Catalytic conversion of lignin-derived, monomeric platform molecules to value-added chemicals

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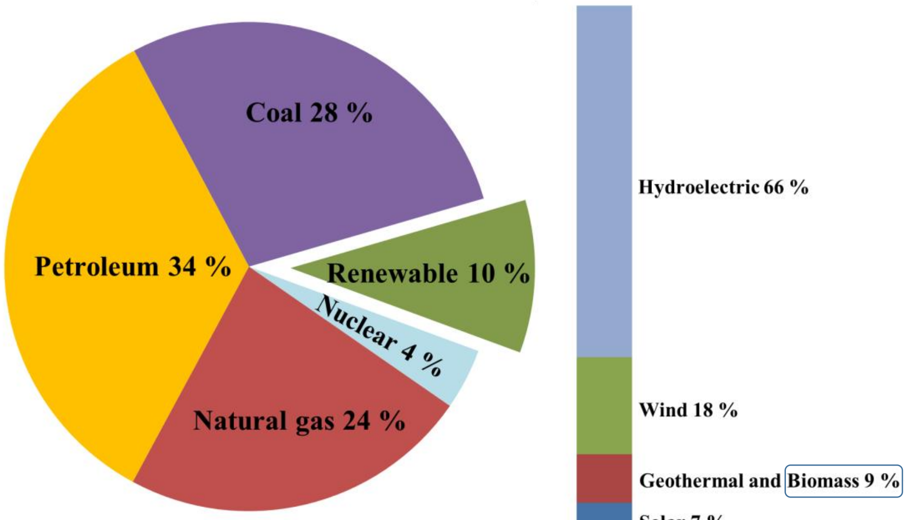
Project meeting
„Joint chemical laboratory for the service of bioeconomy in the Slovak-Hungarian border region"
Interreg, SKHU/1902/4.1/001/Bioeconomy

Faculty of Chemical and Food Technology STU in Bratislava
Radlinského 9, 812 37 Bratislava, Slovak Republic

28 September, 2022

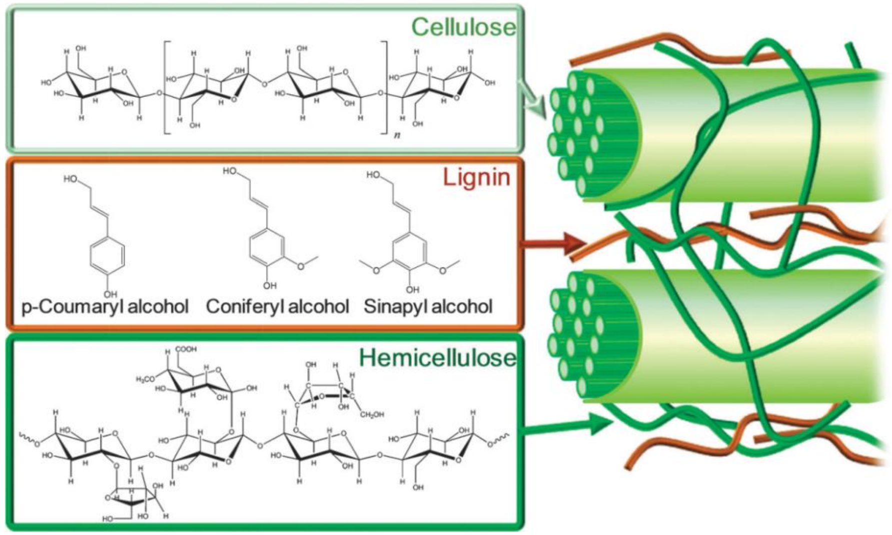
Lignocellulose as source of carbon and energy

Current carbon and energy resources

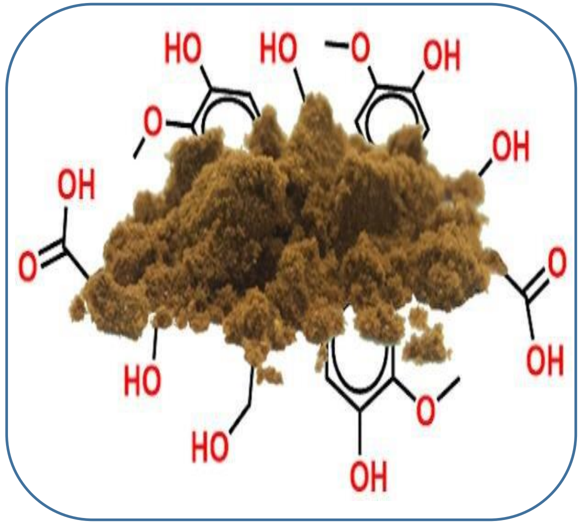


Distribution of energy sources
(BP Statistical Review of World Energy)

