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

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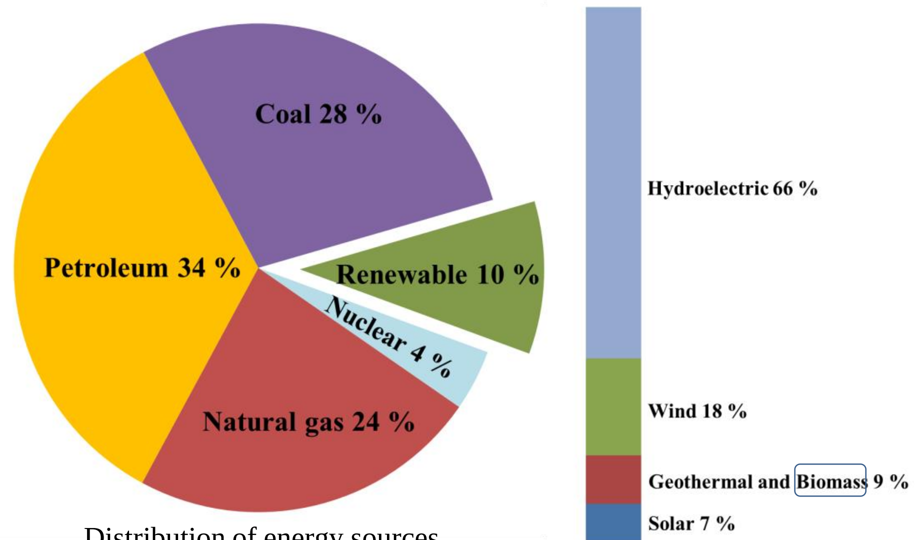
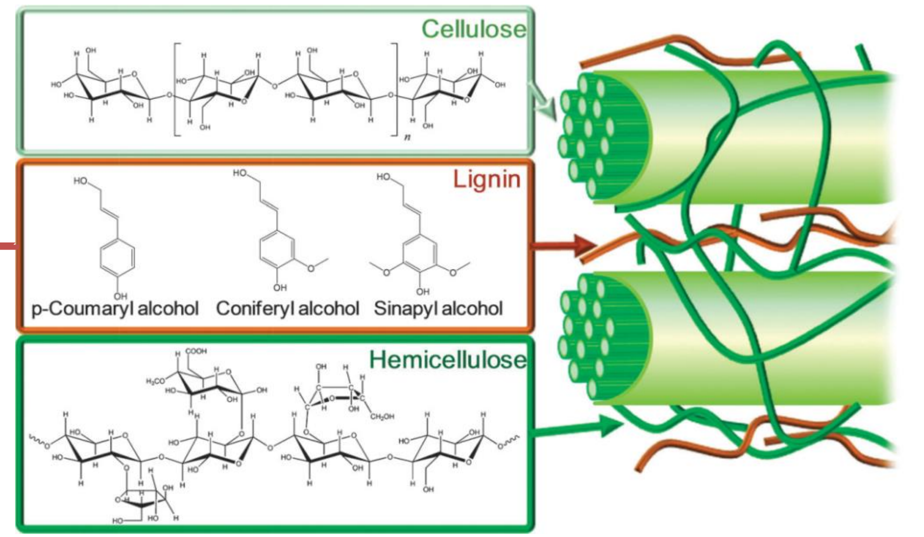
Lignocellulose as source of carbon and energy

Current carbon and energy resources

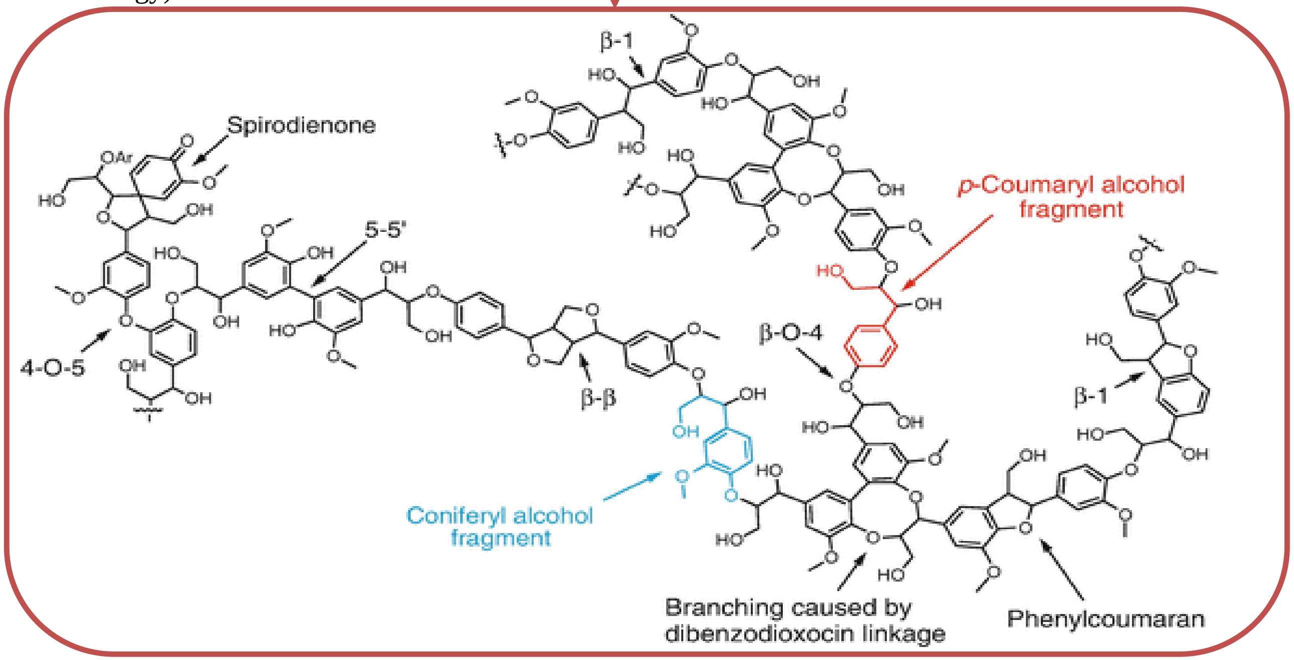


Distribution of energy sources
(BP Statistical Review of World Energy)

