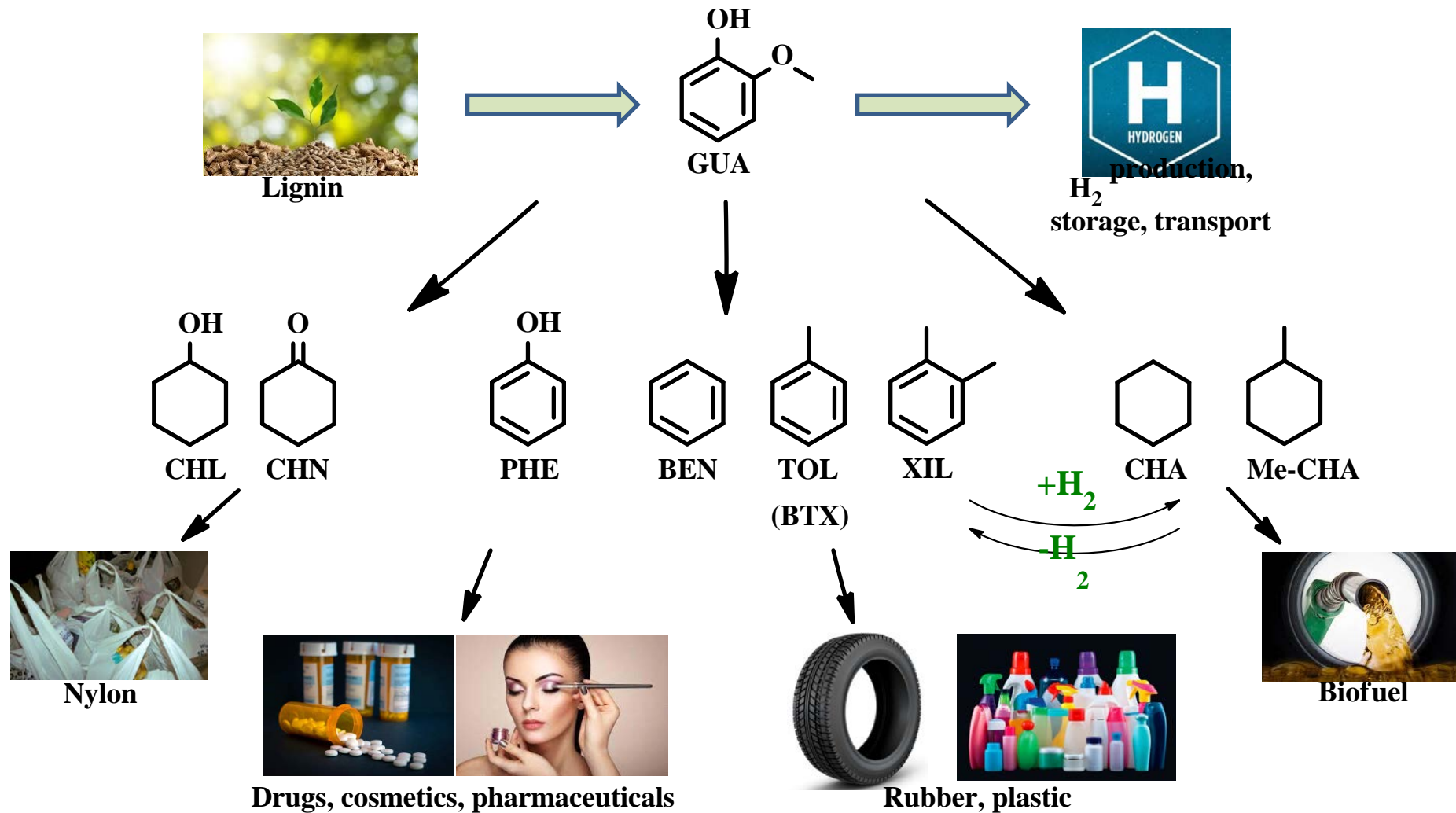
Lignin

chemical/thermal
depolymerization



Bio-oxygenates

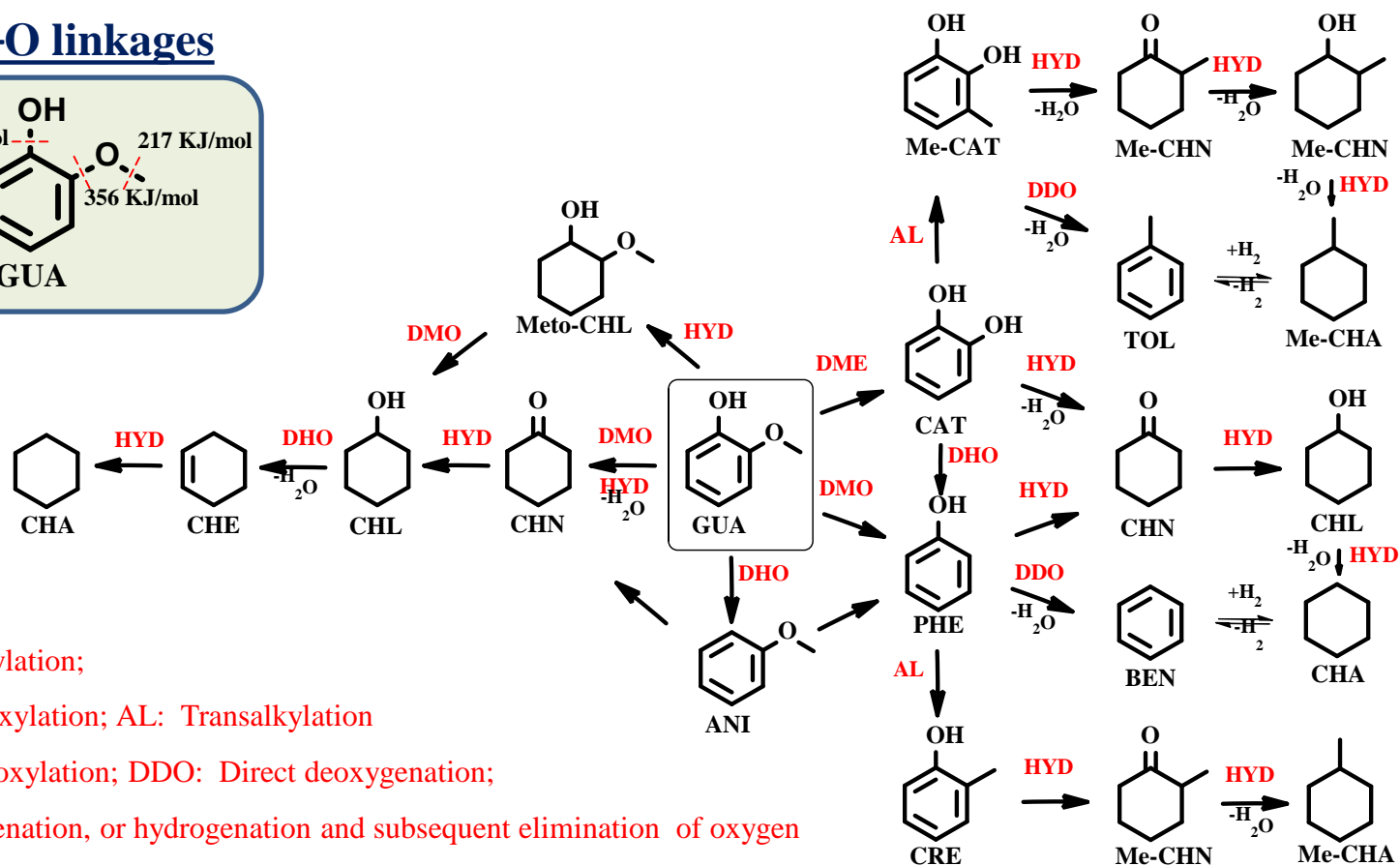
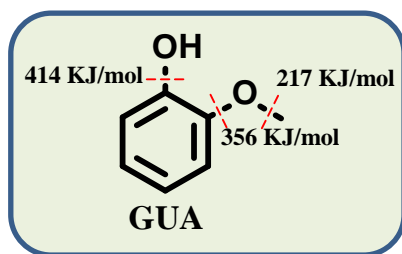
Guaiacol-based chemicals



➤ Products from GUA could replace the materials of fossil origin

Reaction pathways of guaiacol hydrodeoxygenation

C–O linkages



DME: Demethylation;

DHO: Dehydroxylation; AL: Transalkylation

DMO: Demethoxylation; DDO: Direct deoxygenation;

HYD: Hydrogenation, or hydrogenation and subsequent elimination of oxygen

ChemCatChem 4 (2012) 64; ACS Catal. 3 (2013) 1774; App. Cat. A 512 (2016) 93; App. Cat. B 270 (2020) 118890

Objectives:

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

Catalyst preparation

Catalyst	Precursor	Support
Pd/Al ₂ O ₃	Pd(NH ₃) ₄ (NO ₃) ₂	γ-Al ₂ O ₃ (Alfa Aesar)