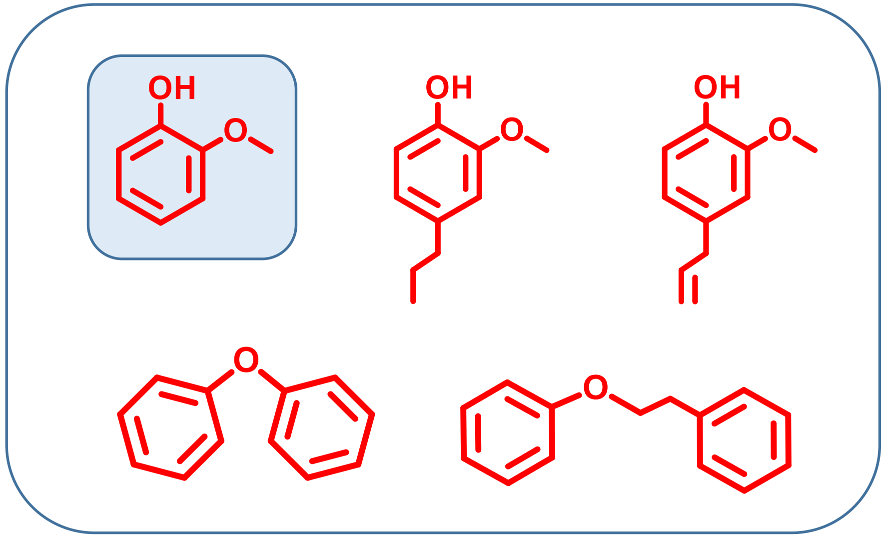
Structure of lignocellulose



Chem. Soc. Rev. 41 (2012) 8075



chemical/thermal depolymerization

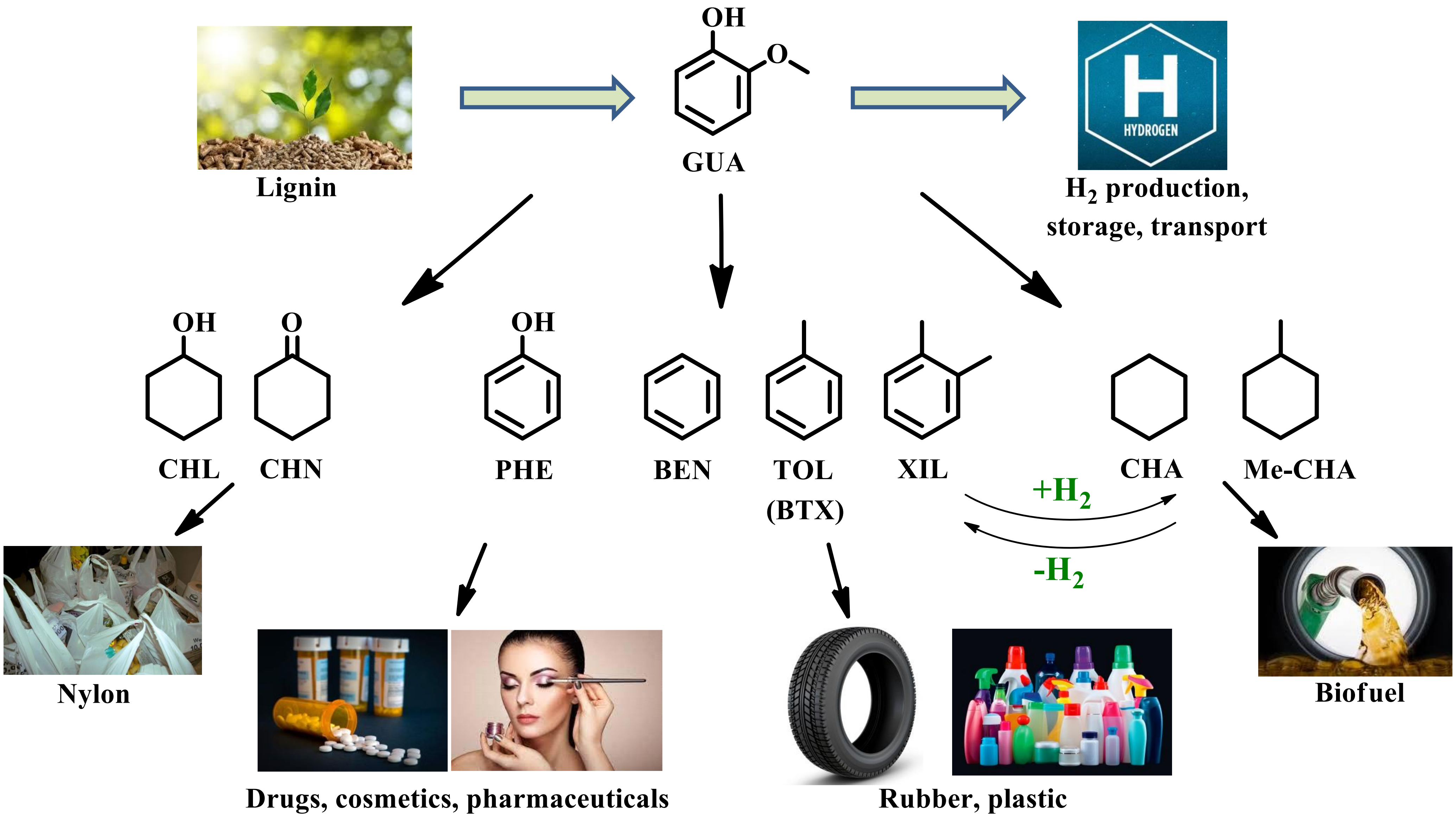


Lignin

Chem. Rev. 110 (2010) 3552; App. Cat. B 257 (2019) 117936

Bio-oxygenates

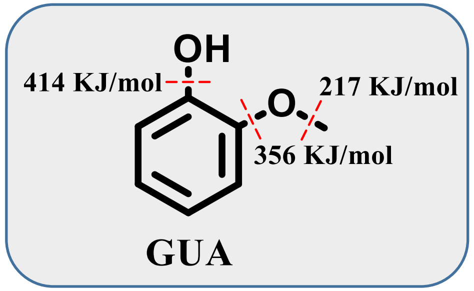
Guaiacol-based chemicals



- ➢ Products from GUA could replace the materials of fossil origin

Reaction pathways of guiacol hydrodeoxygenation

C–O linkages

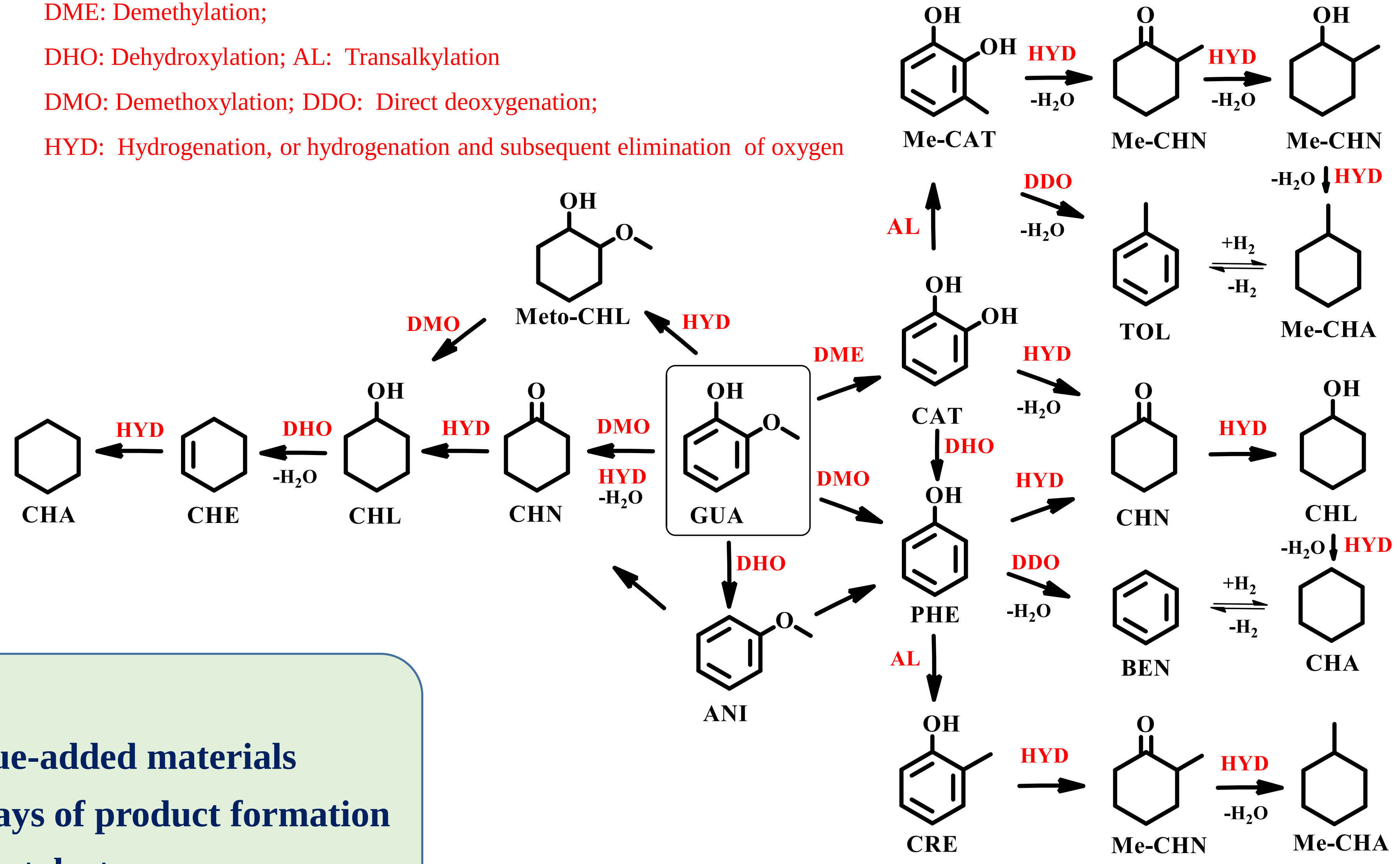


DME: Demethylation;

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
Ni/Al_2O_3	$Ni(NO_3)_2 \cdot 6H_2O$	$\gamma-Al_2O_3$ (Alfa Aesar)
Ni/Al_2O_3 (P)	$Ni(NO_3)_2 \cdot 6H_2O$	$\gamma-Al_2O_3$ (Alfa Aesar) impregnated with H_3PO_4 solution, dried and calcined (550 °C, 4h)

- **Impregnation: metal salt solution**
  - **Calcination: 450 °C, 4h**
    - **In situ reduction: 450 °C, 2h, H_2**

