

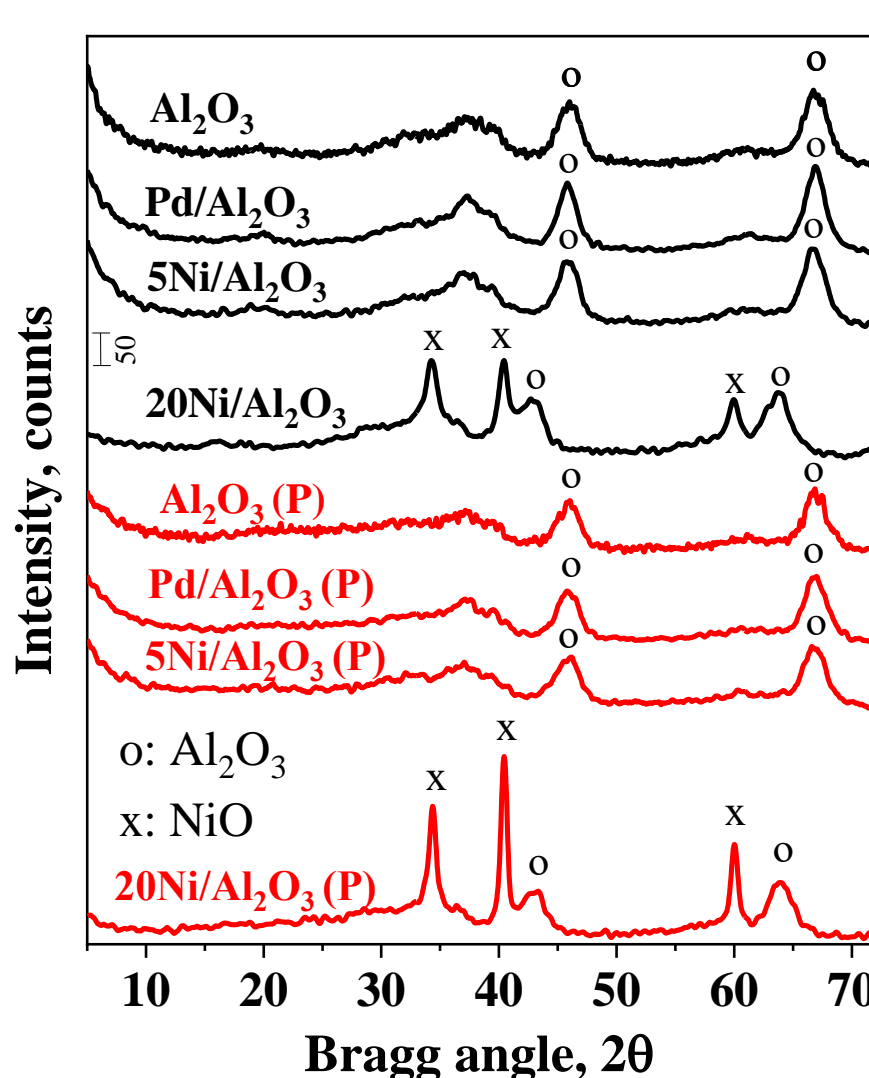
Introduction

- Lignocellulose is the most widely available renewable organic material, which is composed of polymeric cellulose, hemicellulose and lignin. Depolymerizations of lignin results in lower molecular weight polymers and phenolic monomers. Guaiacol (GUA) is a model compound that contains both major functional groups of lignin-derived phenolics, such as hydroxyl (-OH) and methoxy (-O-CH₃). Catalytic hydrodeoxygenation (HDO) of GUA can produce value-added products which have large market potential [1].
- Liquid hydrocarbons obtained by total HDO of GUA can be used as biofuel. The selective partial HDO of GUA results in the formation of oxygenated products like cyclohexanone (CHN) and cyclohexanol (CHL). These oxygenates are precursors of adipic acid, caprolactone, caprolactam and industrial precursors of nylons. The demethylation and/or demethoxylation of GUA leads to the formation of aromatic products like benzene, toluene, xylenes (BTX), phenols and catechols, which are important precursors for many commercial chemicals, pharmaceuticals and polymers [2,3,4].
- In the present study γ -Al₂O₃ and phosphorous-modified γ -Al₂O₃-supported Pd and Ni catalysts were investigated in HDO of GUA using a fixed-bed flow-through microreactor.

