

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

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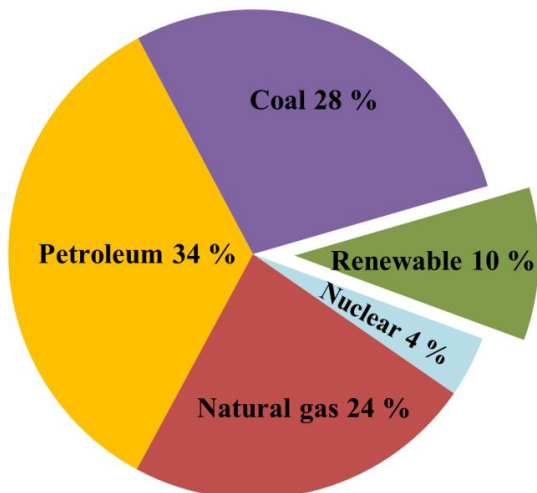
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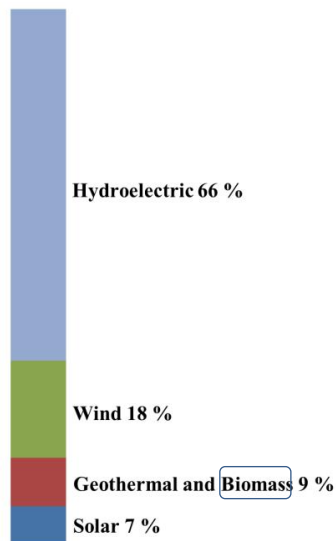


# Lignocellulose as source of carbon and energy

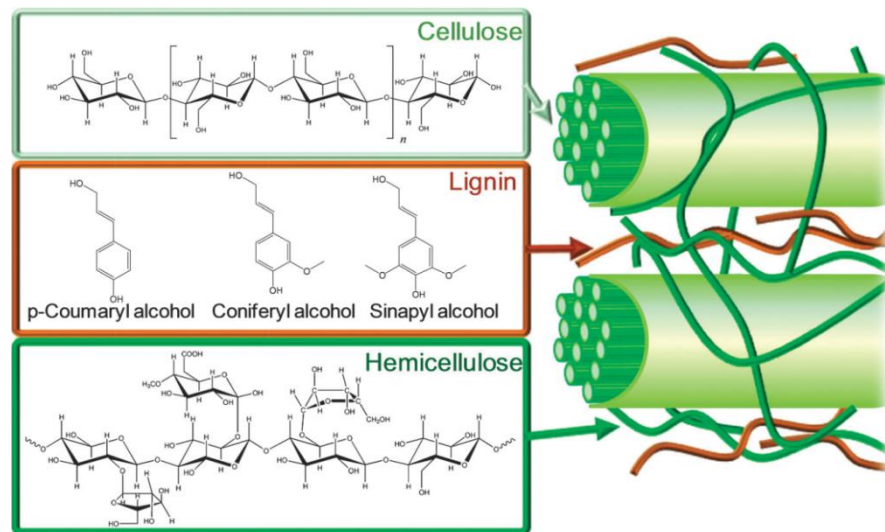
## Current carbon and energy resources



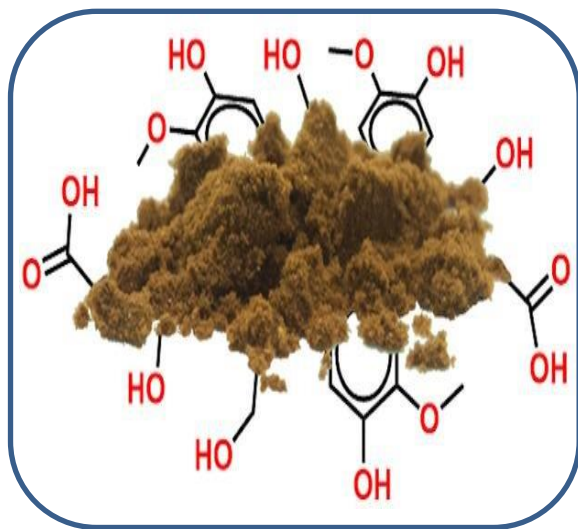
Distribution of energy sources  
(BP Statistical Review of World Energy)