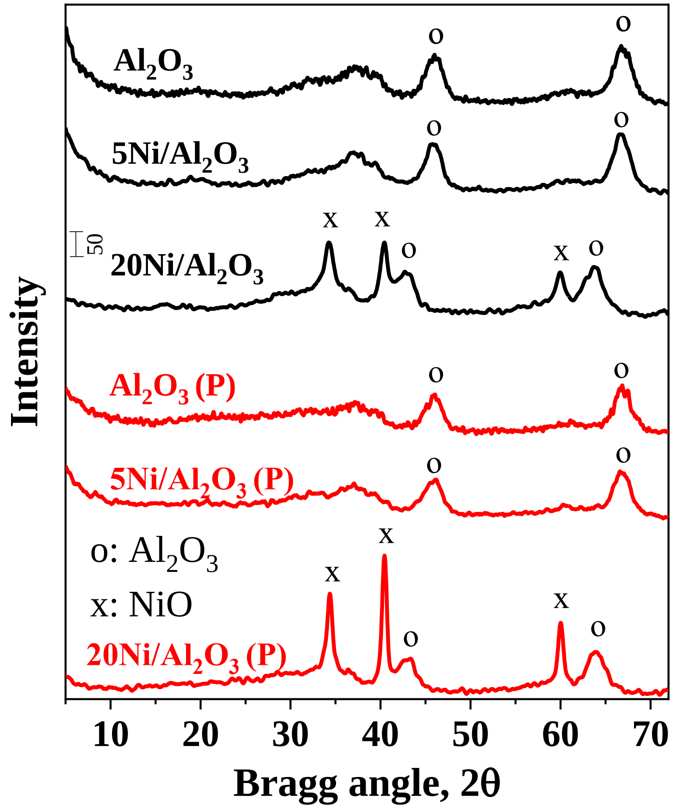
- Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor

Catalyst characterization

Metal and P content; Specific surface area (SSA)

Supports and catalysts	Metal content wt%	P content wt%	SSA m^2/g
Al_2O_3	-	-	196
$5Ni/Al_2O_3$	5.21	-	192
$20Ni/Al_2O_3$	19.87	-	190
Al_2O_3 (P)	-	4.85	167
$5Ni/Al_2O_3$ (P)	5.06	4.82	165
$20Ni/Al_2O_3$ (P)	20.12	4.82	131

X-ray diffraction (XRD)

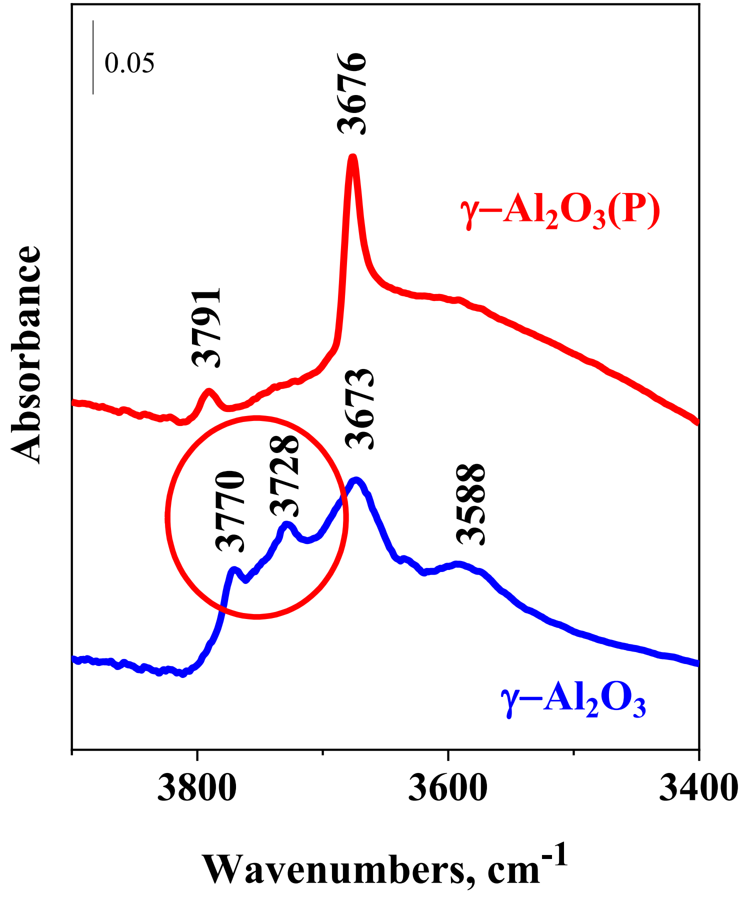


- Metal impregnation has no influence on SSA
- Impregnation of Al_2O_3 support with H_3PO_4 solution reduces SSA

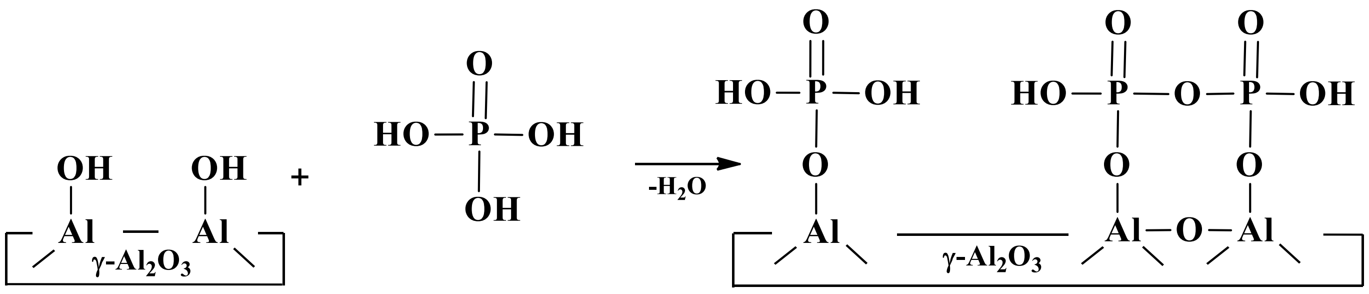
- γ-Al_2O_3 is the only detectable phase of catalysts with low metal loading (NiO crystallites are well dispersed on the Al_2O_3 surface)
- The XRD pattern of $20Ni/Al_2O_3$ and $20Ni/Al_2O_3$(P) catalysts show the reflections of NiO (NiO particle size was about 30 nm)

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-Al_2O_3

- **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**

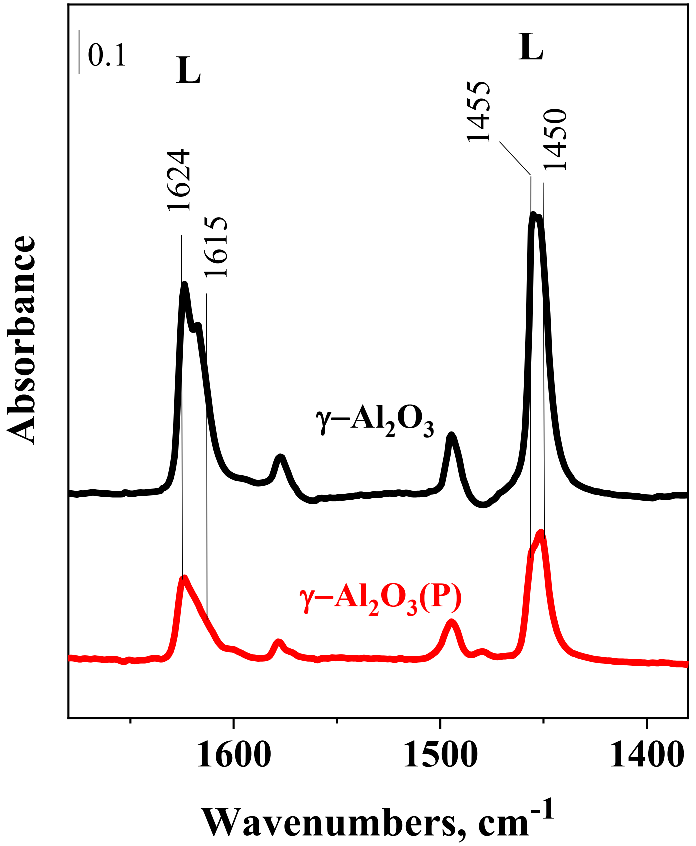
γ-Al_2O_3(P)