[1] M.J. Climent et al. Green Chem. 2014, 16, 516; [2] H. Zhou et al. Appl. Catal. B 2020, 270, 118890; [3] H. Wang et al. ChemSusChem 2017, 10, 1846; [4] G.Y. Xu et al. Green Chem. 2016, 18, 5510

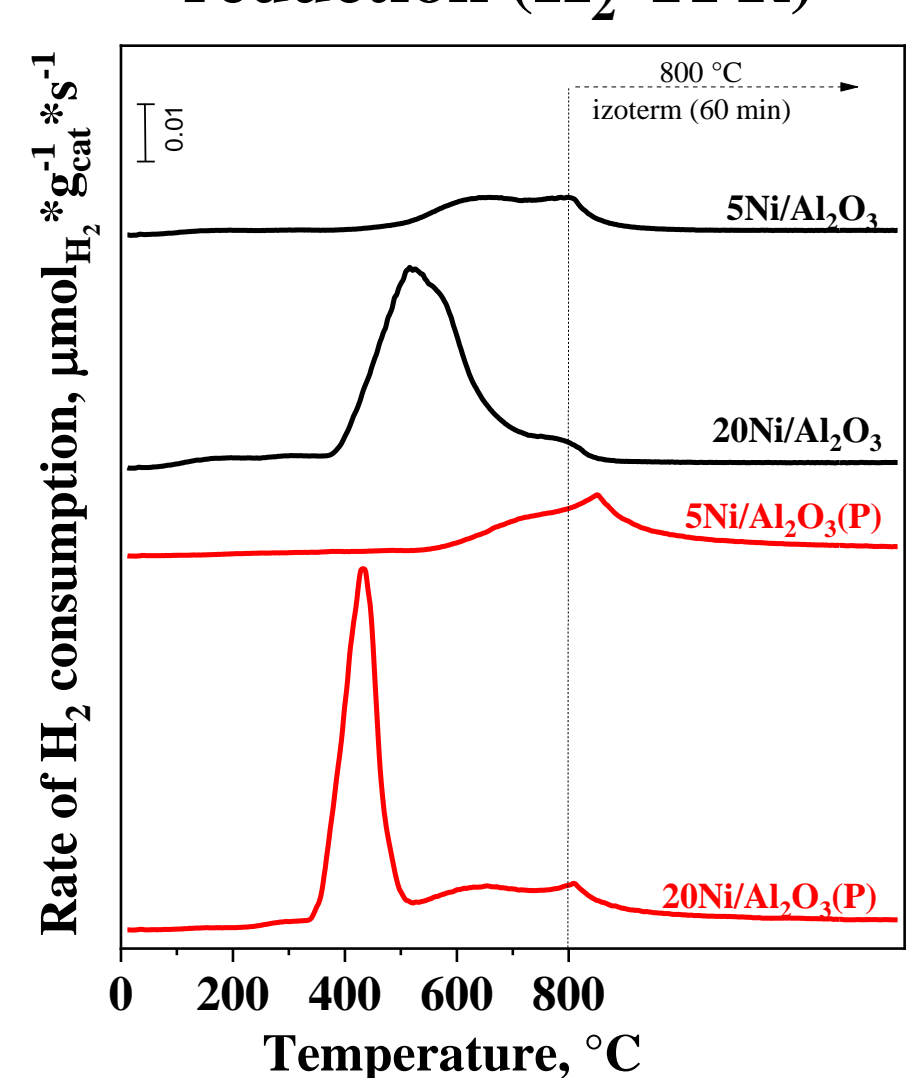
Catalysts preparation and characterization

X-ray diffraction (XRD)



- γ -Al₂O₃ is the only detectable phase of catalysts with low metal loading (NiO and PdO crystallites are well dispersed).
- The XRD pattern of 20Ni/Al₂O₃ and 20Ni/Al₂O₃(P) catalysts show the reflections of NiO (NiO particle size was about 30 nm).