Ni/Al ₂ O ₃	Ni(NO ₃) ₂ ·6H ₂ O	
Pd/Al ₂ O ₃ (P)	Pd(NH ₃) ₄ (NO ₃) ₂	γ-Al ₂ O ₃ (Alfa Aesar) impregnated with H ₃ PO ₄ solution, dried and calcined (550 °C, 4h)
Ni/Al ₂ O ₃ (P)	Ni(NO ₃) ₂ ·6H ₂ O	

➤ **Impregnation: metal salt solution**

➤ **Calcination: 350 °C (Pd), 450 °C (Ni), 4h** \longrightarrow PdO
NiO

➤ **In situ reduction: 350 °C (Pd), 450 °C (Ni), 2h, H₂** \longrightarrow Pd⁰
Ni⁰

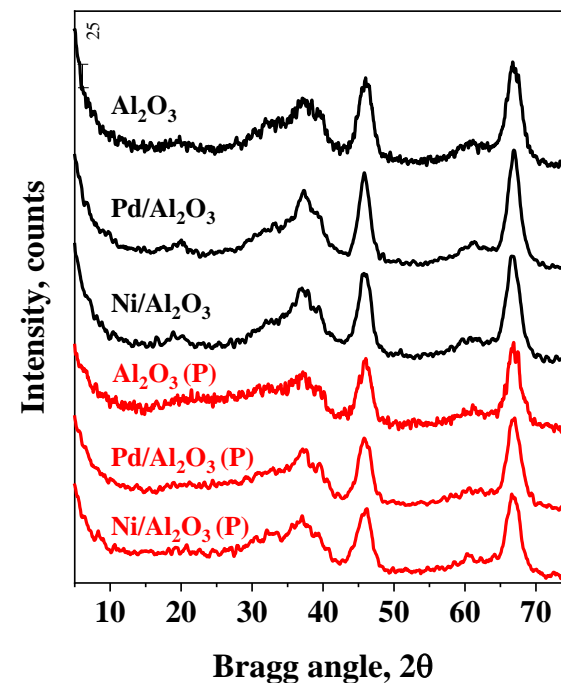
➤ Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor

Catalyst characterization

Metal and P content; Specific surface area (SSA)

Supports and catalysts	Metal content wt%	P content wt%	SSA m ² /g
Al ₂ O ₃	-	-	196
Pd/Al ₂ O ₃	0.47	-	194
Ni/Al ₂ O ₃	5.21	-	192
Al ₂ O ₃ (P)	-	-	167
Pd/Al ₂ O ₃ (P)	0.49	4.87	163
Ni/Al ₂ O ₃ (P)	5.06	4.82	165

X-ray diffraction (XRD)