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

[a]A. Stanislaus, M. Absi-Halabi, K. Al-Doloma et al., Appl. Cat. 39 (1988) 239; A. Vikár, H.E. Solt, Gy. Novodárszki et al., Journal of Catalysis 404 (2021) 67

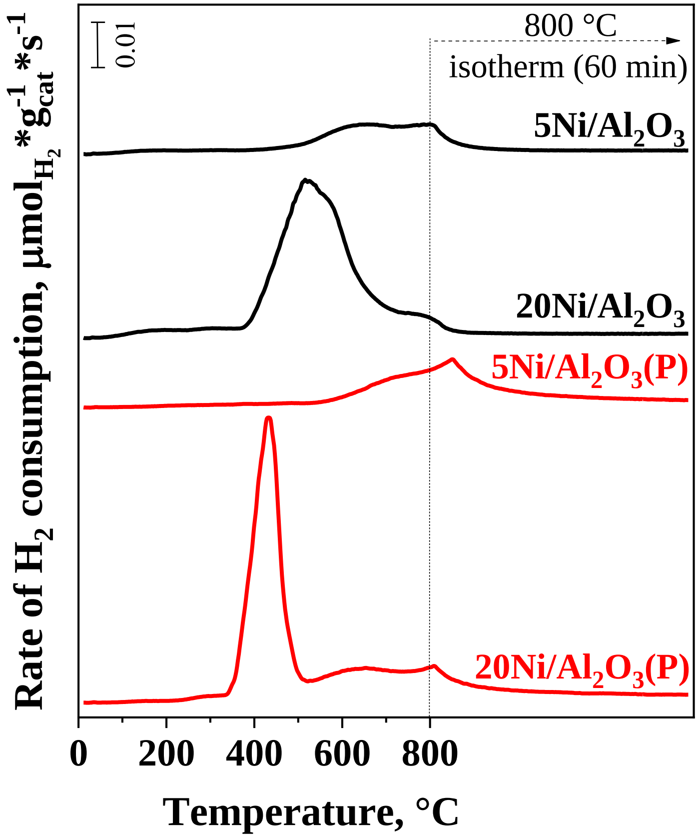
Catalysts acidity and reducibility

FT-IR spectra of adsorbed pyridine



- On the Al_2O_3 (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

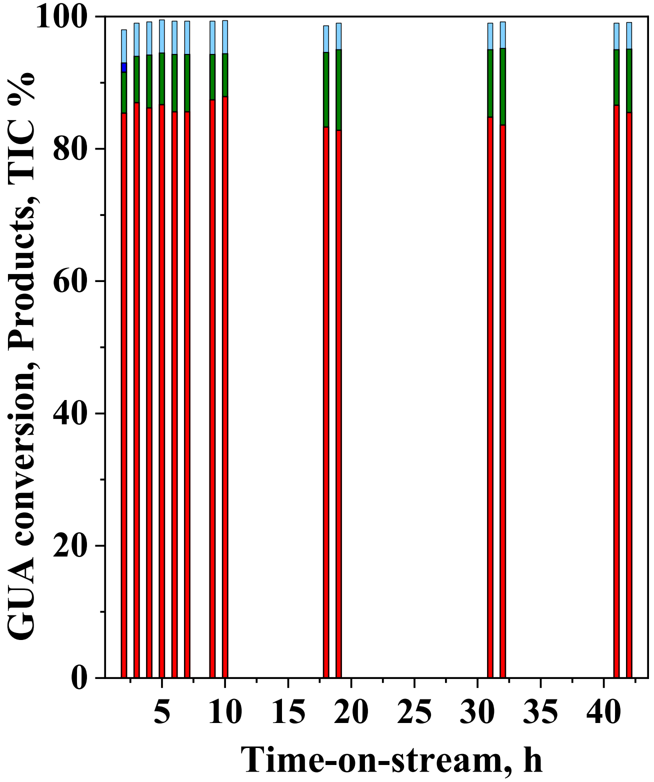
Temperature-programmed reduction (H_2-TPR)



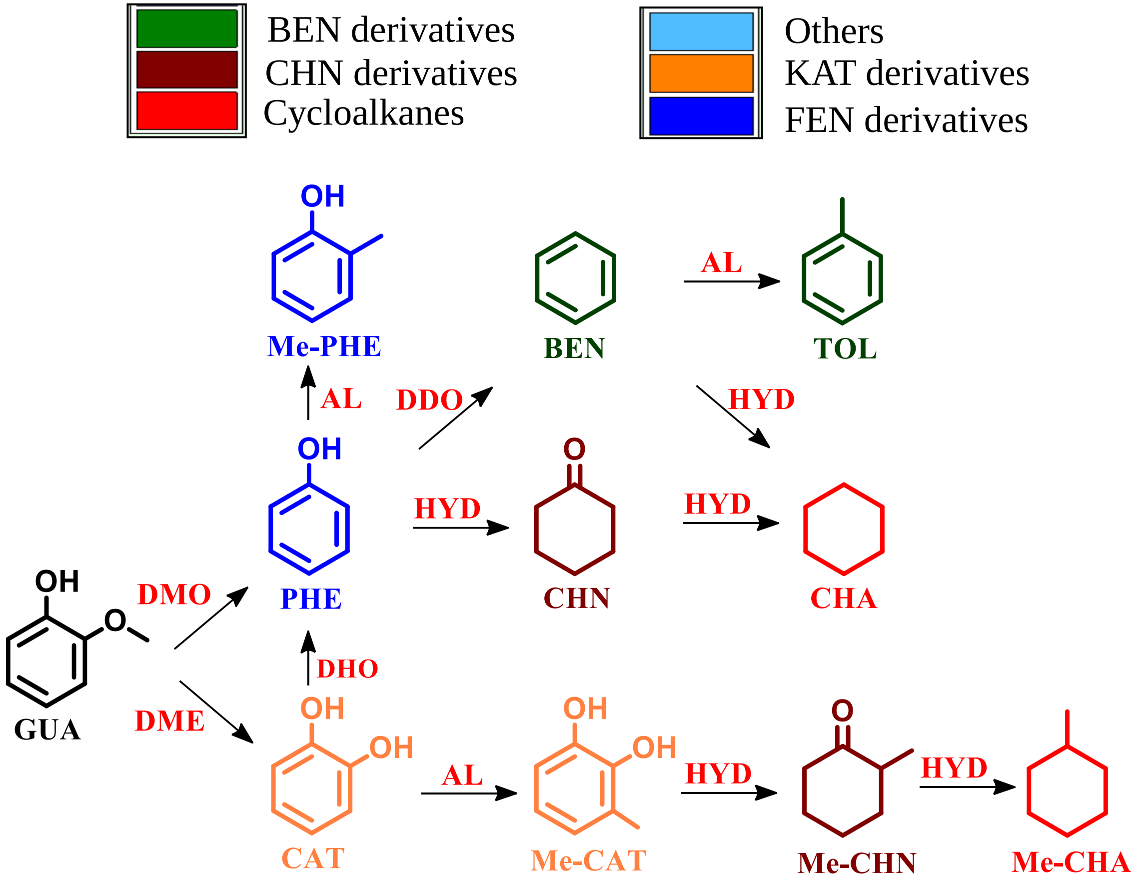
- The degree of reduction at 450 °C:
  - $5Ni/Al_2O_3$ ~ 4.5 % of Ni (H/Ni=0.09)
  - $5Ni/Al_2O_3$ (P) ~ 0.5% (H/Ni=0.01)
  - $20Ni/Al_2O_3$ ~ 68 % (1.37 H/Ni)
  - $20Ni/Al_2O_3$ (P) ~ 65 % (1.3 H/Ni)