## Structure of lignocellulose

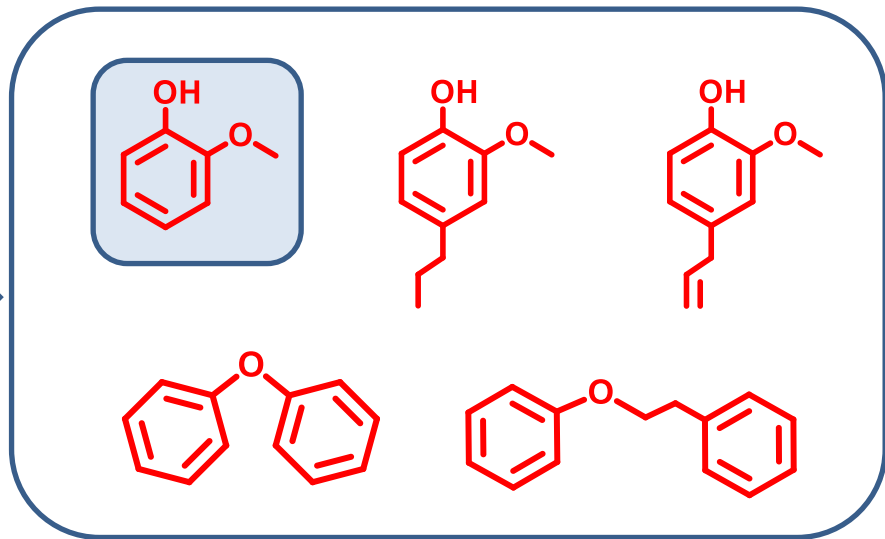


Chem. Soc. Rev. 41 (2012) 8075



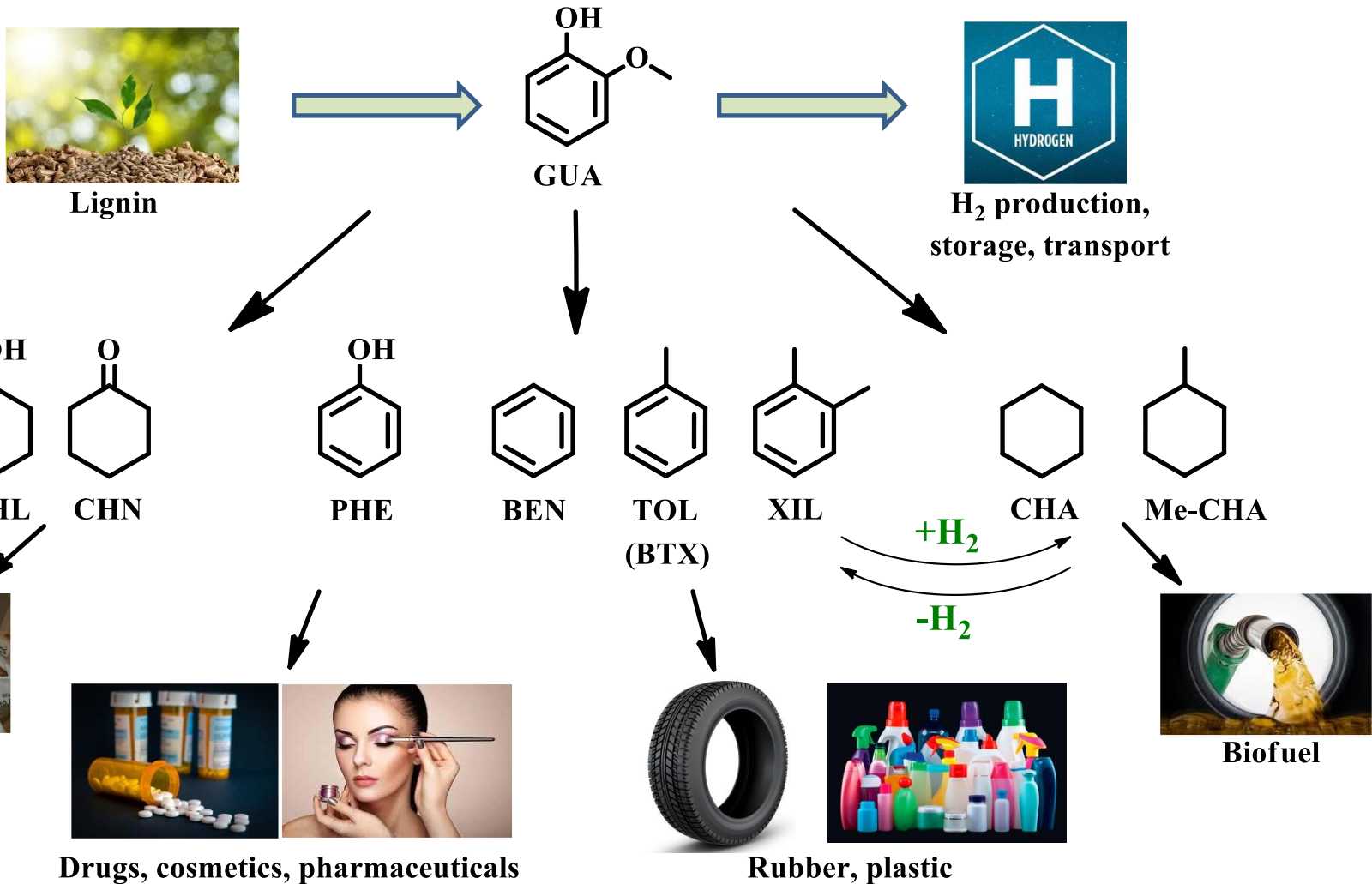
Lignin

chemical/thermal  
depolymerization



Bio-oxygenates

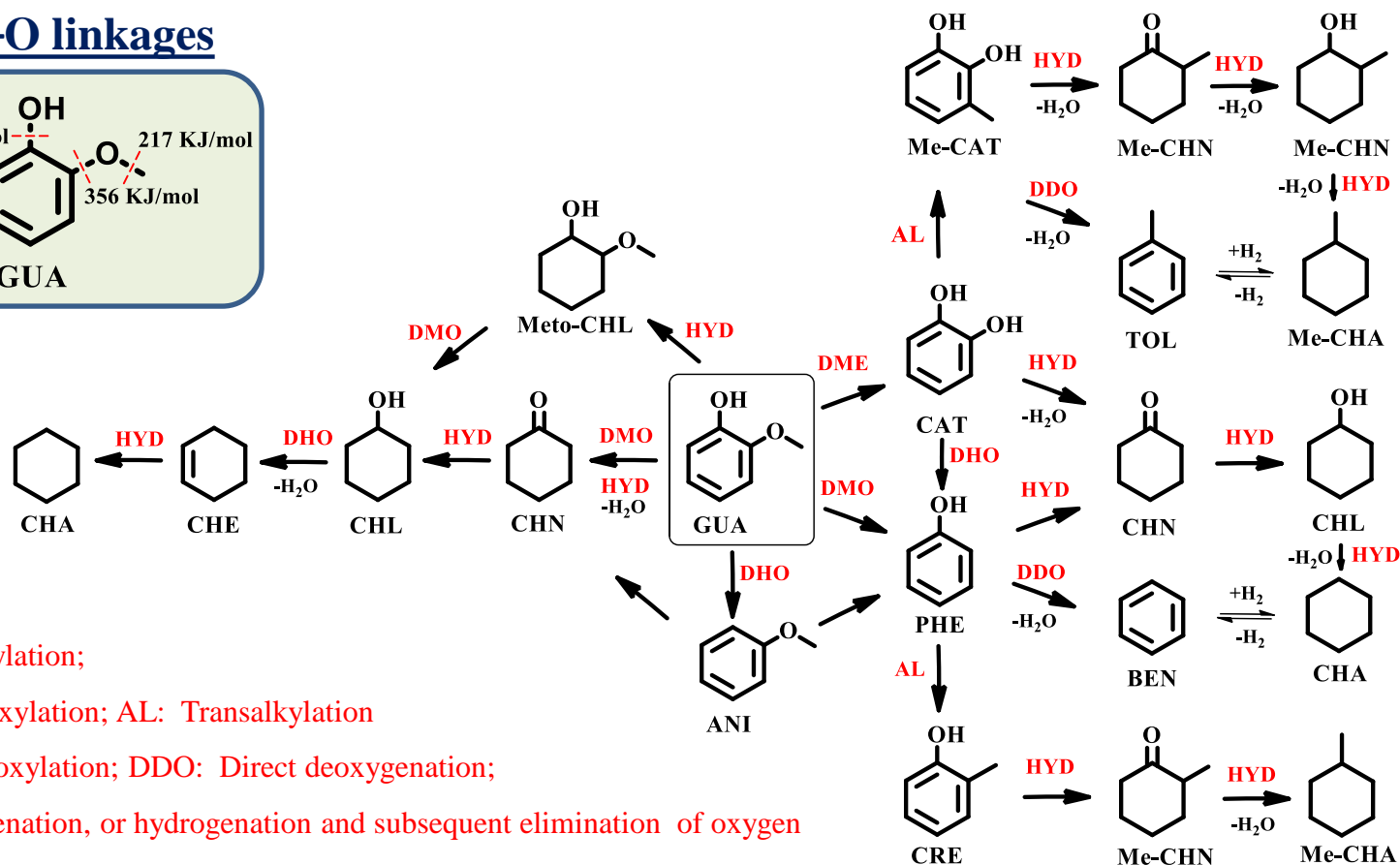
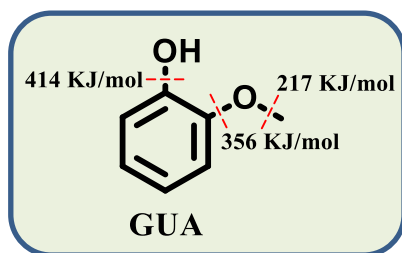
# Guaiacol-based chemicals