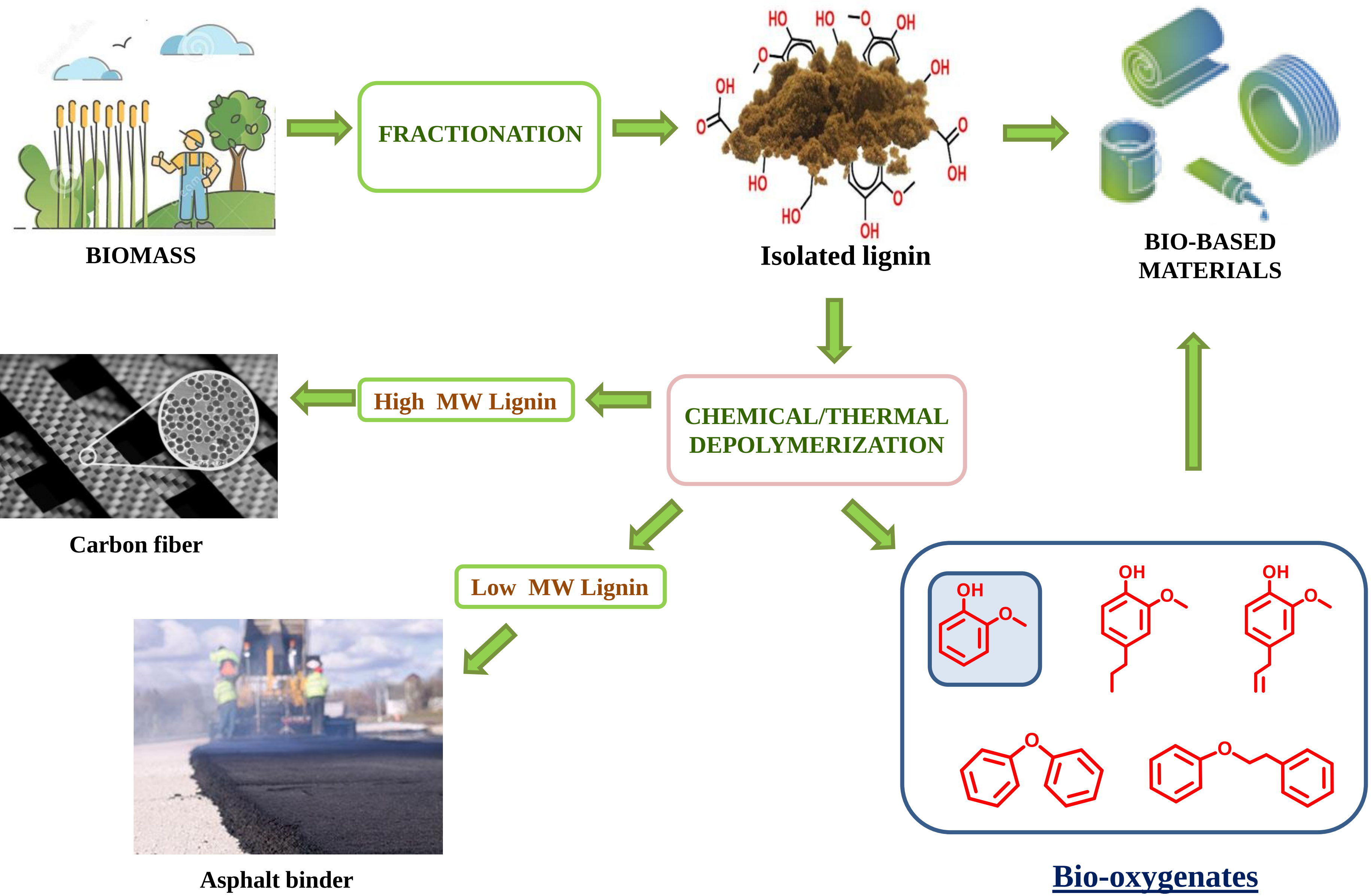
Structure of lignocellulose



Chem. Soc. Rev. 41 (2012) 8075

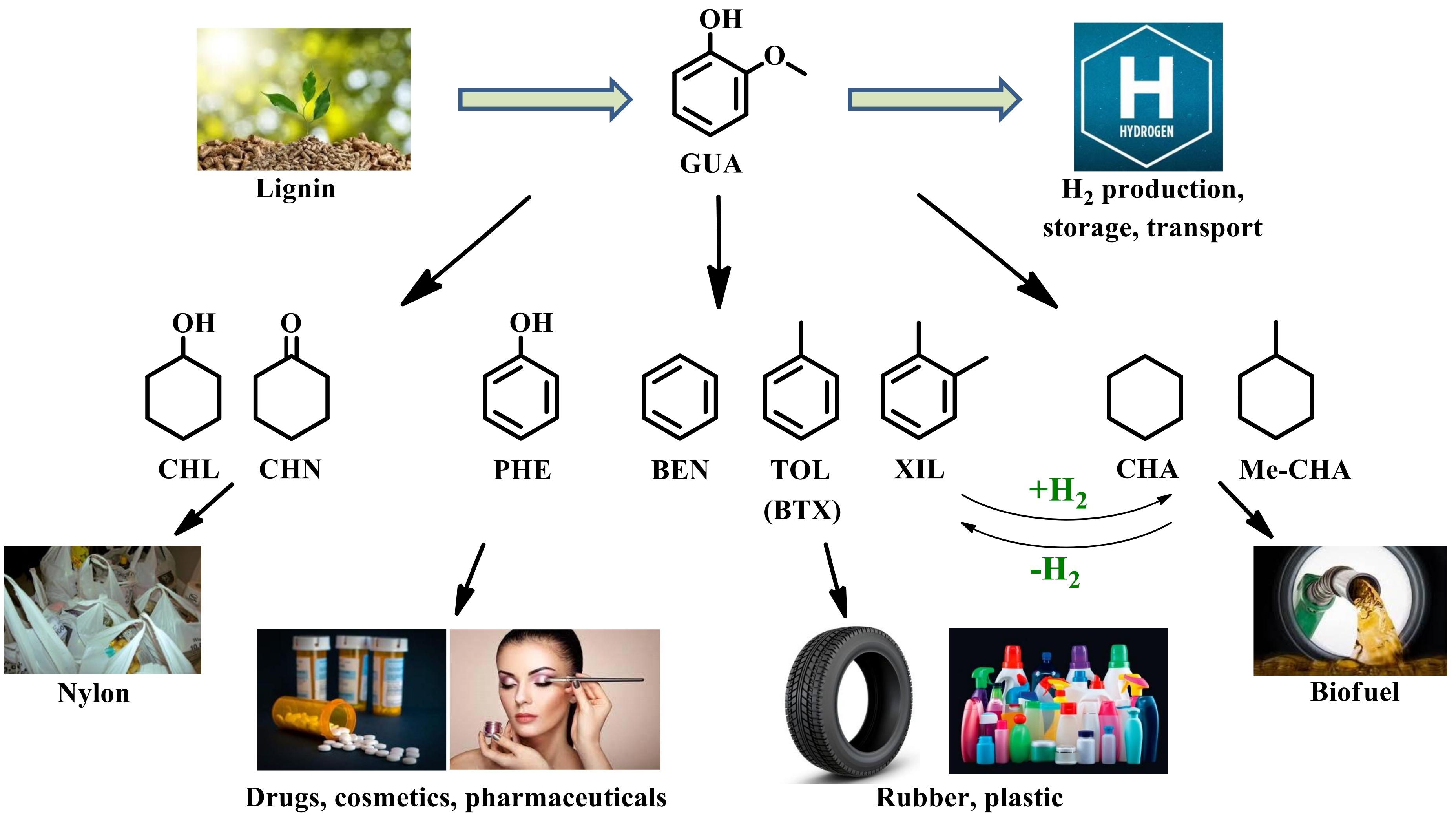


Lignin utilization



http://biomassmagazine.com/articles/14388/researchers-use-waste-lignin-to-make-carbon-fiber

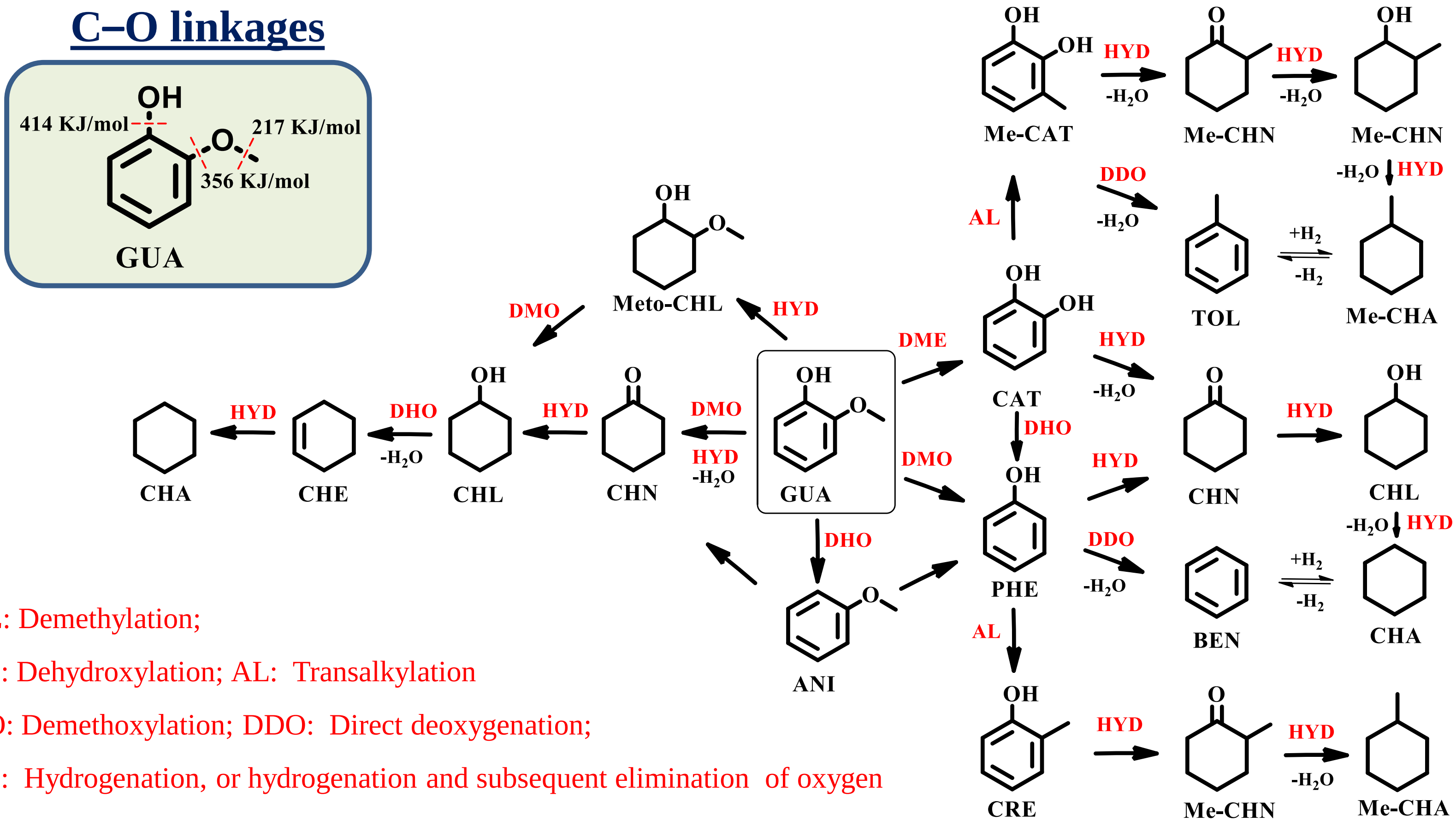
Guaiacol-based chemicals



- 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