Activity of $20Ni/Al_2O_3$ catalyst

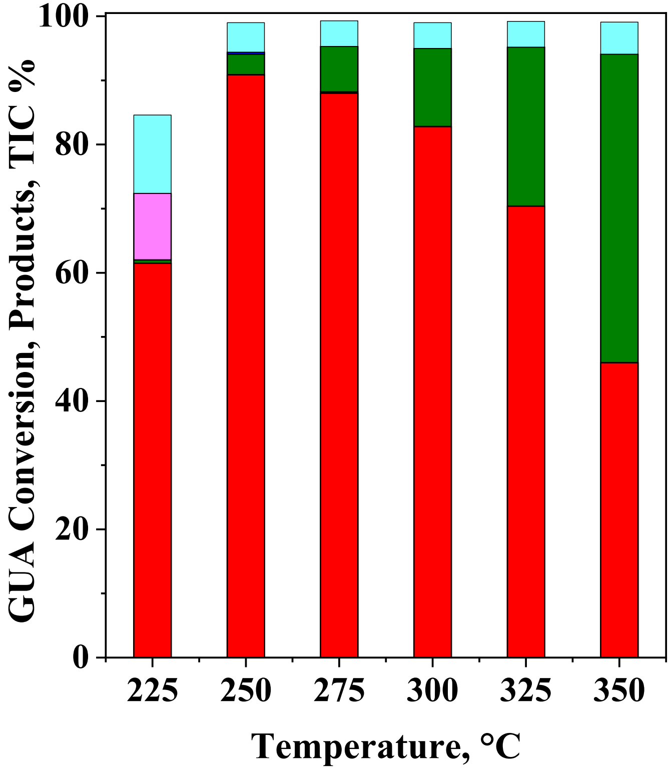
Stability



300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA = 20



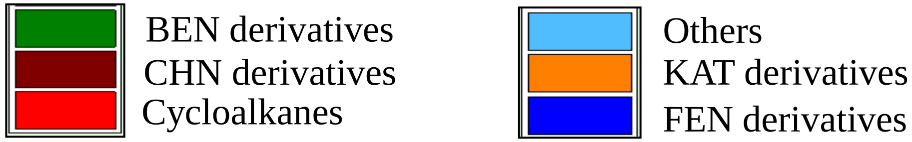
Effect of temperature



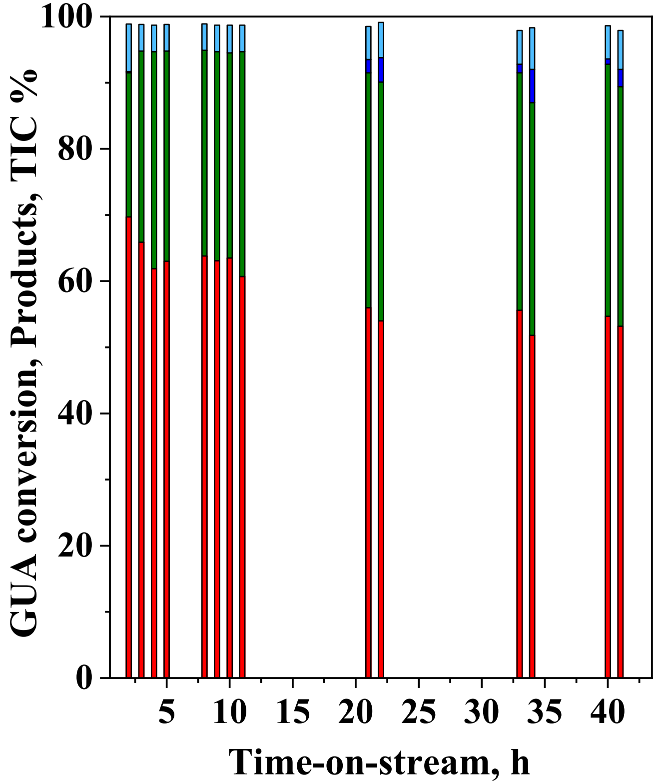
10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA = 20

- The catalyst activity did not change with TOS
- O-free compounds were mainly formed at 300 °C
- At 225 °C CHL-s appear in the product mixture
- With temperature the yield of benzenes increased