Temperature-programmed reduction (H₂-TPR)



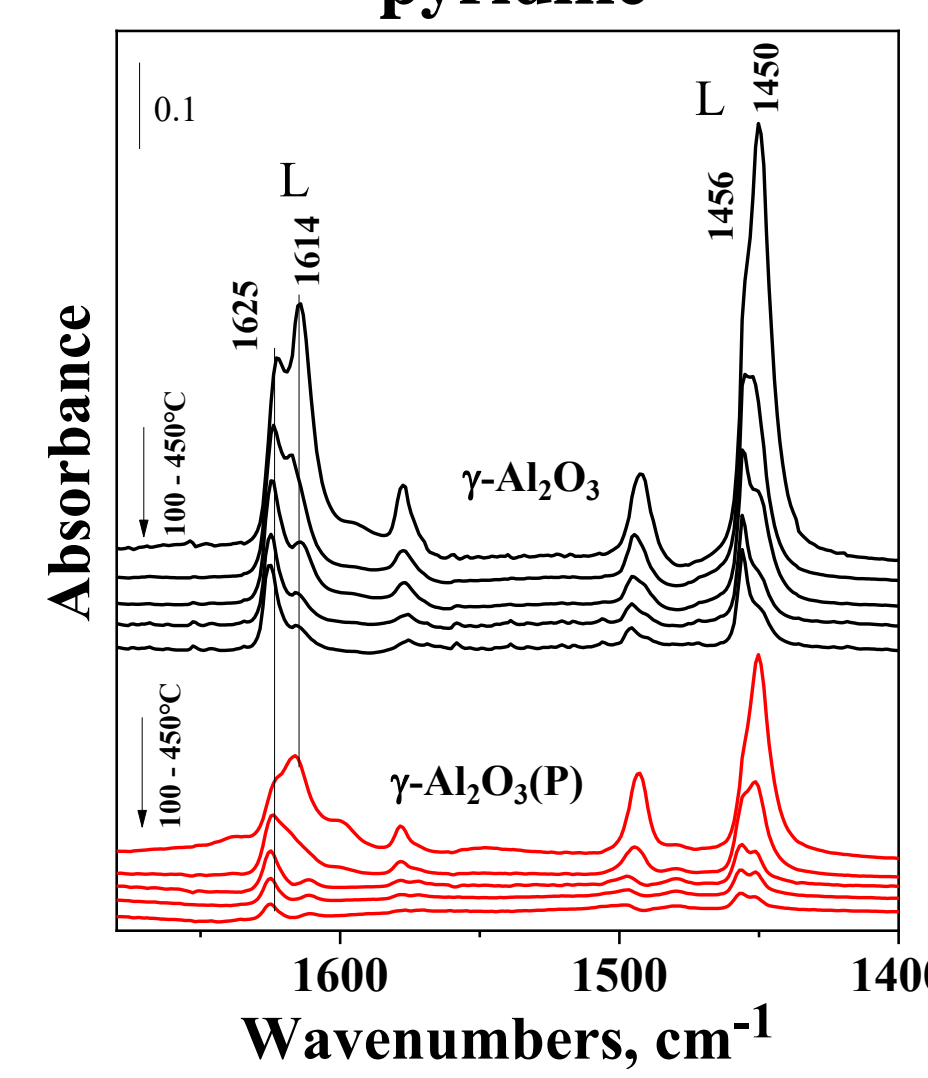
- The catalysts were in situ reduced at 450 °C in the reactor before catalytic run.
- The degree of reduction at 450 °C:
 - 5Ni/Al₂O₃ ~ 4.5 % of Ni (H/Ni=0.09)
 - 5Ni/Al₂O₃ (P) ~ 0.5% (H/Ni=0.01)
 - 5Ni/Al₂O₃ (P) (550) ~ 3.5% (H/Ni=0.07)
 - 20Ni/Al₂O₃ ~ 68 % (1.37 H/Ni)
 - 20Ni/Al₂O₃ (P) ~ 65 % (1.3 H/Ni)

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
5Ni/Al ₂ O ₃	5.21	-	192
20Ni/Al ₂ O ₃	~20	-	190
Al ₂ O ₃ (P)	-	4.85	167
Pd/Al ₂ O ₃ (P)	0.49	4.87	163
5Ni/Al ₂ O ₃ (P)	5.06	4.82	165
20Ni/Al ₂ O ₃ (P)	~20	4.82	131