Pd/Al_2O_3	$Pd(NH_3)_4(NO_3)_2$	$\gamma-Al_2O_3$ (Alfa Aesar)
Ni/Al_2O_3	$Ni(NO_3)_2)\cdot 6H_2O$	
Pd/Al_2O_3 (P)	$Pd(NH_3)_4(NO_3)_2$	$\gamma-Al_2O_3$ (Alfa Aesar) impregnated with H_3PO_4 solution, dried and calcined (550 °C, 4h)
Ni/Al_2O_3 (P)	$Ni(NO_3)_2)\cdot 6H_2O$	

- **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**

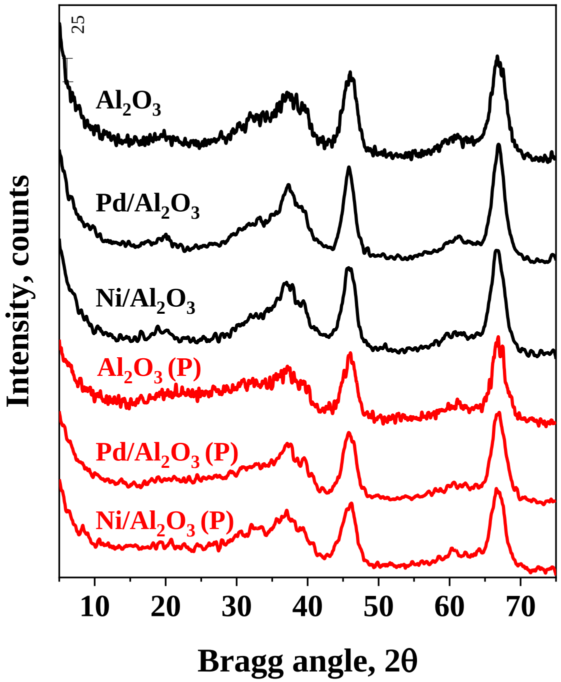
- Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor

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
Pd/Al_2O_3	0.47	-	194
Ni/Al_2O_3	5.21	-	192
Al_2O_3 (P)	-	4.85	167
Pd/Al_2O_3 (P)	0.49	4.87	163
Ni/Al_2O_3 (P)	5.06	4.82	165

X-ray diffraction (XRD)



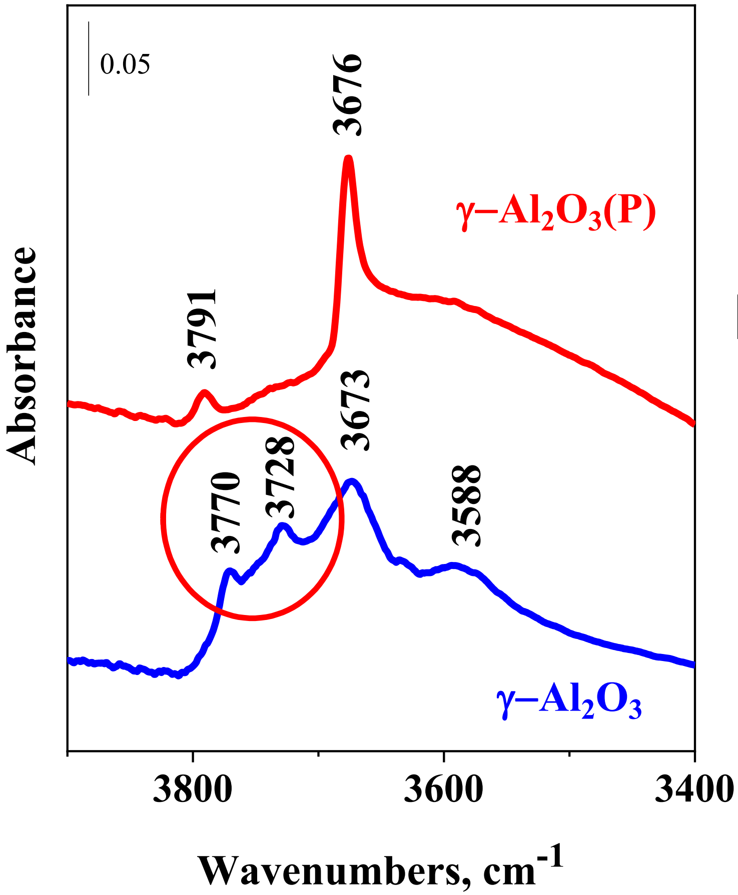
- Metal impregnation has no influence on SSA
- Impregnation of Al_2O_3 support with H_3PO_4 solution reduces SSA

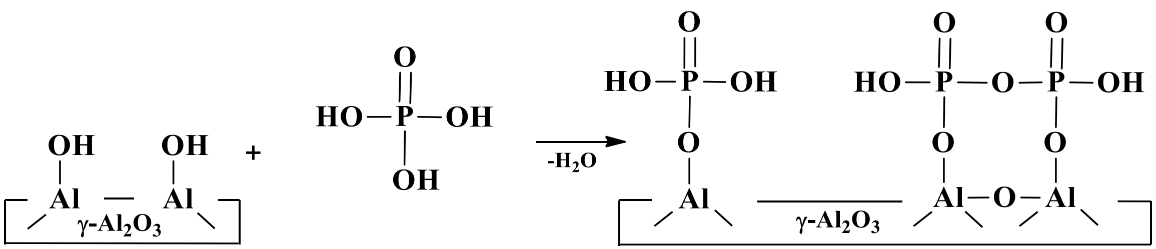
- Al_2O_3 is the only detectable phase
- NiO and PdO crystallites are well dispersed on the Al_2O_3 surface

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-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**

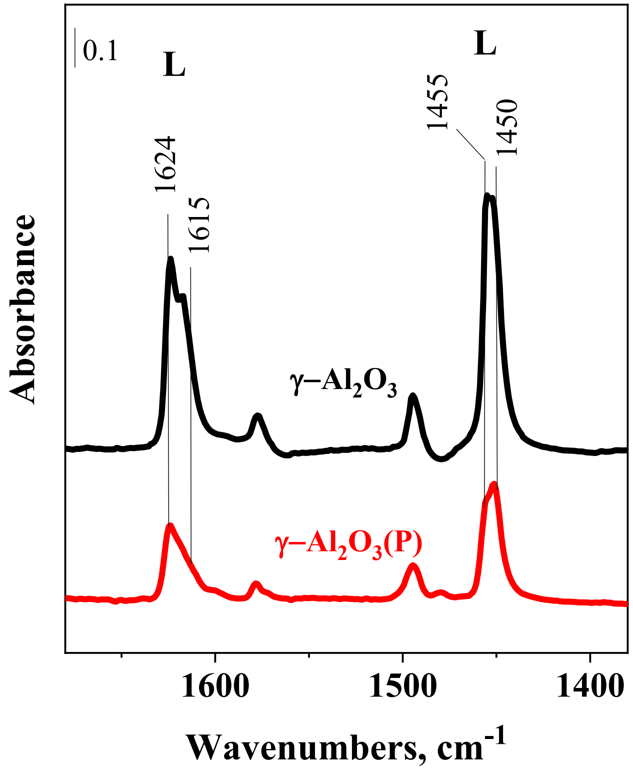
γ-Al_2O_3(P)

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

[a]Stanislaus et al., Appl. Cat. 39 (1988) 239; A. Vikár et al., Journal of Catalysis (2021) 10.1016/j.jcat.2021.08.052