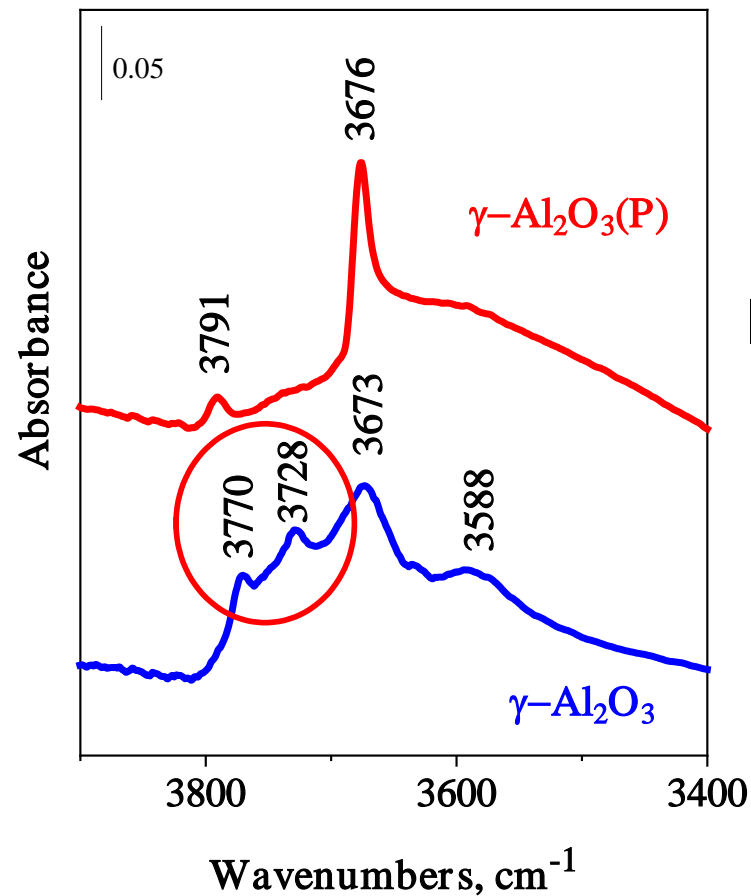


- Metal impregnation has no influence on SSA
- Impregnation of Al₂O₃ support with H₃PO₄ solution reduces SSA

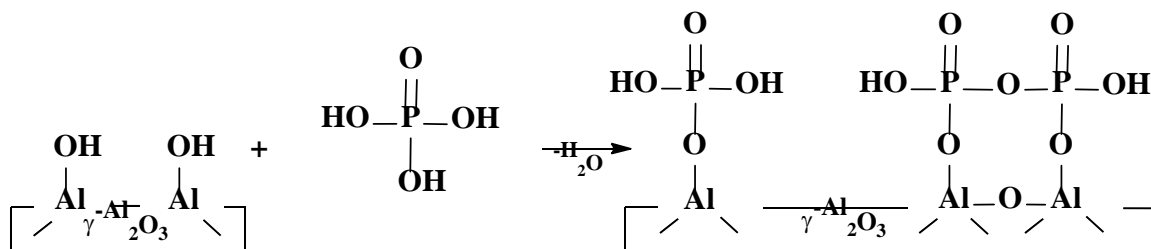
- Al₂O₃ is the only detectable phase
- NiO and PdO crystallites are well dispersed on the Al₂O₃ surface

Surface structure of phosphated γ -alumina

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



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



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

γ -Al₂O₃

- 3770 cm⁻¹, □-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

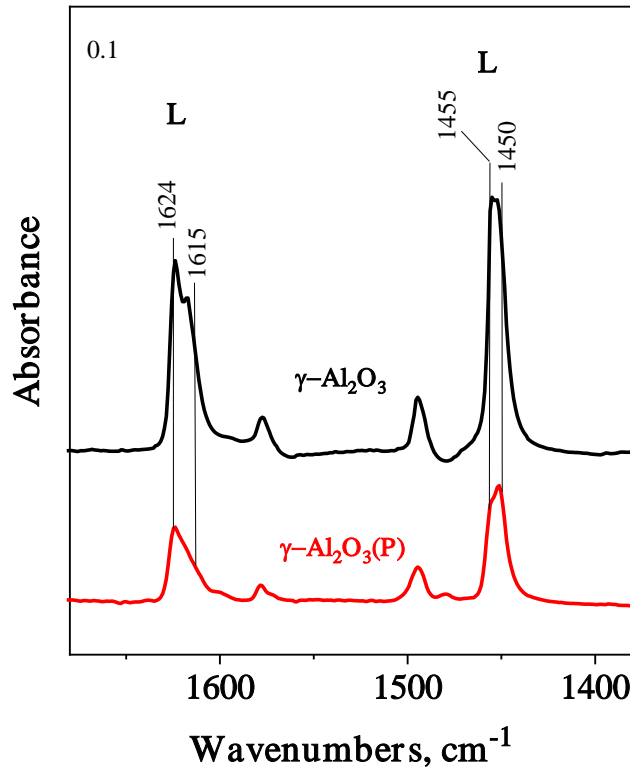
γ -Al₂O₃(P)

- 3791 cm⁻¹, Al^{IV}-OH, (terminal)_{tetr}
- 3676 cm⁻¹, P-OH on phosphates

^aStanislaus et al., Appl. Cat. 39 (1988) 239; A. Vikár et al., manuscript under preparation