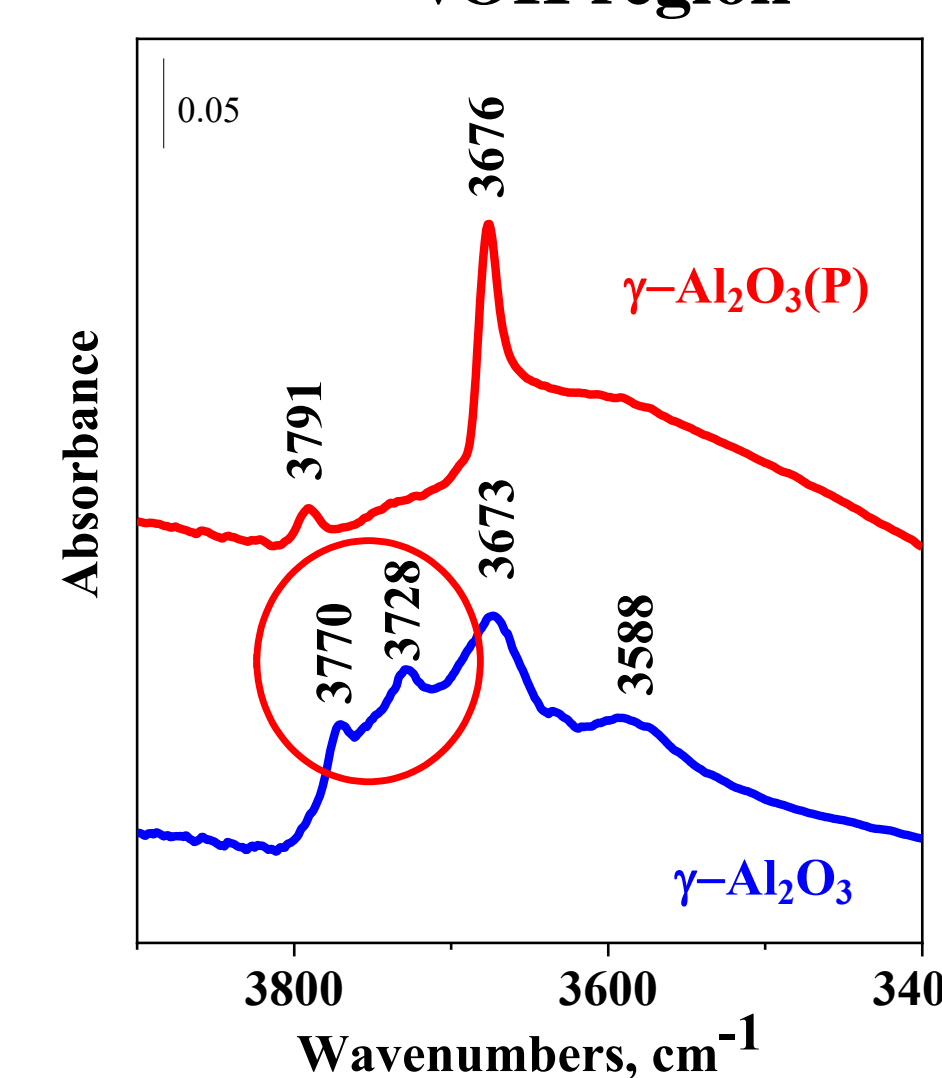
- Commercial γ -Al₂O₃ and phosphorous (P)-modified γ -Al₂O₃ were used as support.
- The phosphorous (P) modification was done with H₃PO₄ solution.
- The SSA decreased upon P-modification.
- The Pd- and Ni-containing catalysts were prepared by wet impregnation method.
- Metal impregnation has no influence on SSA and pore volume.
- Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor.

FT-IR spectra of adsorbed pyridine



- On Al₂O₃ (P) support the intensity of bands at 1450, 1455 cm⁻¹ and 1615, 1624 cm⁻¹ is lower, indicating its lower Lewis acidity.
- Phosphorus modification reduces the Lewis acidity of the alumina support.