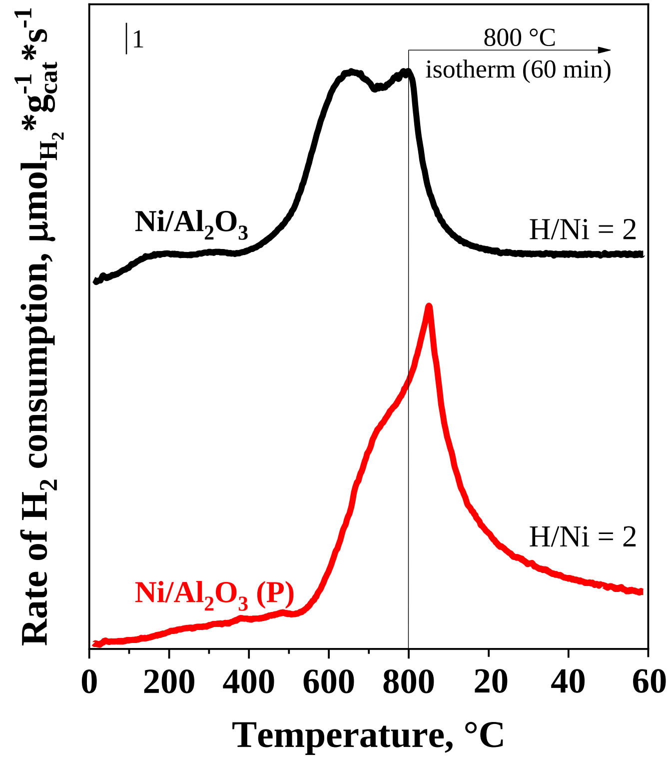
Catalysts acidity and reducibility

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)



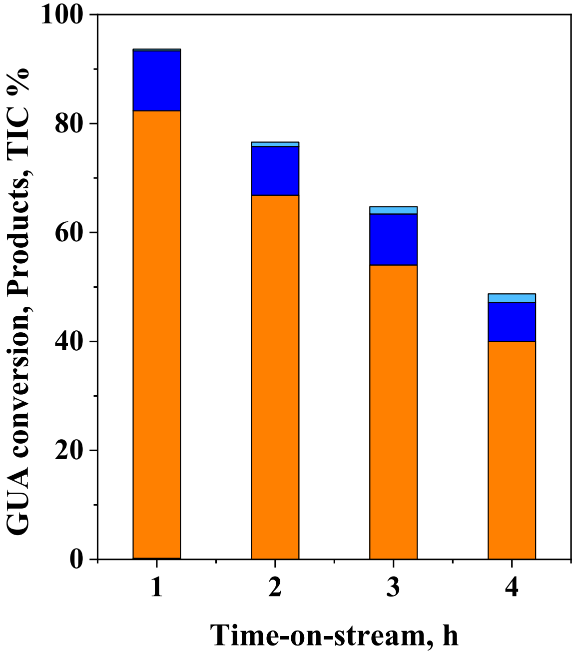
- Pd can be easily reduced around 100 °C (not shown in the figure)
- The degree of reduction at 450 °C:
  - -Ni/Al_2O_3 ~ 4.5 % of Ni (H/Ni=0.09)
  - -Ni/Al_2O_3 (P) ~ 0.5% (H/Ni=0.01)
  - *Ni/Al_2O_3 (P) (550) ~ 3.5% (H/Ni=0.07)

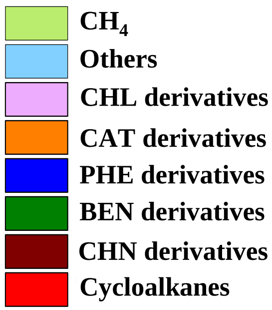
Activity of Al_2O_3 and Al_2O_3 (P) supports

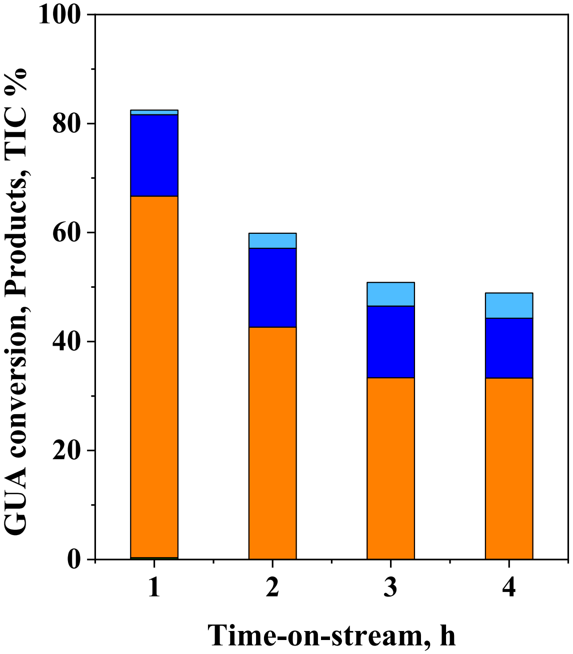
Al_2O_3

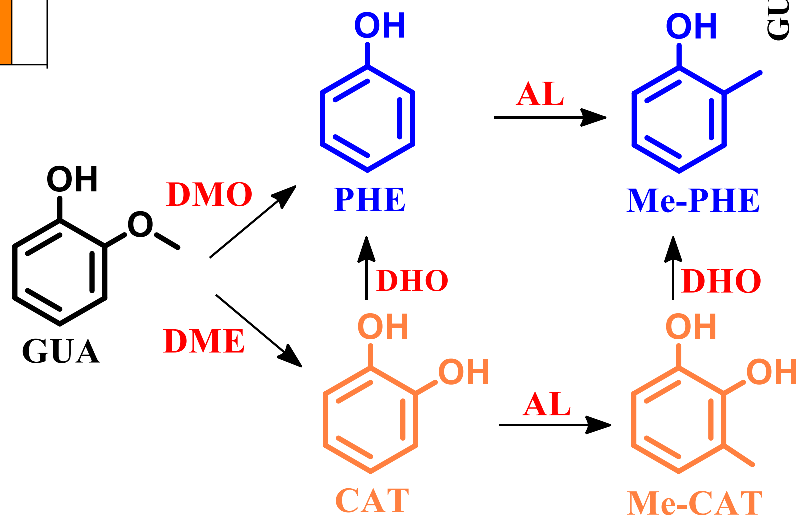
300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20

Al_2O_3 (P)