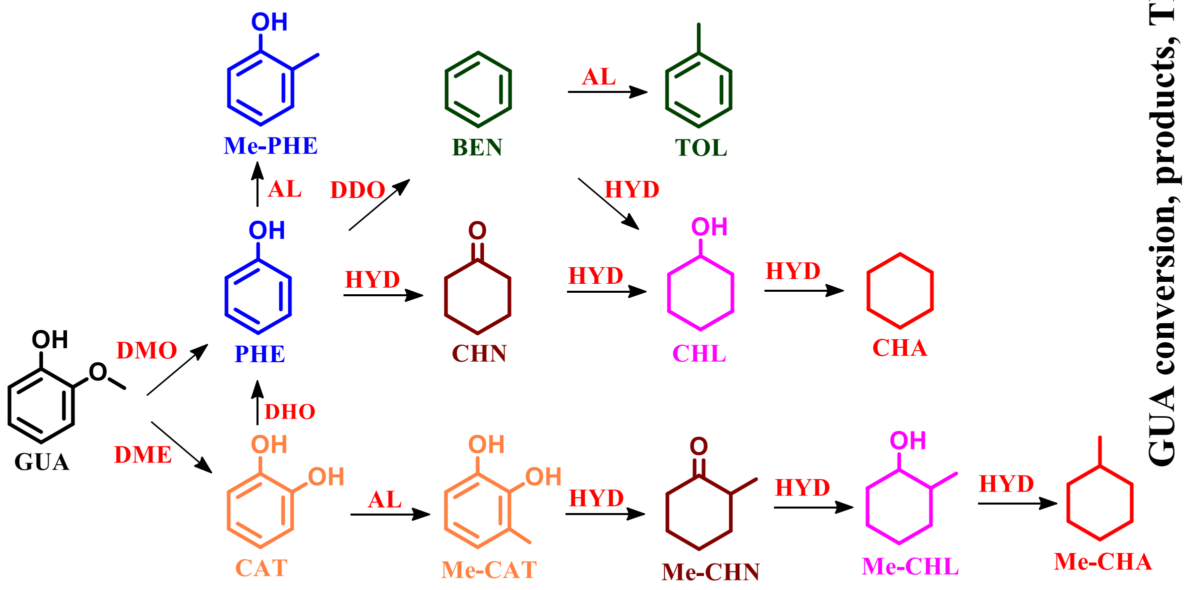
Activity of 5Ni/Al_2O_3 catalyst



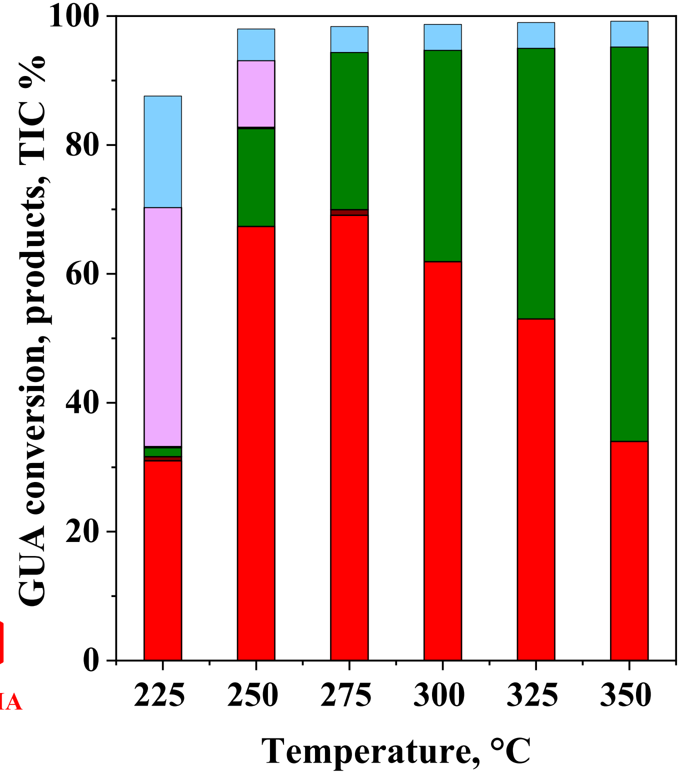
Stability



300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA = 20



Effect of temperature



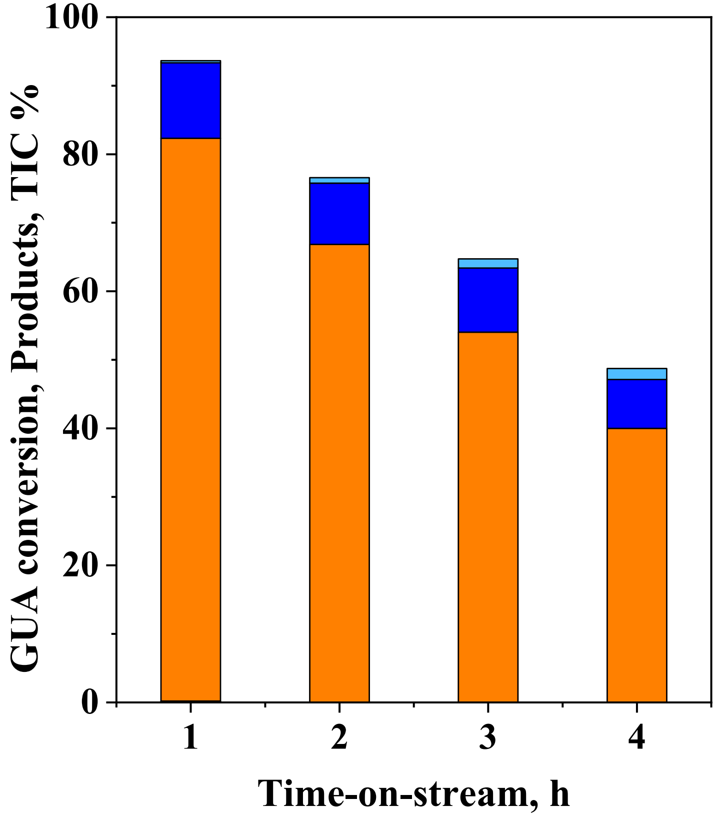
10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA = 20

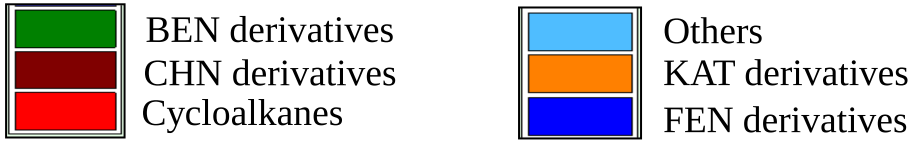
- The catalyst activity did not change with TOS
- O-free compounds were mainly formed at 300 °C

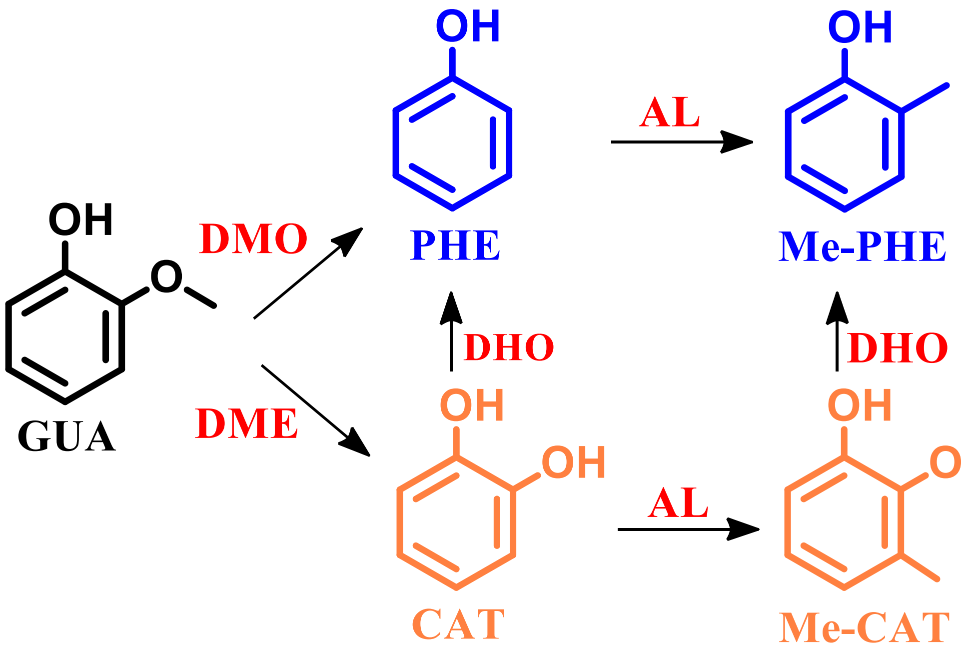
- At 225 °C cyclohexanols were the main products
- With temperature the yield of benzenes increased

Activity of Al_2O_3 and Al_2O_3 (P) supports

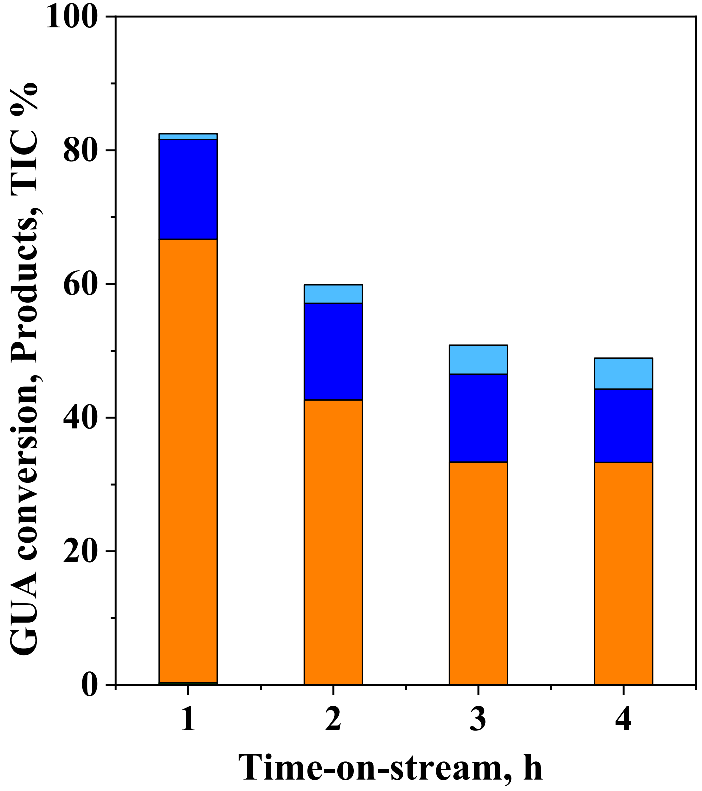
Al_2O_3







Al_2O_3 (P)