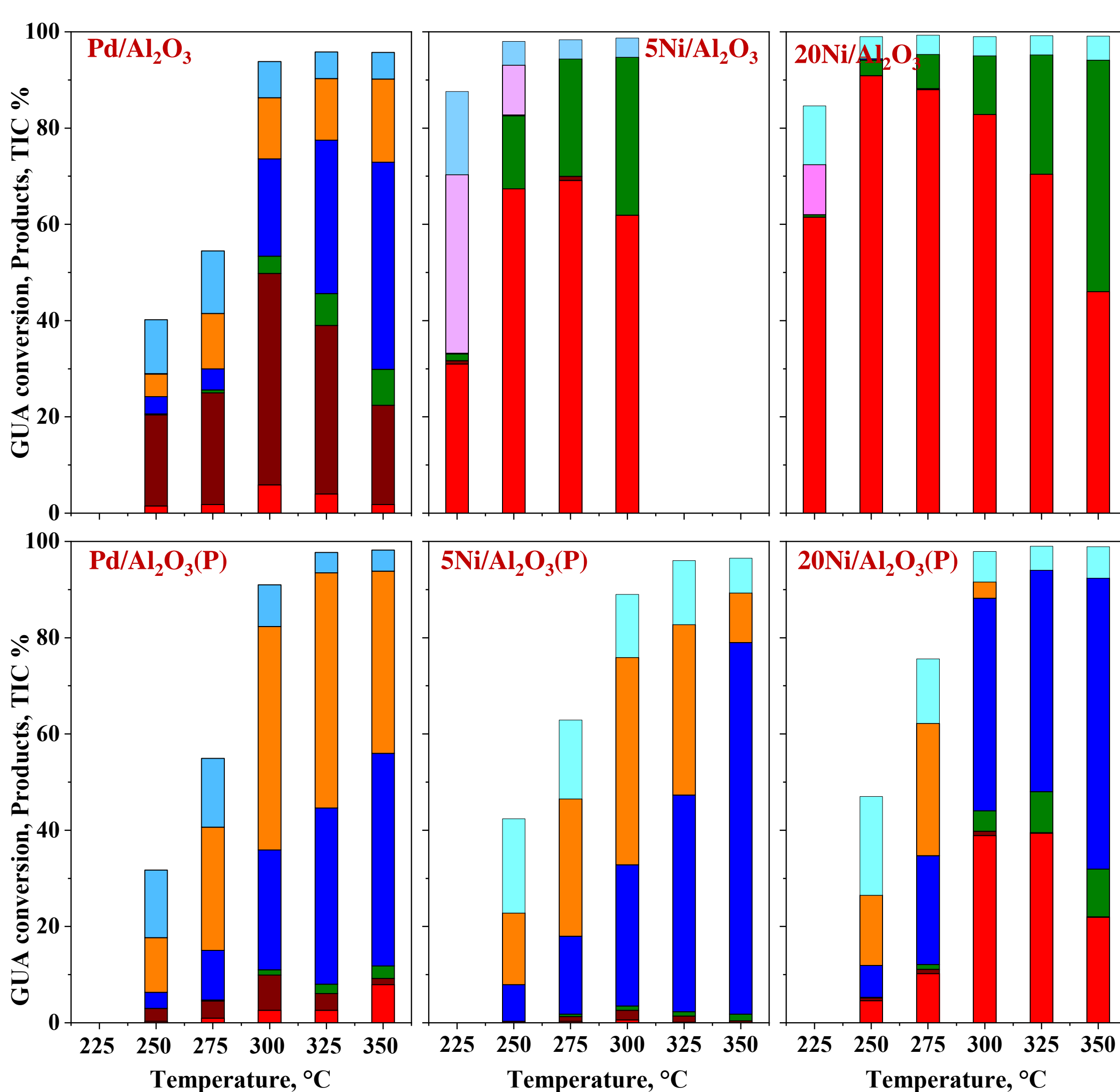
FT-IR spectra in the vOH region



- γ -Al₂O₃
 - 3770 cm⁻¹, □-O-Al^{IV}-OH, (terminal)_{tet}
 - 3728 cm⁻¹, Al^{IV}-OH, (terminal)_{oct}
 - 3673 cm⁻¹, Al-O(H)-Al, bridged
 - 3588 cm⁻¹, triple-bridged
- γ -Al₂O₃(P)
 - 3791 cm⁻¹, Al^{IV}-OH, (terminal)_{tet}
 - 3676 cm⁻¹, P-OH on phosphates
- Phosphoric acid reacts with the hydroxyls of alumina and monomeric and polymeric phosphate species are formed.