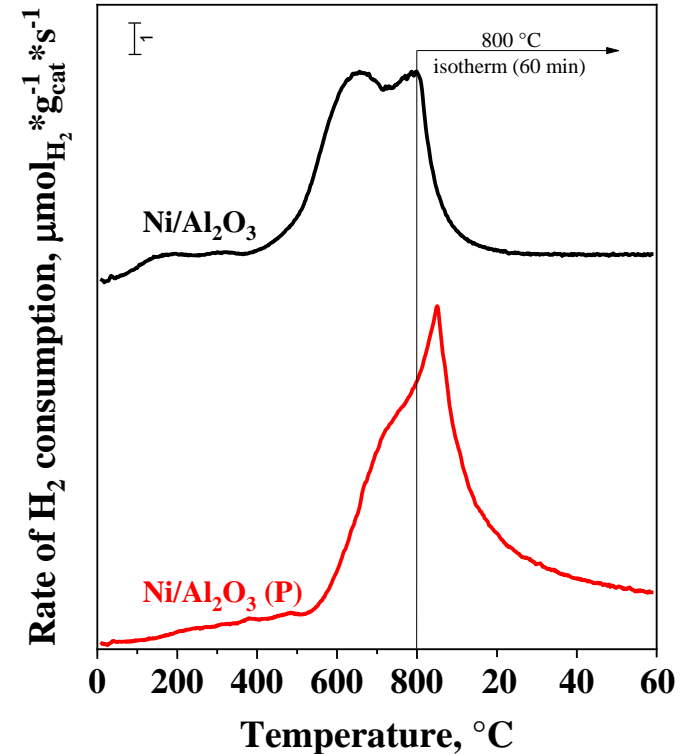
Catalysts acidity and reducibility

FT-IR spectra of adsorbed pyridine



- On the $\text{Al}_2\text{O}_3(\text{P})$ support the intensity of bands at 1450, 1455 cm^{-1} and 1615, 1624 cm^{-1} is lower \longrightarrow lower Lewis acidity
- Phosphorus modification reduces the Lewis acidity of the alumina support

Temperature-programmed reduction (TPR)



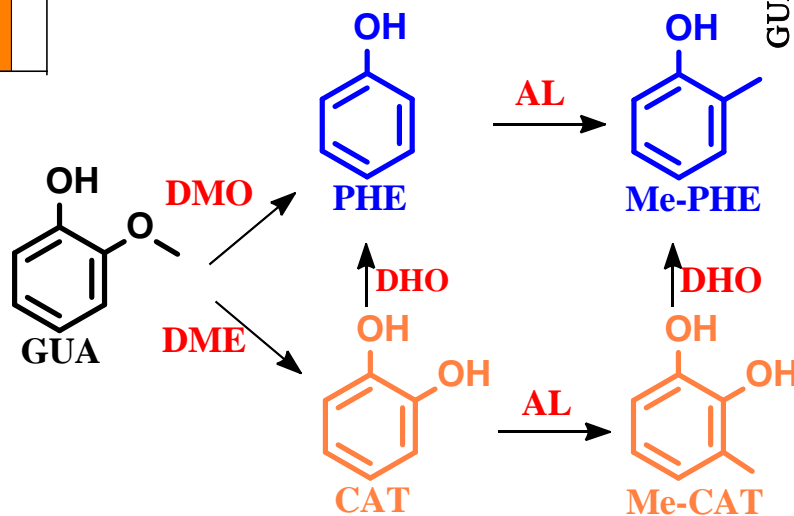
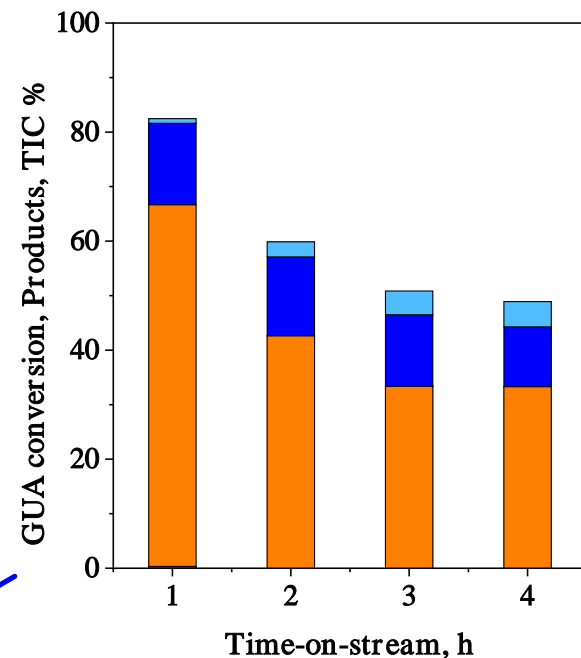
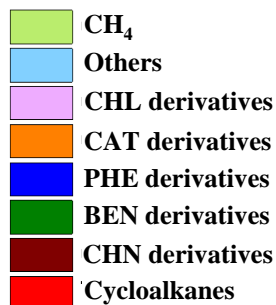
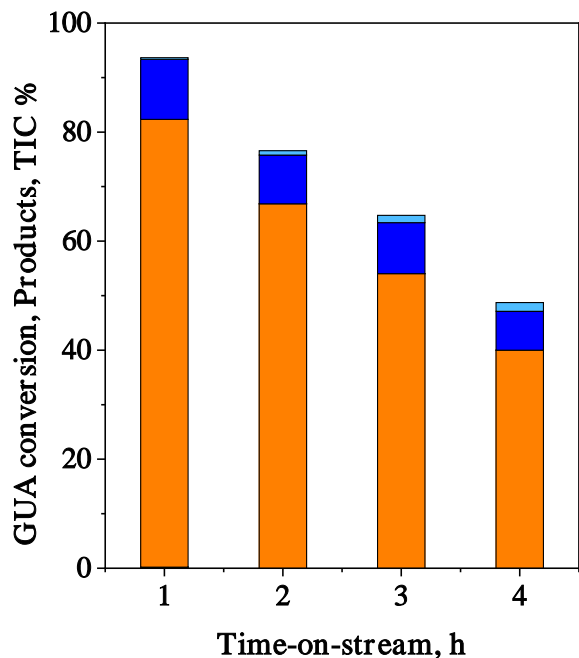
- Pd can be reduced at room temperature (not shown in the figure)
- The degree of reduction at 450 $^{\circ}\text{C}$:
 - $\text{Ni}/\text{Al}_2\text{O}_3 \sim 4.5\%$ of Ni ($\text{H}/\text{Ni}=0.09$)
 - $\text{Ni}/\text{Al}_2\text{O}_3(\text{P}) \sim 0.5\%$ ($\text{H}/\text{Ni}=0.01$)

Activity of Al₂O₃ and Al₂O₃ (P) supports

Al₂O₃

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

Al₂O₃ (P)