➤ 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 <sub>2</sub> O <sub>3</sub>     | Pd(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> | γ-Al <sub>2</sub> O <sub>3</sub> (Alfa Aesar)   |
| Ni/Al <sub>2</sub> O <sub>3</sub>     | Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O              |   |
| Pd/Al <sub>2</sub> O <sub>3</sub> (P) | Pd(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> | γ-Al <sub>2</sub> O <sub>3</sub> (Alfa Aesar)<br>impregnated with H <sub>3</sub> PO <sub>4</sub> solution,<br>dried and calcined (550 °C, 4h) |
| Ni/Al <sub>2</sub> O <sub>3</sub> (P) | Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 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, H<sub>2</sub>**  $\longrightarrow$  Pd<sup>0</sup>  
Ni<sup>0</sup>

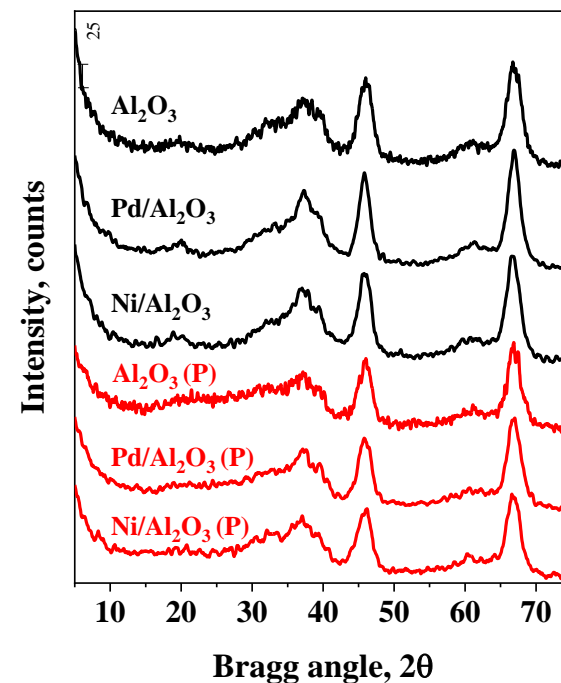
➤ Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor

# Catalyst characterization

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

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

## X-ray diffraction (XRD)

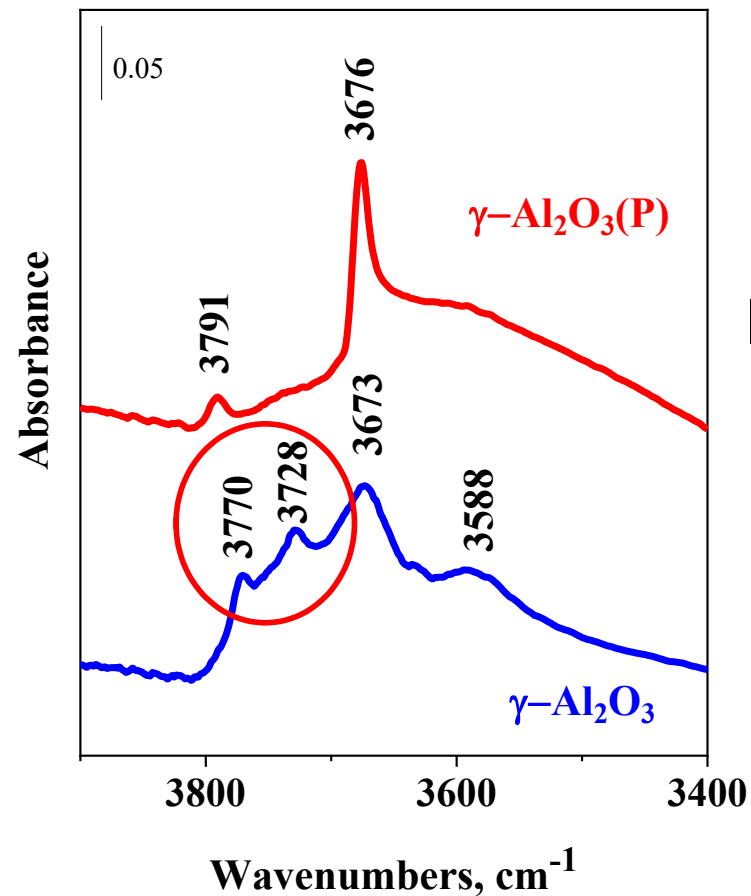


- Metal impregnation has no influence on SSA
- Impregnation of Al<sub>2</sub>O<sub>3</sub> support with H<sub>3</sub>PO<sub>4</sub> solution reduces SSA

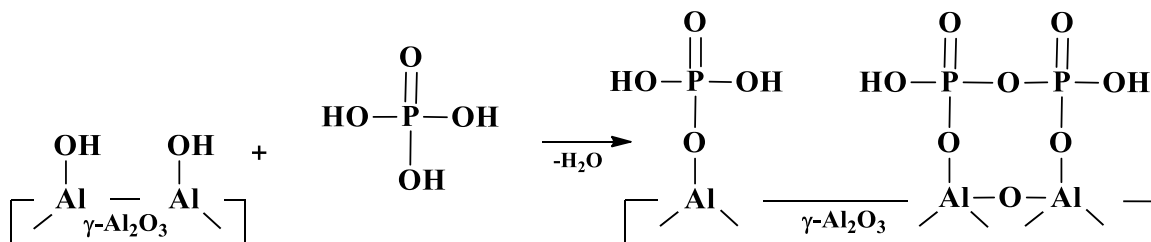
- Al<sub>2</sub>O<sub>3</sub> is the only detectable phase
- NiO and PdO crystallites are well dispersed on the Al<sub>2</sub>O<sub>3</sub> surface

# Surface structure of phosphated $\gamma$ -alumina

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



Phosphoric acid reacts with the hydroxyls of alumina  $\longrightarrow$  monomeric and polymeric phosphate species are formed<sup>a</sup>