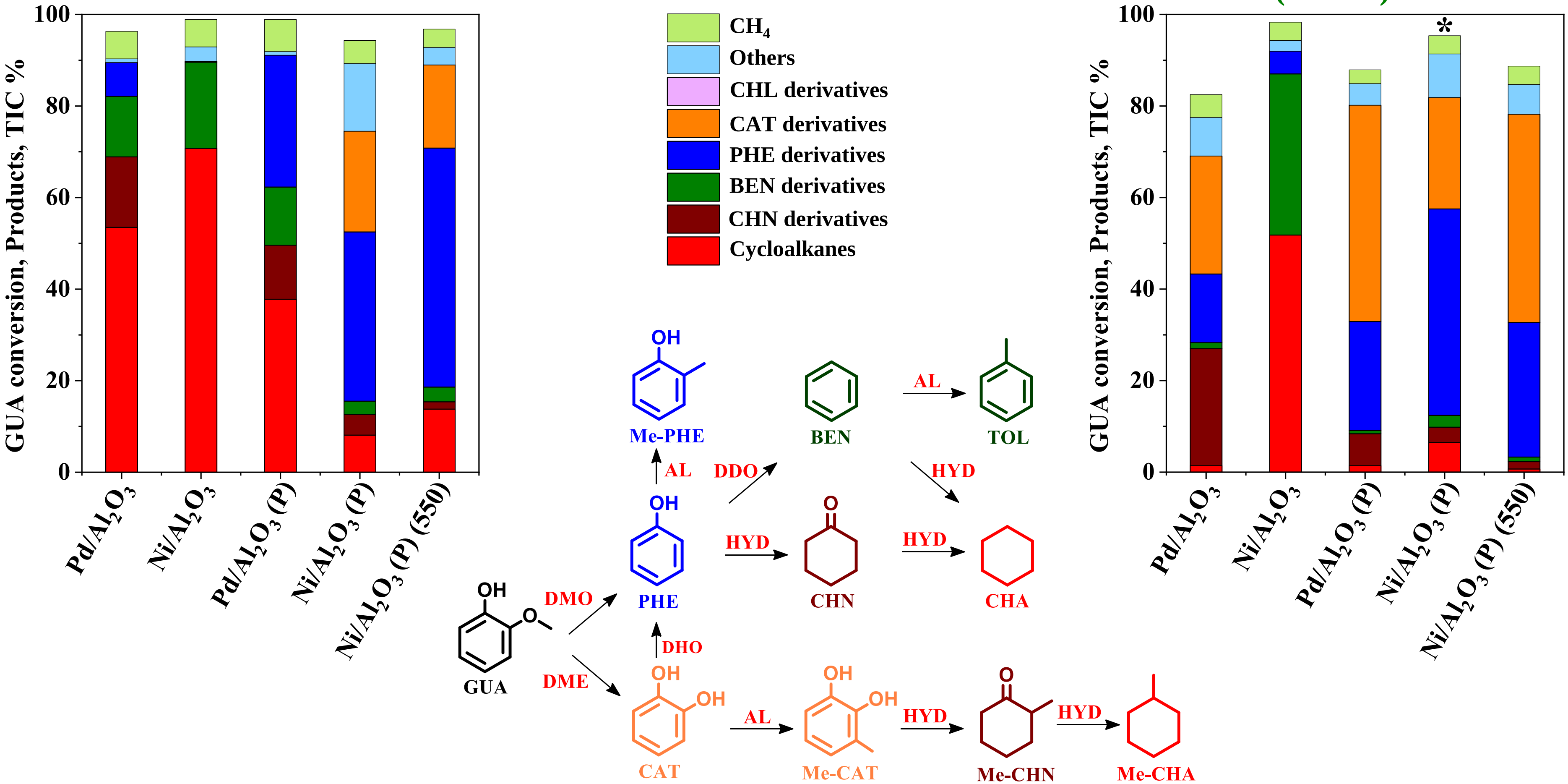
- Demethylation (DME) and transalkylation (AL) are the main reactions
- CAT derivatives are the main products
- Demethoxylation (DMO) and dehydroxylation (DHO) also takes place
- PHE derivatives were also formed

Comparison of catalysts activity

300 °C, 10 bar, 1 g_{cat}/g_{GUA}*h

H_2/GUA=20, time-on-stream = 2 h

H_2/GUA=20, time-on-stream = 38 h (* = 4 h)



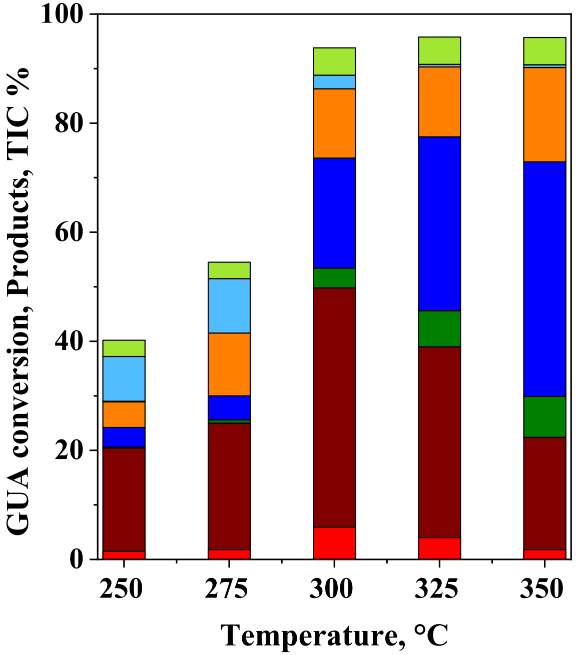
- Cyclohexanones and cycloalkanes are the main products on Pd/Al_2O_3
- O-free compounds were mainly formed on Ni/Al_2O_3
- Aromatics (phenols, catechols) were formed on Ni/Al_2O_3 (P) and Ni/Al_2O_3 (P)(550)