➤ Demethylation (DME) and transalkylation (AL) are the main reactions

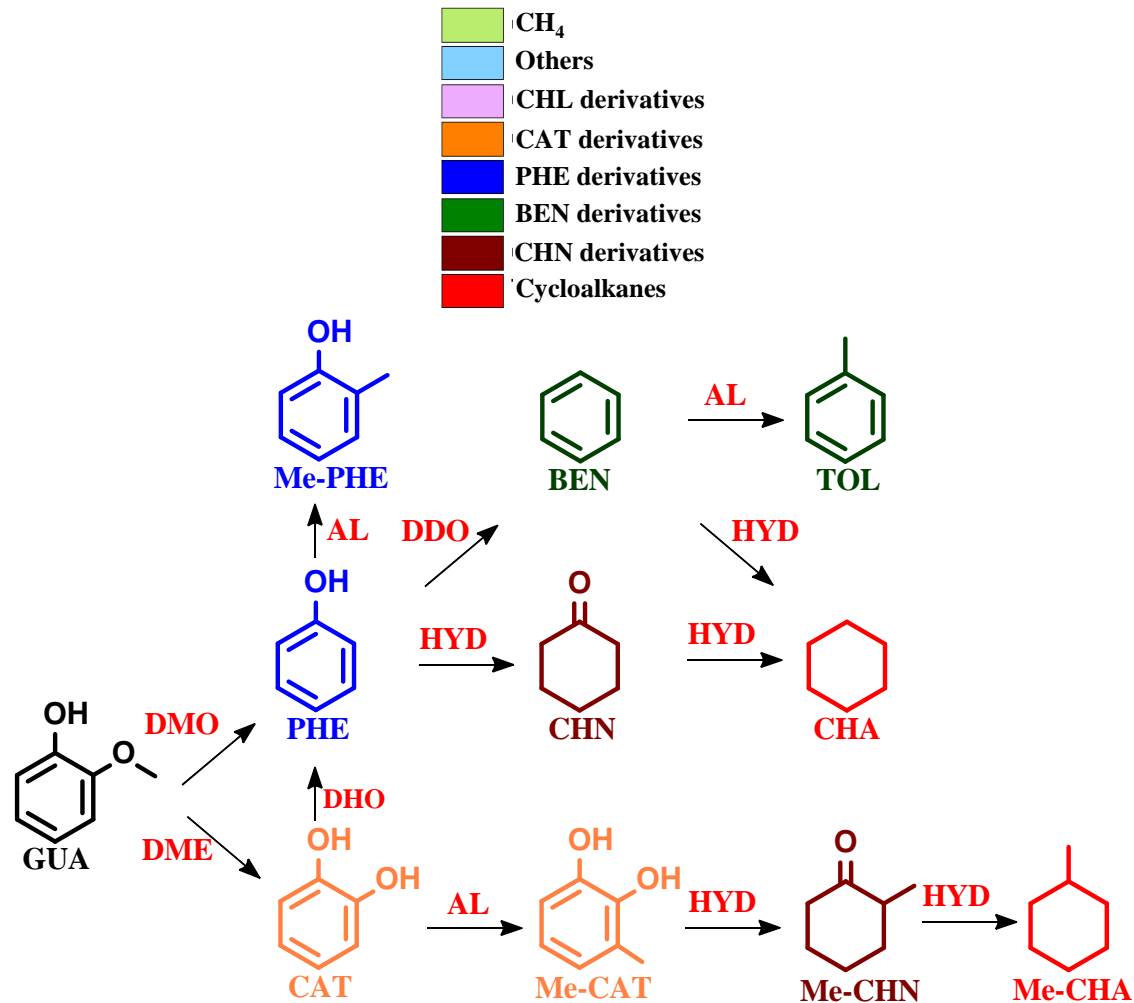
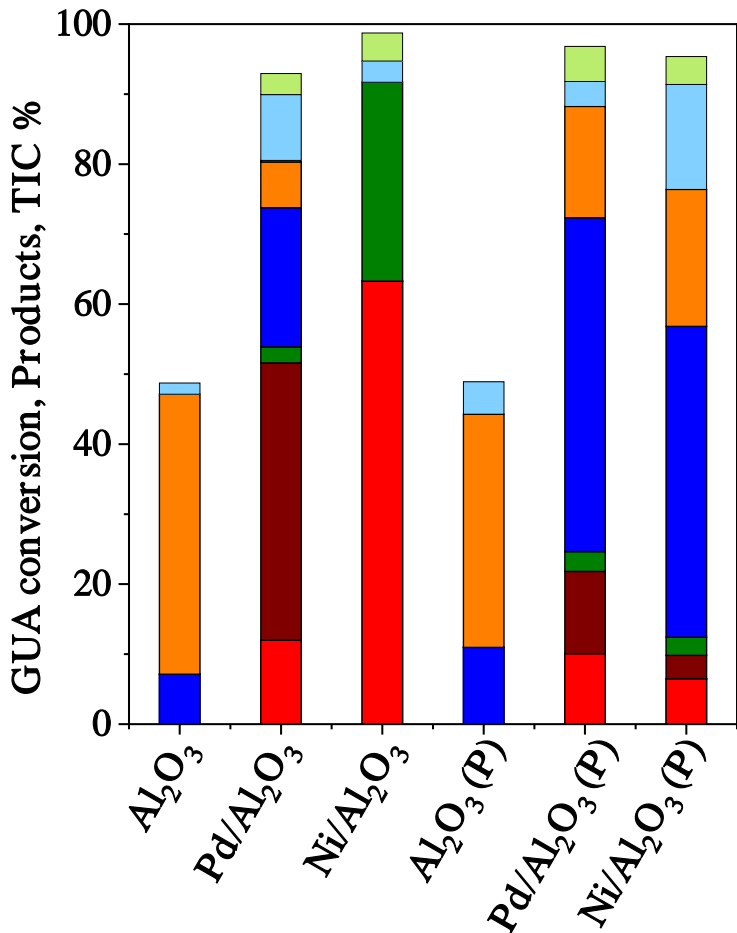
➤ CAT derivatives are the main products