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

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

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

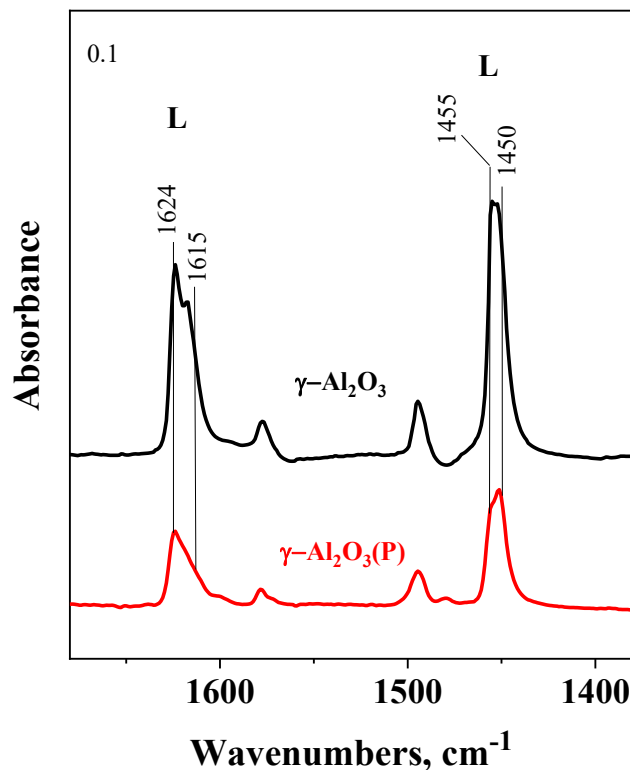
$\gamma\text{-Al}_2\text{O}_3(\text{P})$

- 3791  $\text{cm}^{-1}$ ,  $\text{Al}^{\text{IV}}\text{-OH}$ , (terminal)<sub>tetr</sub>
- 3676  $\text{cm}^{-1}$ ,  $\text{P-OH}$  on phosphates

<sup>a</sup>Stanislaus et al., Appl. Cat. 39 (1988) 239; A. Vikár et al., manuscript under preparation

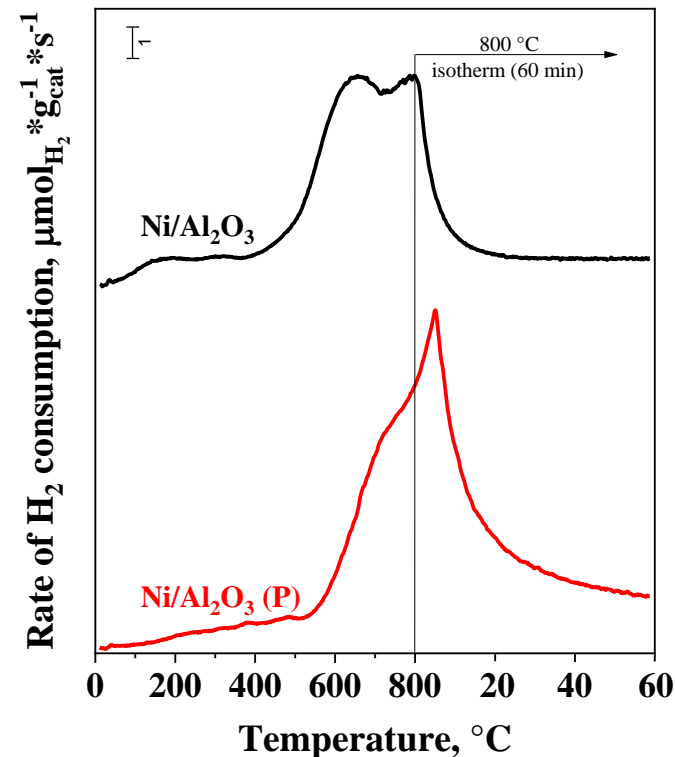
# Catalysts acidity and reducibility

## FT-IR spectra of adsorbed pyridine



- On the  $\text{Al}_2\text{O}_3(\text{P})$  support the intensity of bands at 1450, 1455  $\text{cm}^{-1}$  and 1615, 1624  $\text{cm}^{-1}$  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 ( $\text{H}/\text{Ni}=0.09$ )
  - $\text{Ni}/\text{Al}_2\text{O}_3(\text{P}) \sim 0.5\%$  ( $\text{H}/\text{Ni}=0.01$ )

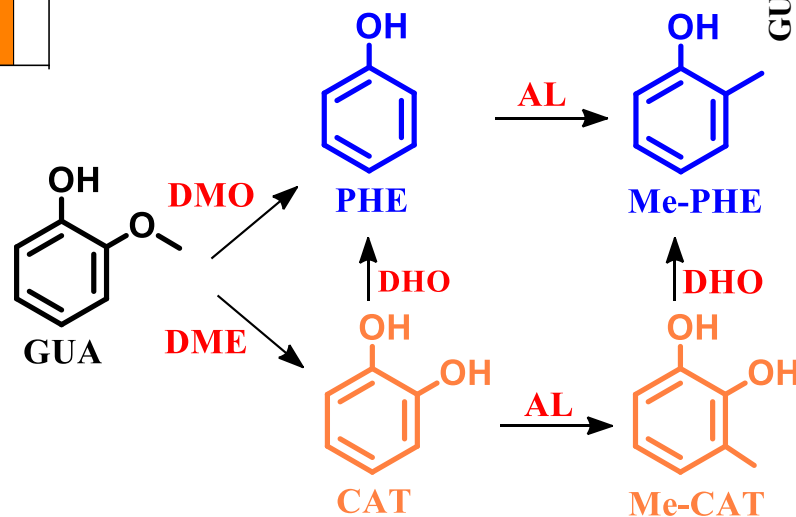
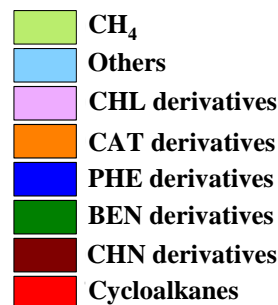
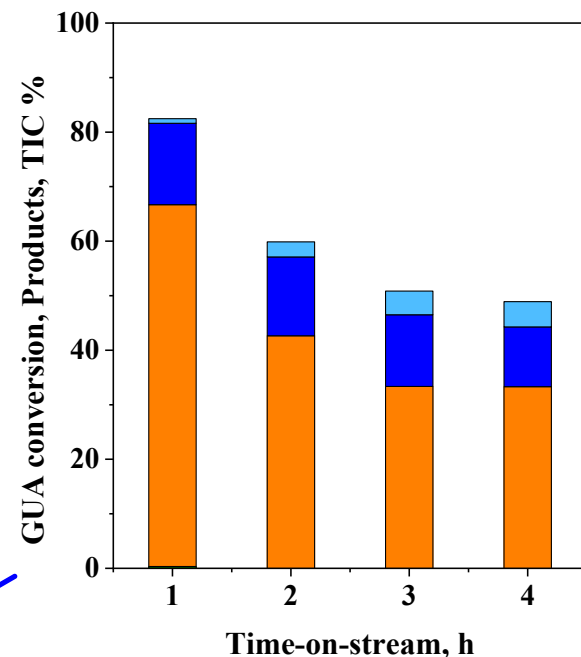
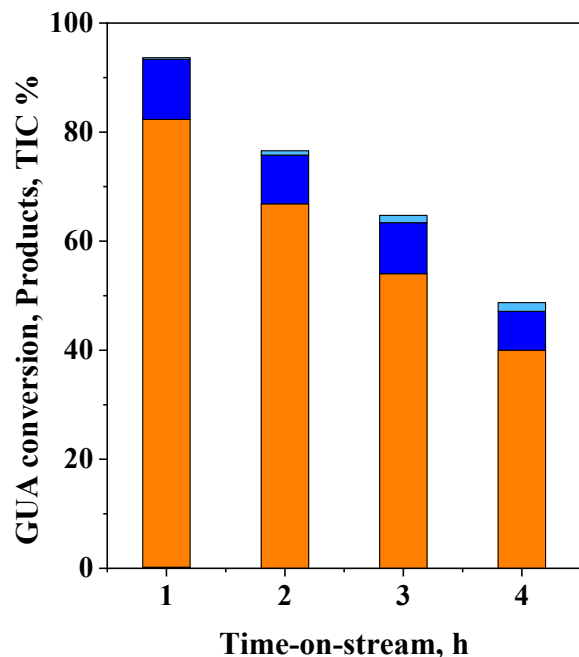