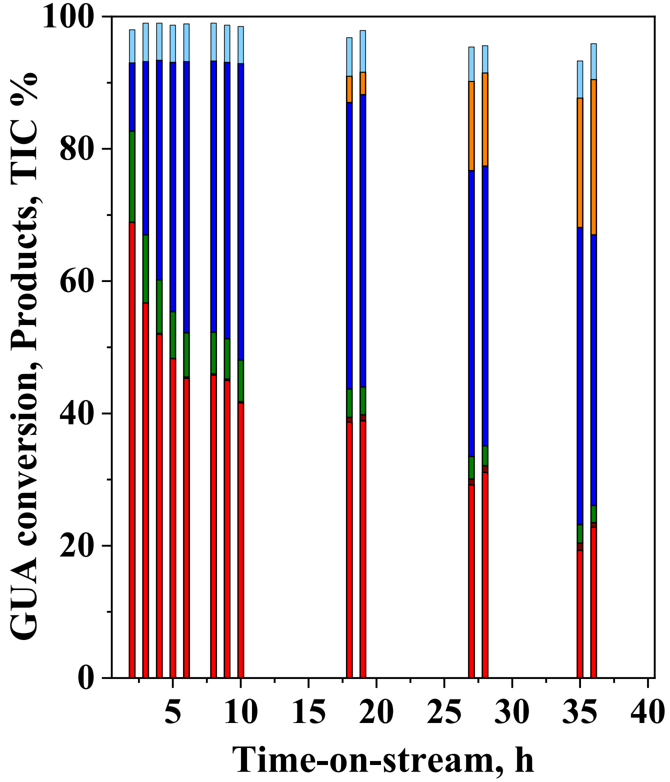


300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20

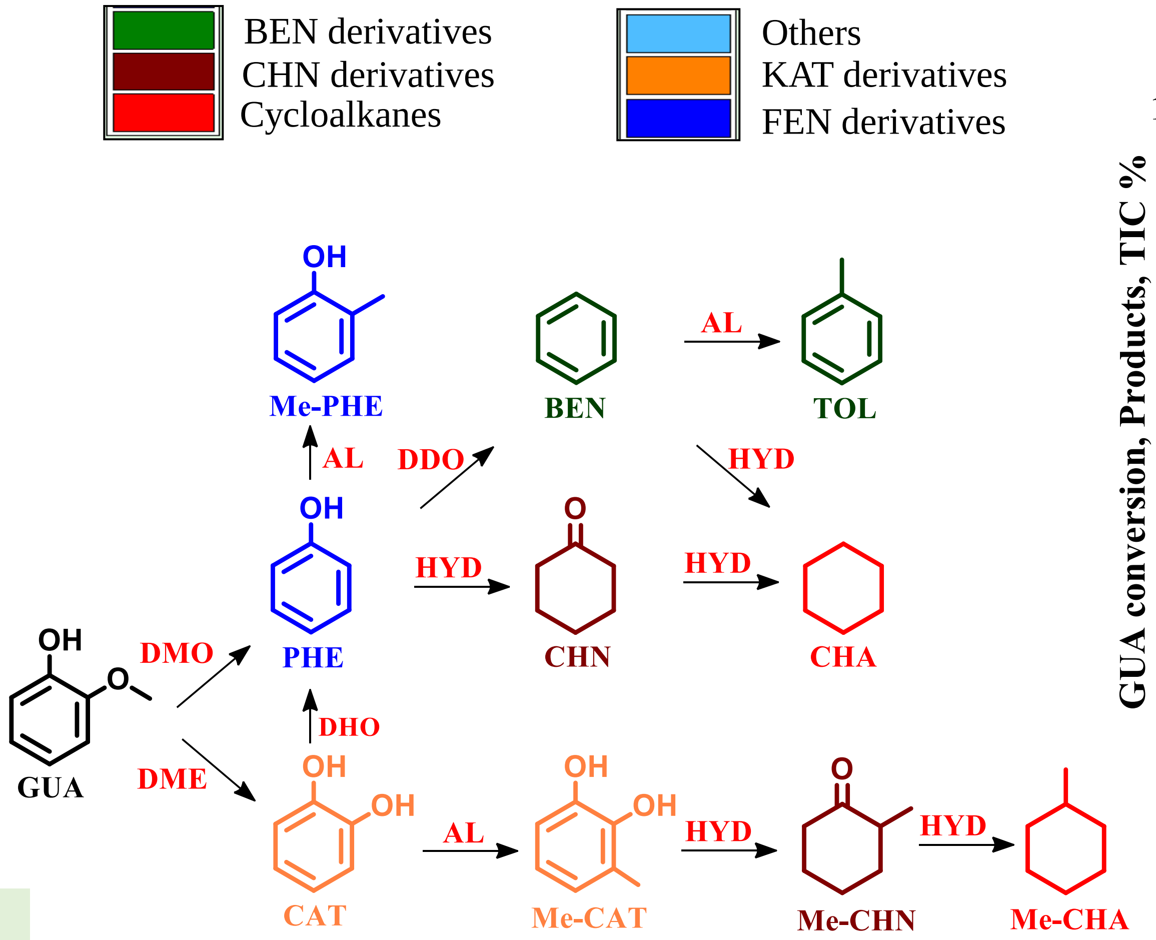
- Demethylation (DME) and transalkylation (AL) are the main reactions
- CAT derivatives are the main products
- Demethoxylation (DMO) and dehydroxylation (DHO) also takes place
- PHE derivatives were also formed