➤ 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,
H₂/GUA=20, time-on-stream = 4 h



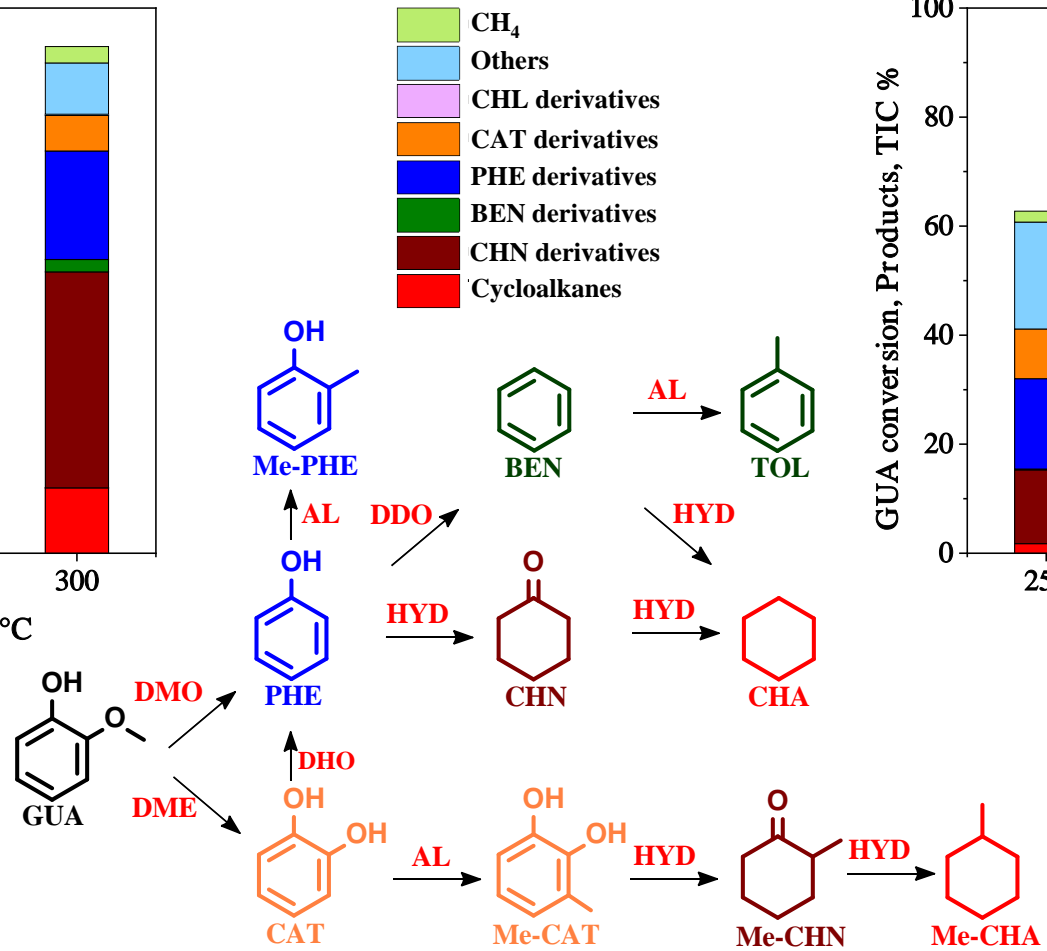
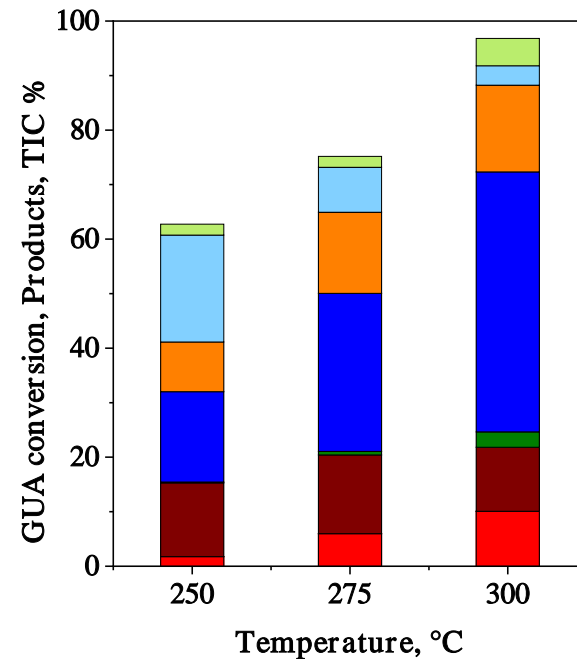
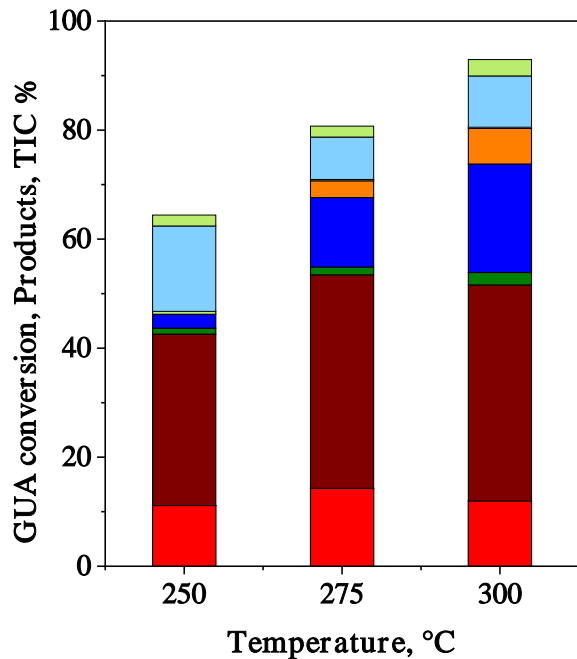
- Cyclohexanones and cycloalkanes are the main products on Pd/Al₂O₃
- O-free compounds were mainly formed on Ni/Al₂O₃
- Aromatics (phenols, catechols) were formed on Pd/Al₂O₃ (P) and Ni/Al₂O₃ (P)