# Activity of $\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ (P) supports

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

300 °C, 10 bar, 1 g<sub>cat</sub>/g<sub>GUA</sub>\*h, H<sub>2</sub>/GUA=20

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



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

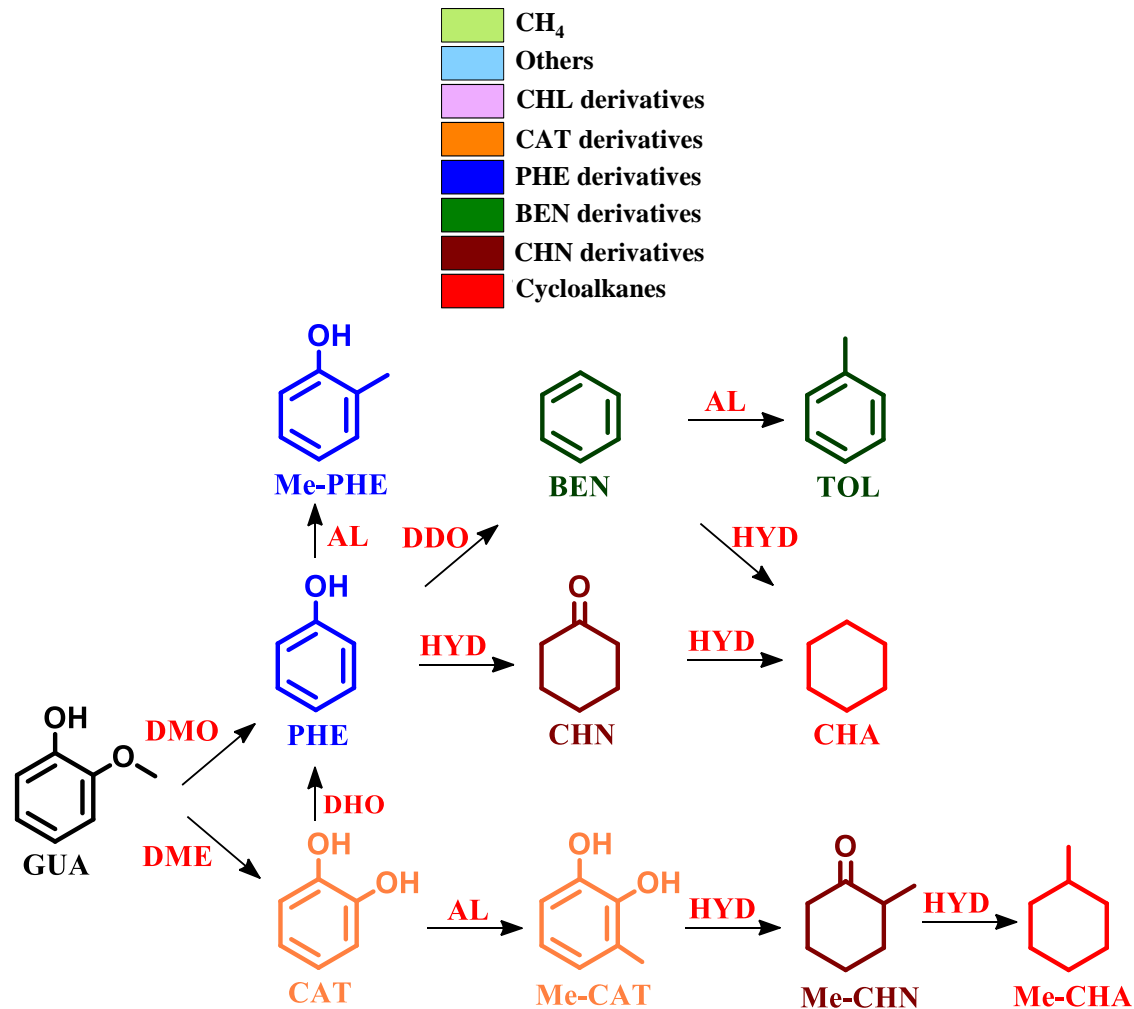
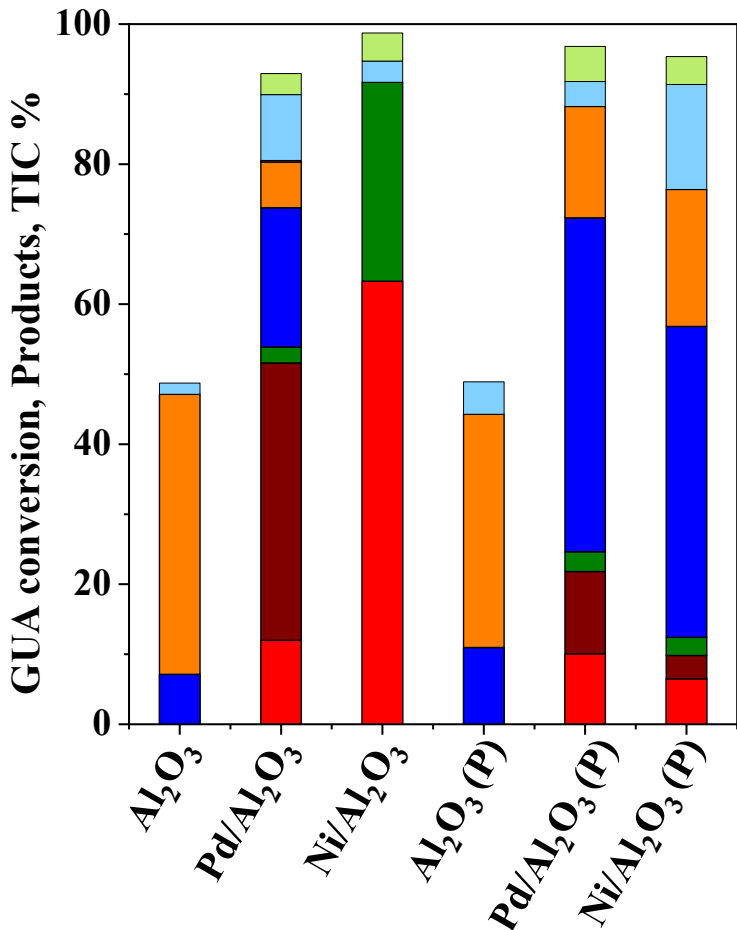
➤ CAT derivatives are the main products