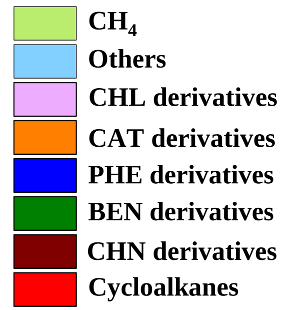
Effect of temperature

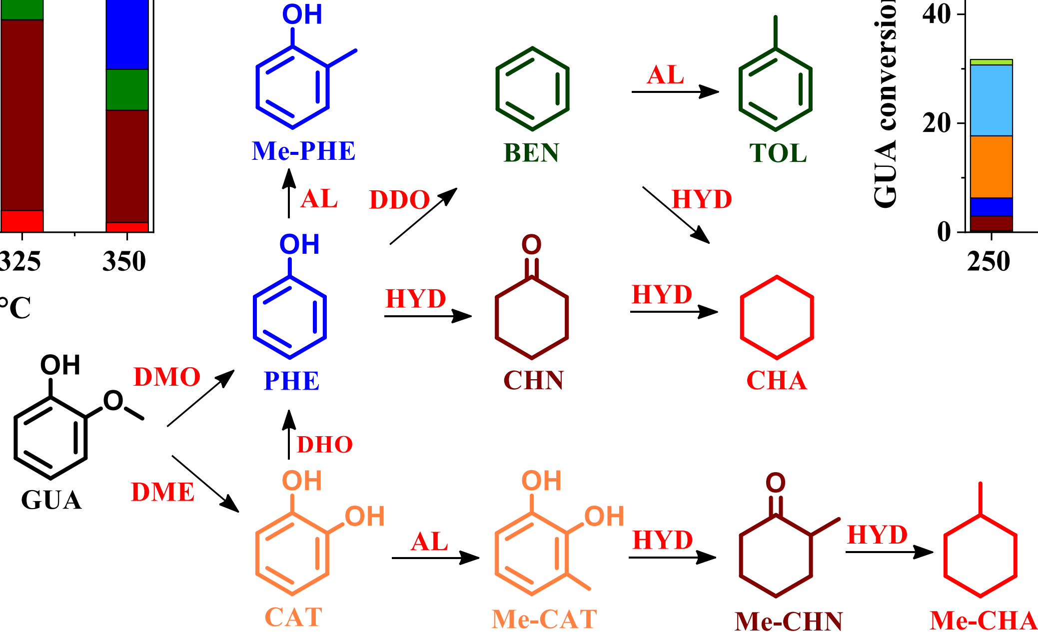
Pd/Al_2O_3

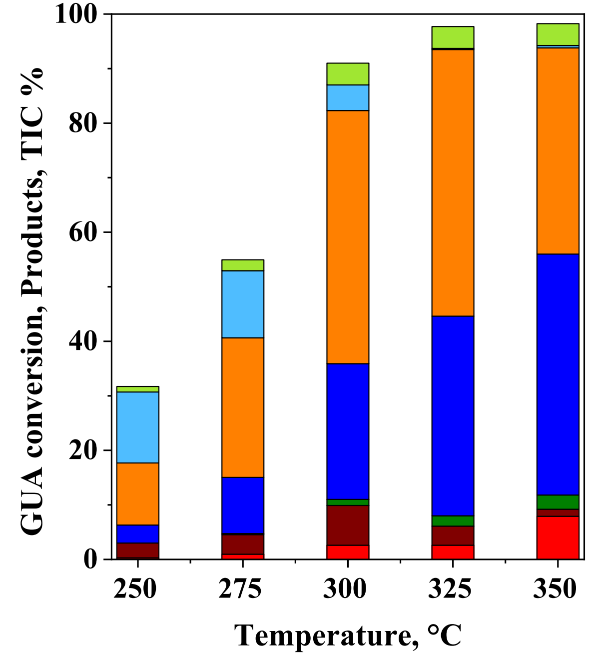
10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20

Pd/Al_2O_3 (P)









- The yield of phenols increases with temperature
- 1-Methoxycyclohexane and 2-methoxy-cyclohexanone were also formed (not shown)

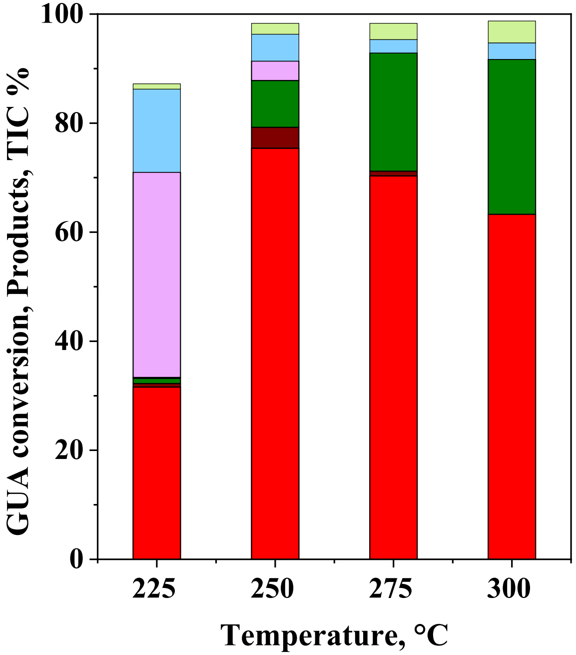
- The yield of aromatics (phenols, catechols) increases with temperature
- 1,2-Dimethoxybenzene was also formed at lower temperature (not shown)