Effect of temperature

Pd/Al₂O₃

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

Pd/Al₂O₃ (P)



- The yield of CHN derivatives is high at 250 °C and does not change with temperature
- 1-Methoxycyclohexane and 2-methoxycyclohexanone were also formed (not shown)

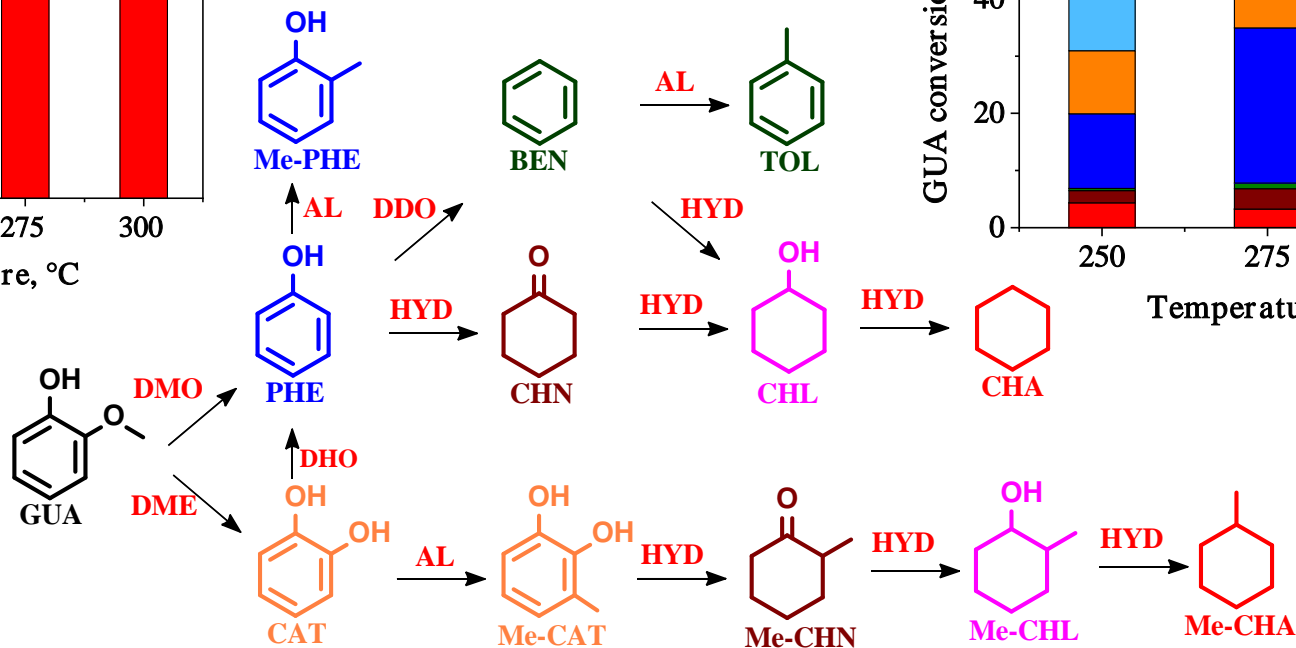
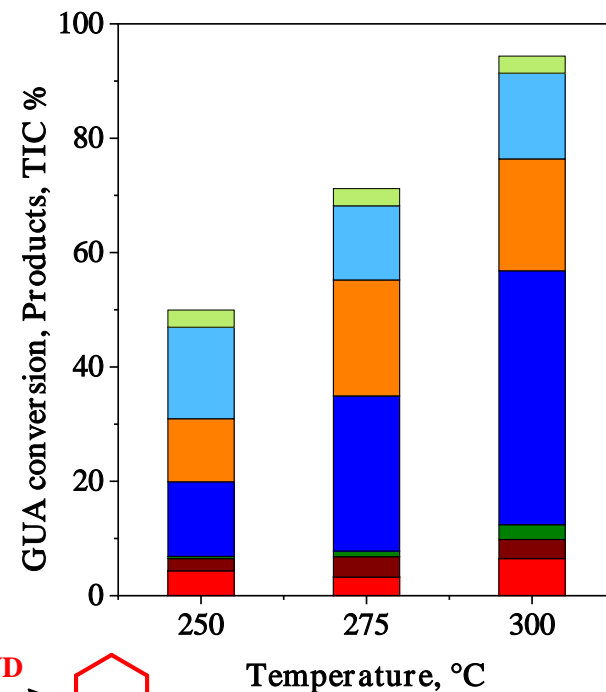
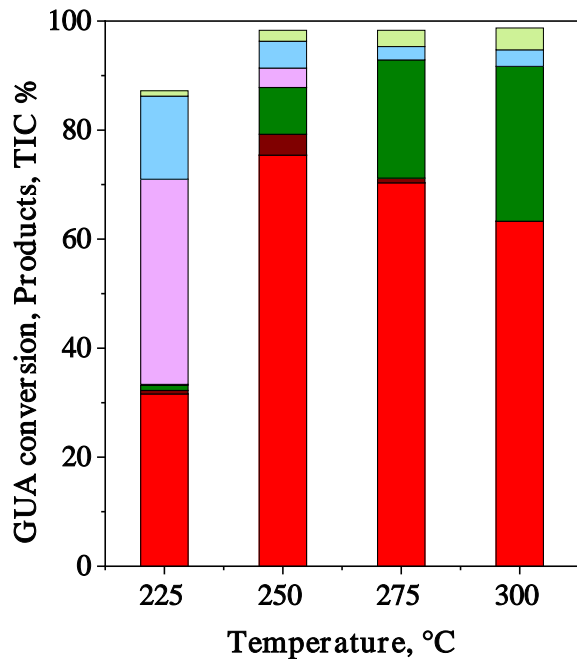
- The yield of aromatics (phenols, catechols) increases with temperature
- 1,2-Dimethoxybenzene was also formed at lower temperature (not shown)

Effect of temperature

Ni/Al₂O₃

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

Ni/Al₂O₃ (P)