➤ Demethoxylation (DMO) and dehydroxylation (DHO) also takes place

➤ PHE derivatives were also formed

# Comparison of catalysts activity

300 °C, 10 bar, 1 g<sub>cat</sub>/g<sub>GUA</sub>\*h,  
H<sub>2</sub>/GUA=20, time-on-stream = 4 h



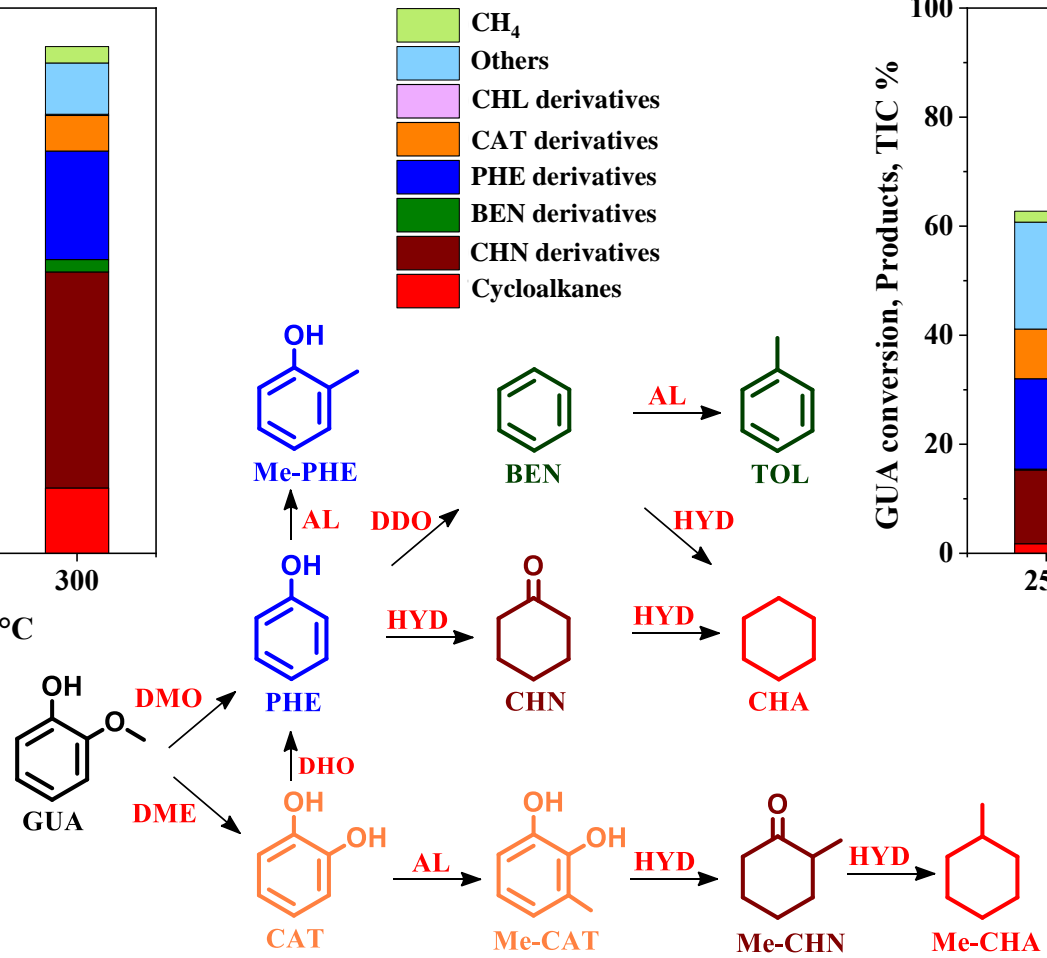
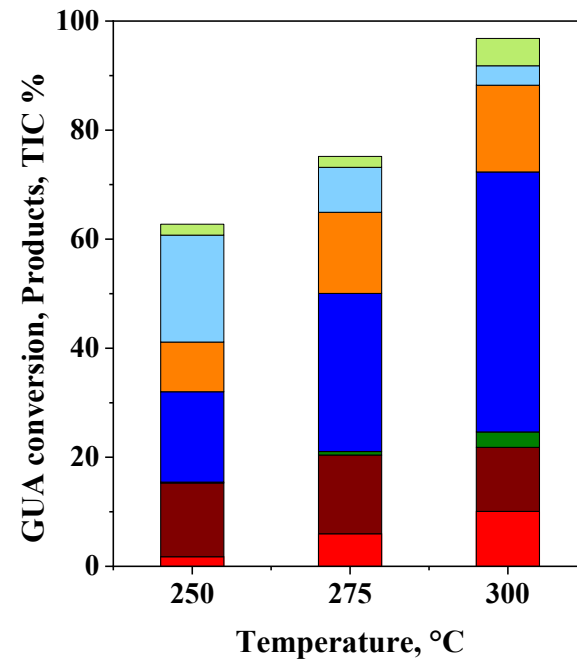
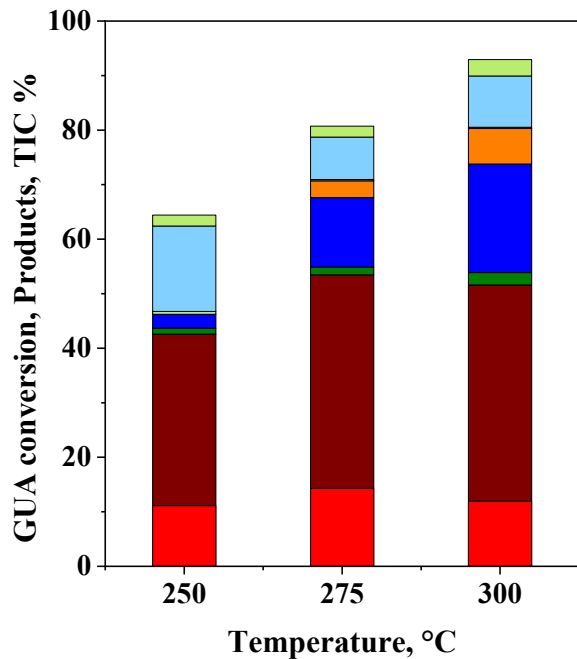
- Cyclohexanones and cycloalkanes are the main products on Pd/Al<sub>2</sub>O<sub>3</sub>
- O-free compounds were mainly formed on Ni/Al<sub>2</sub>O<sub>3</sub>
- Aromatics (phenols, catechols) were formed on Pd/Al<sub>2</sub>O<sub>3</sub> (P) and Ni/Al<sub>2</sub>O<sub>3</sub> (P)