Activity of $20Ni/Al_2O_3$(P) catalyst

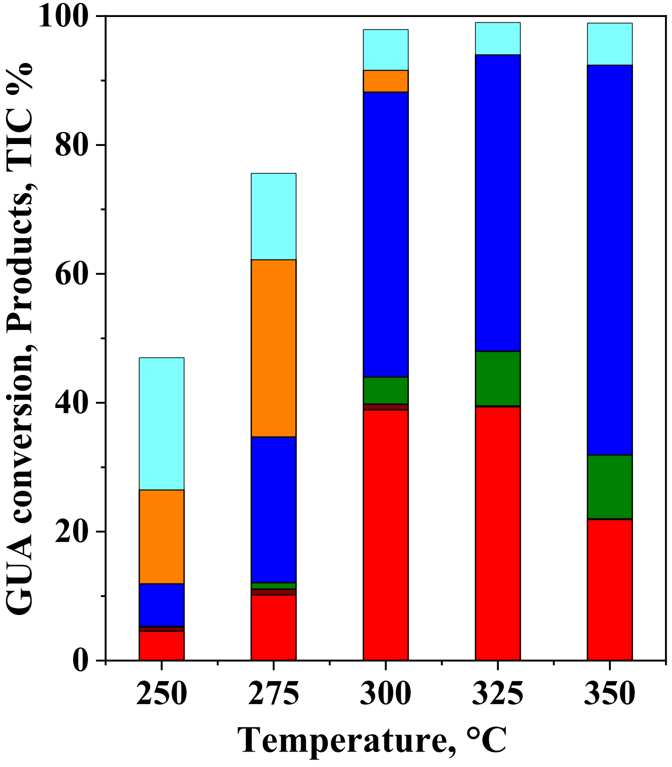
Stability



300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20



Effect of temperature

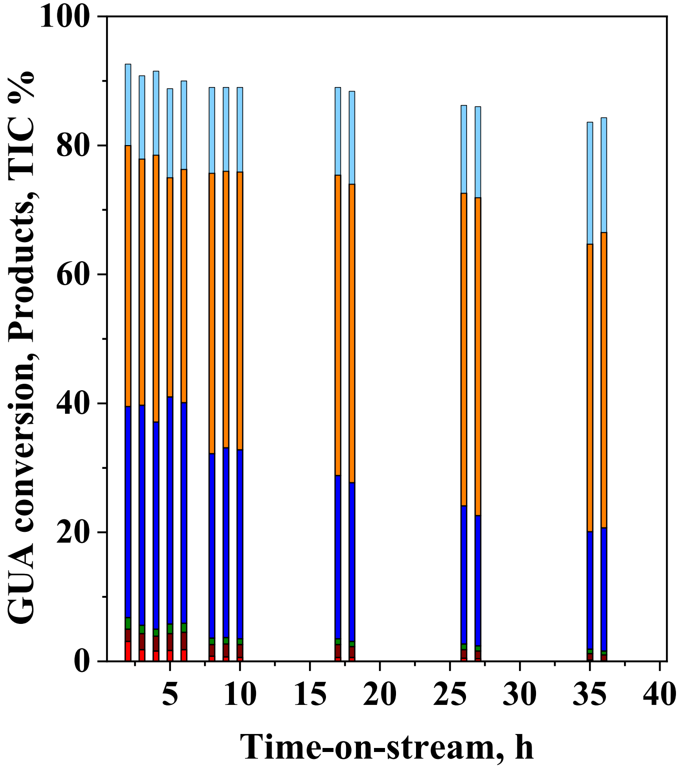


10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20

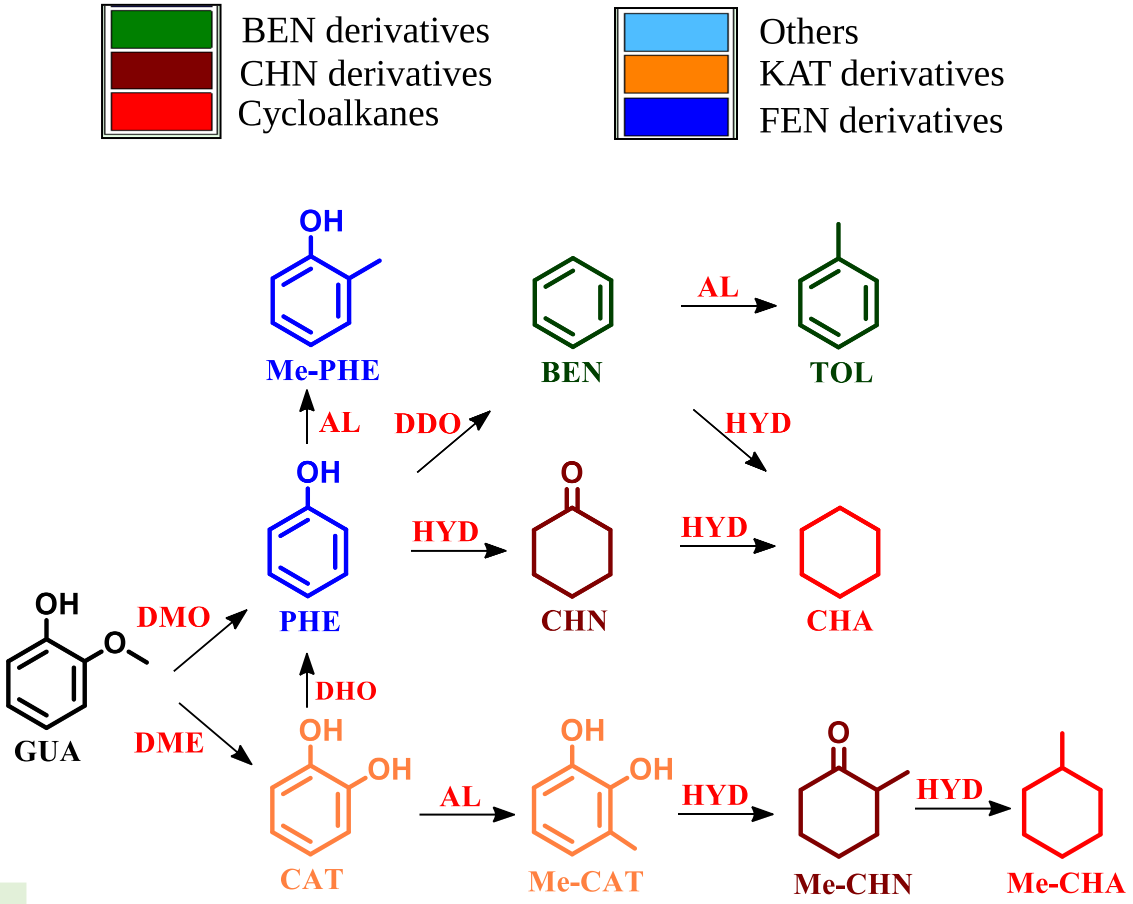
- The catalyst selectivity change in funcion of TOS
- Phenols were formed on modified $20Ni/Al_2O_3$(P) catalyst
- Catechols also appear in product mixture
- The amount of PHE derivatives increased with temperature

Activity of $5Ni/Al_2O_3(P)$ catalyst

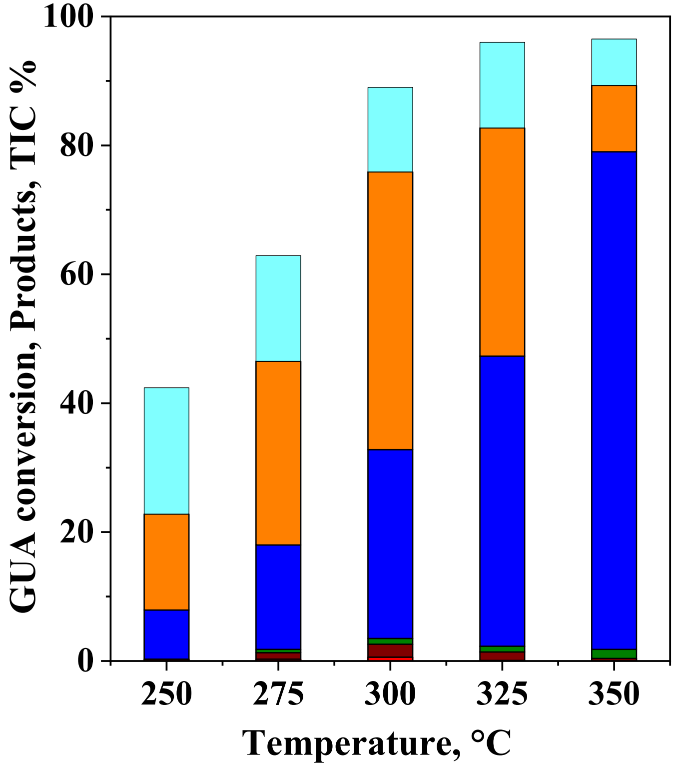
Stability



300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20



Effect of temperature



10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20

- Catechols were formed on modified $5Ni/Al_2O_3(P)$ catalyst
- The amount of PHE derivatives increased with temperature

Conclusions

- The sequential steps of GUA hydrodeoxygenation can be controlled by modifying the alumina support.
- Demethylation of GUA on Al_2O_3 and phosphorous modified Al_2O_3(P) supports leads to catechol formation.
- Ni/Al_2O_3 catalyzed hydrodeoxygenation of GUA to O-free compounds like cyclohexane.
- At lower temperature cyclohexanols were formed in large amounts.
- Ni/Al_2O_3(P) catalysts are selective to aromatics (phenols, catechols).
- At higher temperature phenols were the main products.
- Ni/Al_2O_3(P) catalysts remain active in demethylation and demethoxylation, but lose their ability to hydrogenate the aromatic ring. (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

Interreg Slovakia-Hungary

Building Partnership

www.ttk.hu/palyazatok/bioeconomy