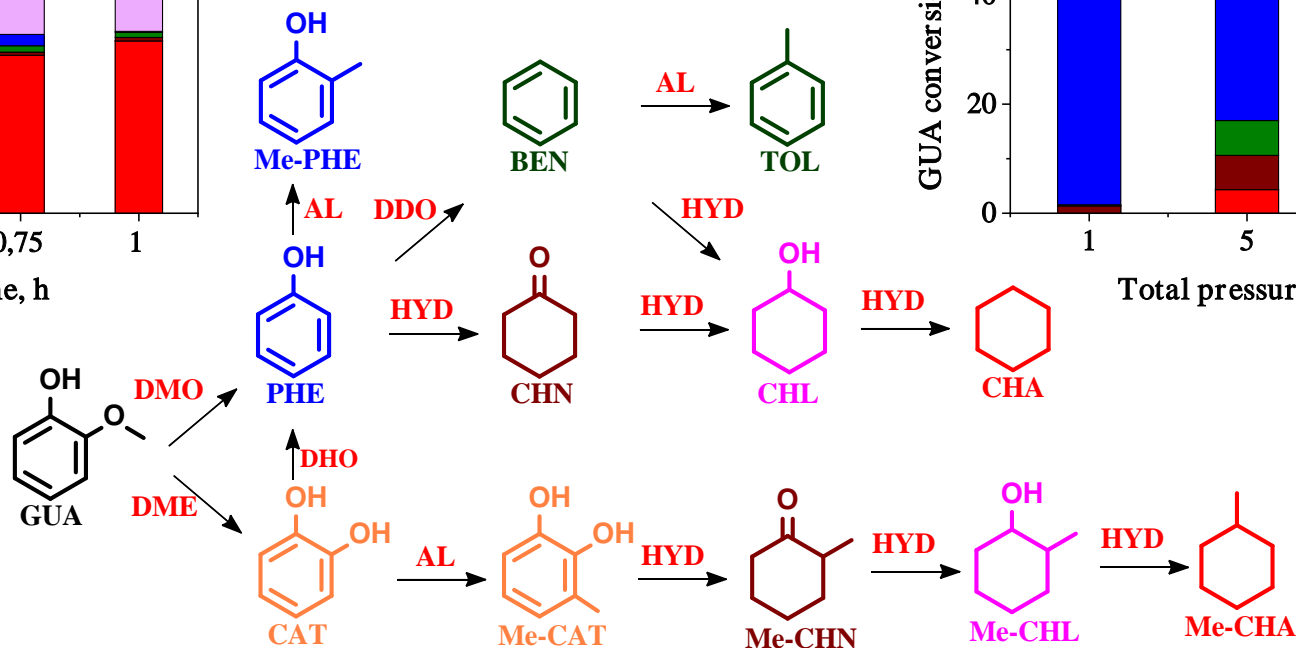
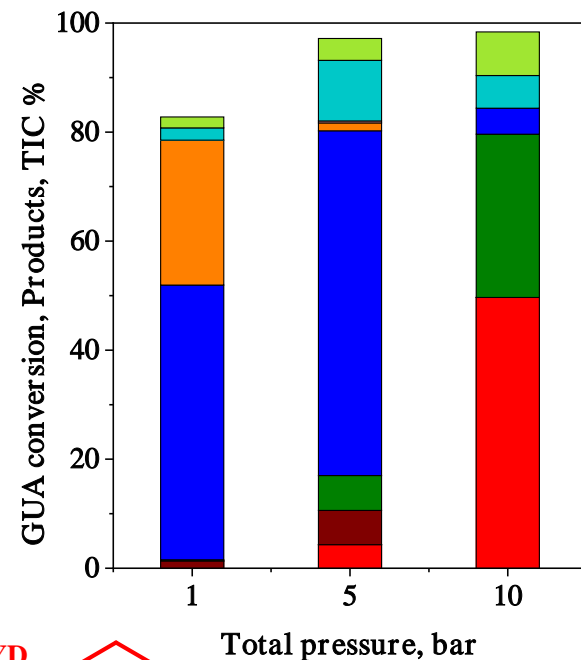
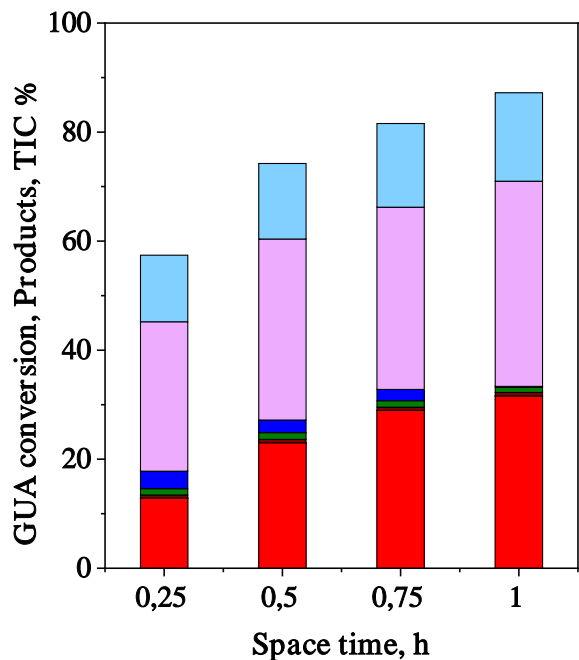
- At 225 °C cyclohexanols were the main products
- At 250 °C high yield and selectivity to CHA
- With temperature the yield of benzenes increased as dehydrogenation is accelerated

- 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

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



- 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_2O_3 supports are active in demethylation of GUA to form catechol.
- ✓ $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst shows high activity and selectivity in GUA hydrodeoxygenation to cyclohexanones.
- ✓ $\text{Ni}/\text{Al}_2\text{O}_3$ 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.
- ✓ $\text{Pd}/\text{Al}_2\text{O}_3(\text{P})$ and $\text{Ni}/\text{Al}_2\text{O}_3(\text{P})$ 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

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