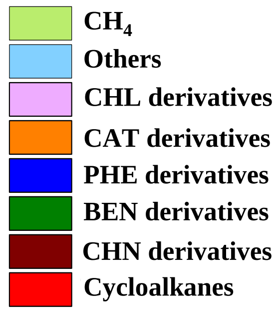
Effect of temperature

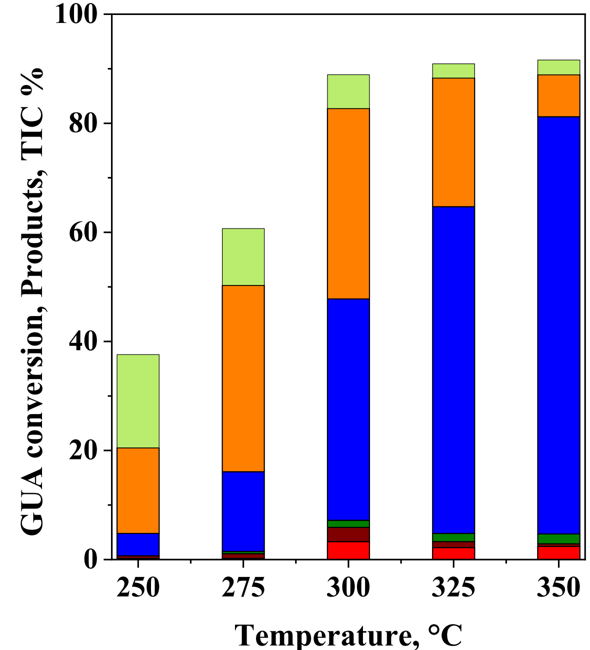
Ni/Al_2O_3

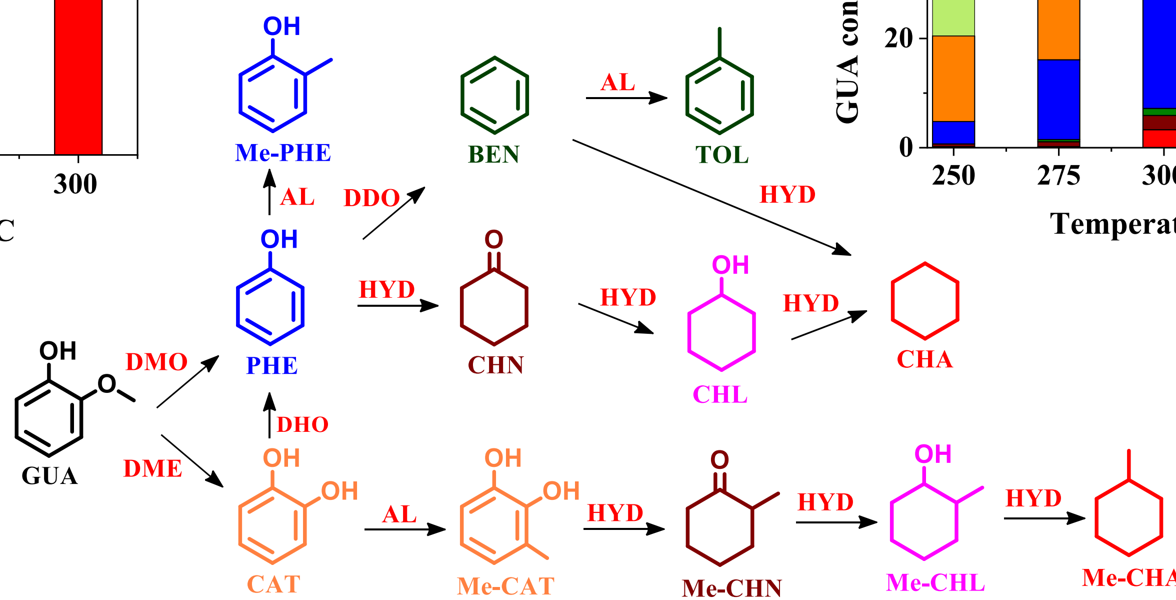
10 bar, 1 g_{cat}/g_{GUA}*h, H_2/GUA=20

Ni/Al_2O_3 (P) (550)







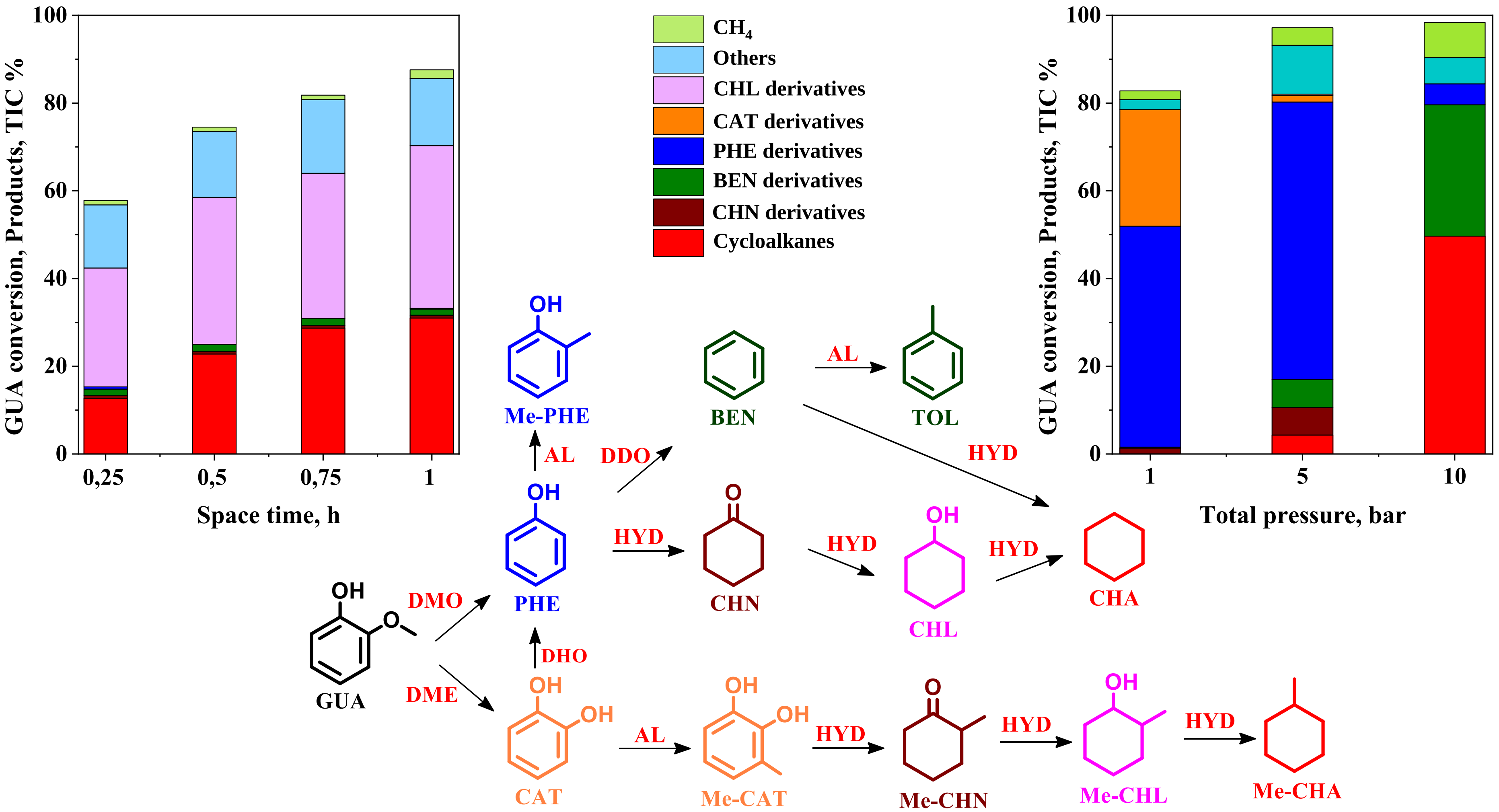


- At 225 °C cyclohexanols were the main products
- At 250 °C high yield and selectivity to CHA
- With temperature the yield of benzenes increased as dehydrogenation is accelerated

- The yield of phenols increases with temperature

Effect of space time and total pressure on Ni/Al_2O_3

225 °C, 10 bar, H_2/GUA=20 | **300 °C, 1 g_{cat}/g_{GUA}*h , H_2/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

- At lower pressure the hydrogenation activity is lower
- With total pressure more hydrogenated products were formed

Conclusions

- ✓ The sequential steps of GUA hydroconversion can be controlled by using noble and non-noble metal and modifying the alumina support.
- ✓ Pd/Al_2O_3 catalyst shows high activity and selectivity in GUA hydrodeoxygenation to cyclohexanones.
- ✓ Ni/Al_2O_3 catalyzed hydroconverzion 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_2O_3(P) and Ni/Al_2O_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**

Interreg Slovakia-Hungary EUROPEAN UNION Building Partnership

www.ttk.hu/palyazatok/bioeconomy