# Effect of temperature

Pd/Al<sub>2</sub>O<sub>3</sub>

10 bar, 1 g<sub>cat</sub>/g<sub>GUA</sub>\*h, H<sub>2</sub>/GUA=20

Pd/Al<sub>2</sub>O<sub>3</sub> (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)

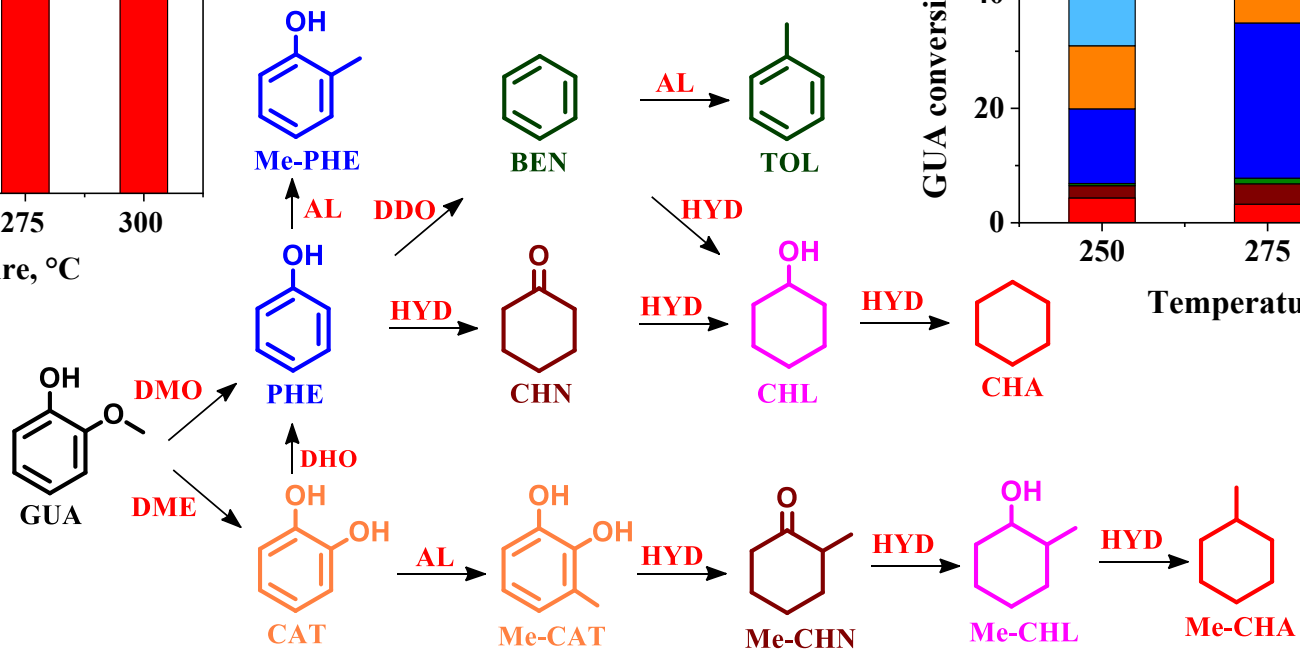
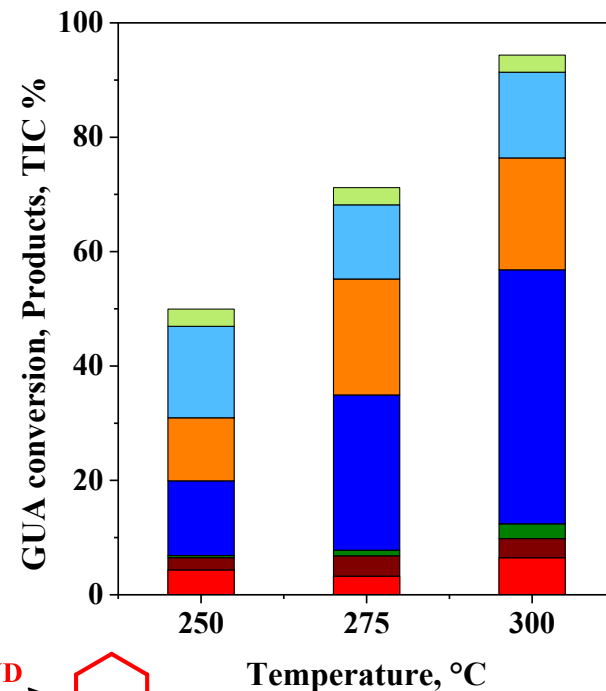
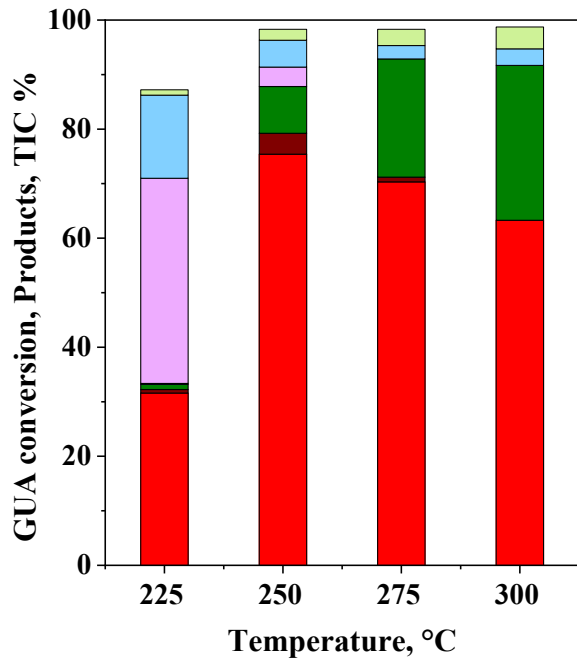
- The yield of aromatics (phenols, catechols) increases with temperature
- 1,2-Dimethoxybenzene was also formed at lower temperature (not shown)

# Effect of temperature

Ni/Al<sub>2</sub>O<sub>3</sub>

10 bar, 1 g<sub>cat</sub>/g<sub>GUA</sub>\*h, H<sub>2</sub>/GUA=20

Ni/Al<sub>2</sub>O<sub>3</sub> (P)



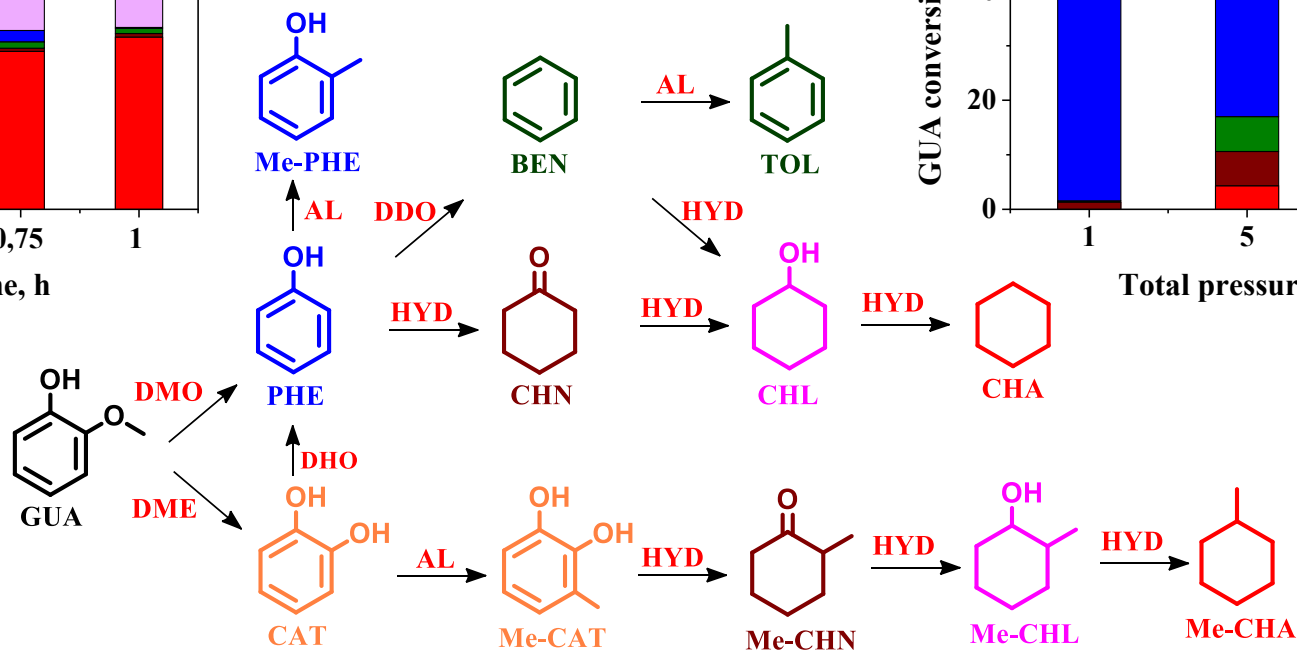
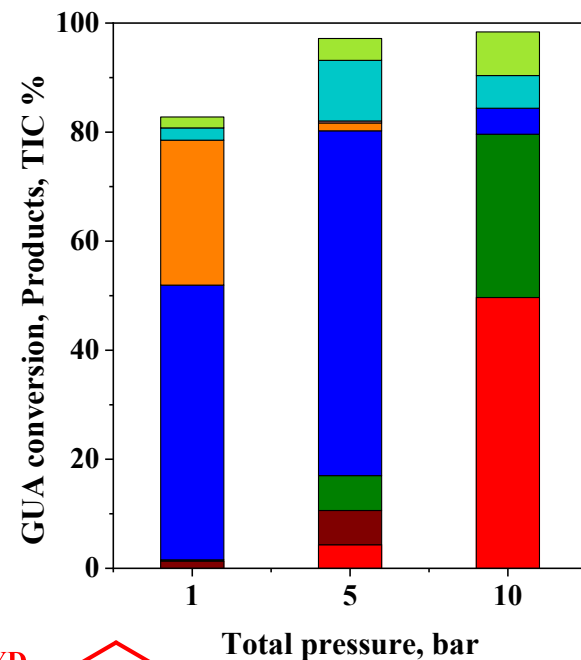
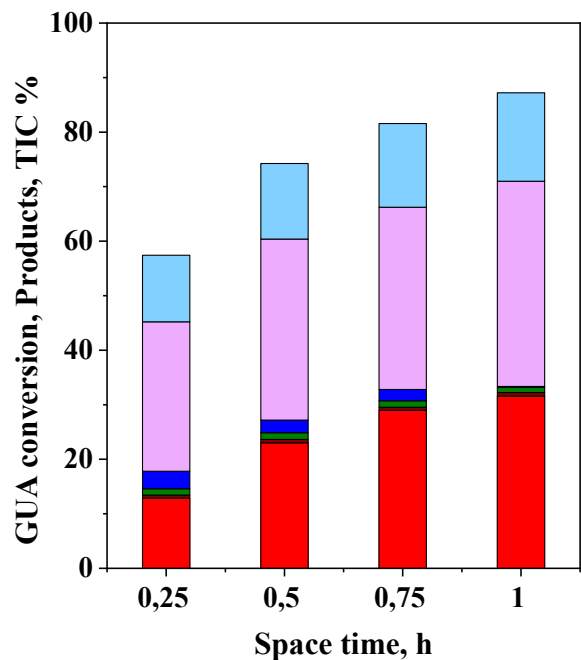
- At 225 °C cyclohexanols were the main products
- At 250 °C high yield and selectivity to CHA
- With temperature the yield of benzenes increased as dehydrogenation is accelerated

- The yield of aromatics (phenols, catechols) increases with temperature

# Effect of space time and total pressure on Ni/Al<sub>2</sub>O<sub>3</sub>

225 °C, 10 bar, H<sub>2</sub>/GUA=20

300 °C, 1 g<sub>cat</sub>/g<sub>GUA</sub>\*h, H<sub>2</sub>/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

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- ✓ 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  $\text{Al}_2\text{O}_3$  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!



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