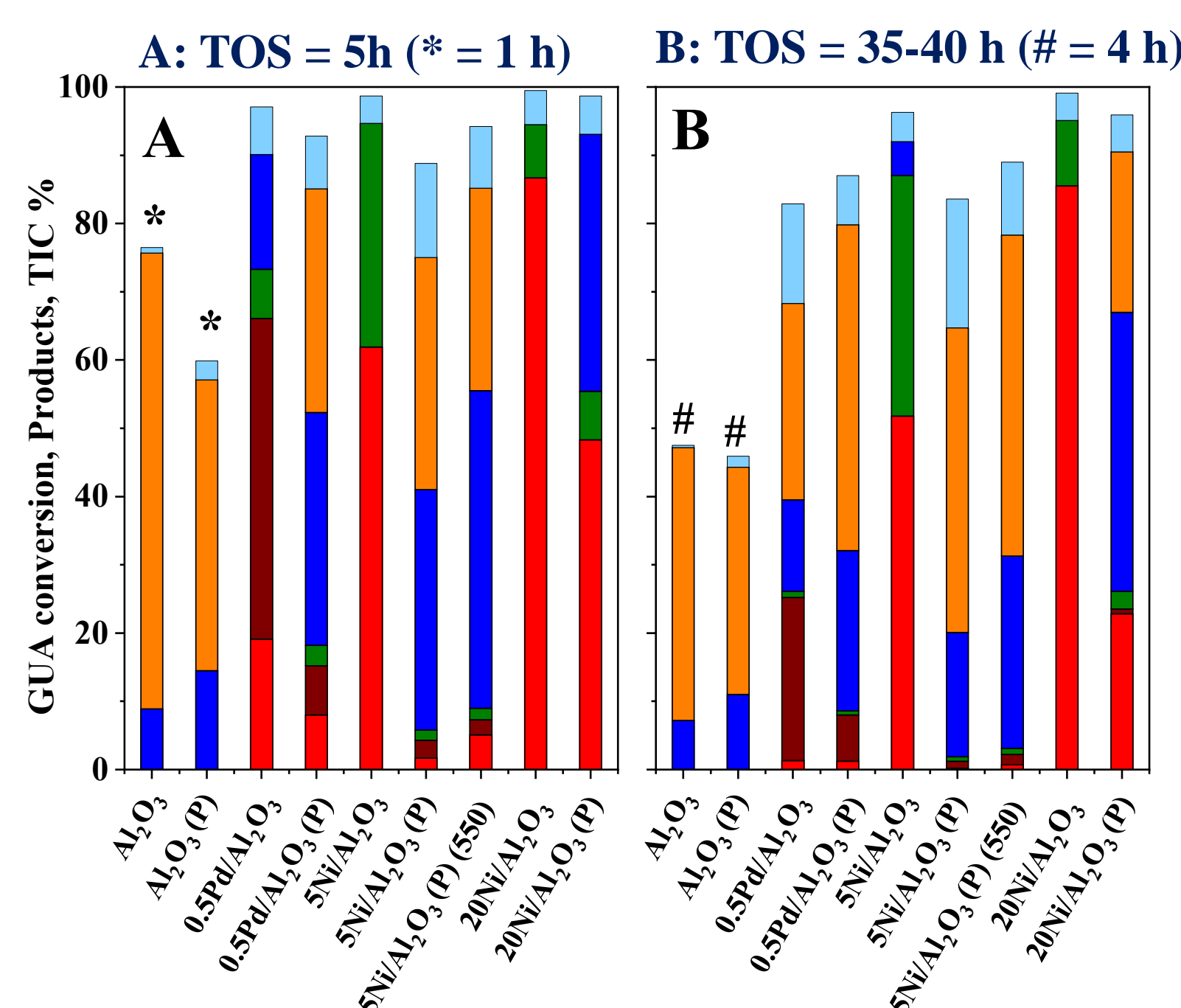
Catalytic hydrodeoxygenation of guaiacol

Effect of temperature



- Over Pd/Al₂O₃ catalyst CHN derivatives were the main products at 300 °C. At higher temperatures (325 and 350 °C) the yield of PHE derivatives increased.
- O-free compounds like cyclohexane (CHA) and Me-CHA were mainly formed over 5Ni/Al₂O₃ and 20Ni/Al₂O₃ at 250 – 300 °C. With temperature the yield of benzenes increased as dehydrogenation of cyclohexanes is accelerated. At 225 °C cyclohexanols were the main products.
- Aromatics (phenols, catechols) were formed on P modified catalysts. The amount of PHE derivatives increased with temperature.

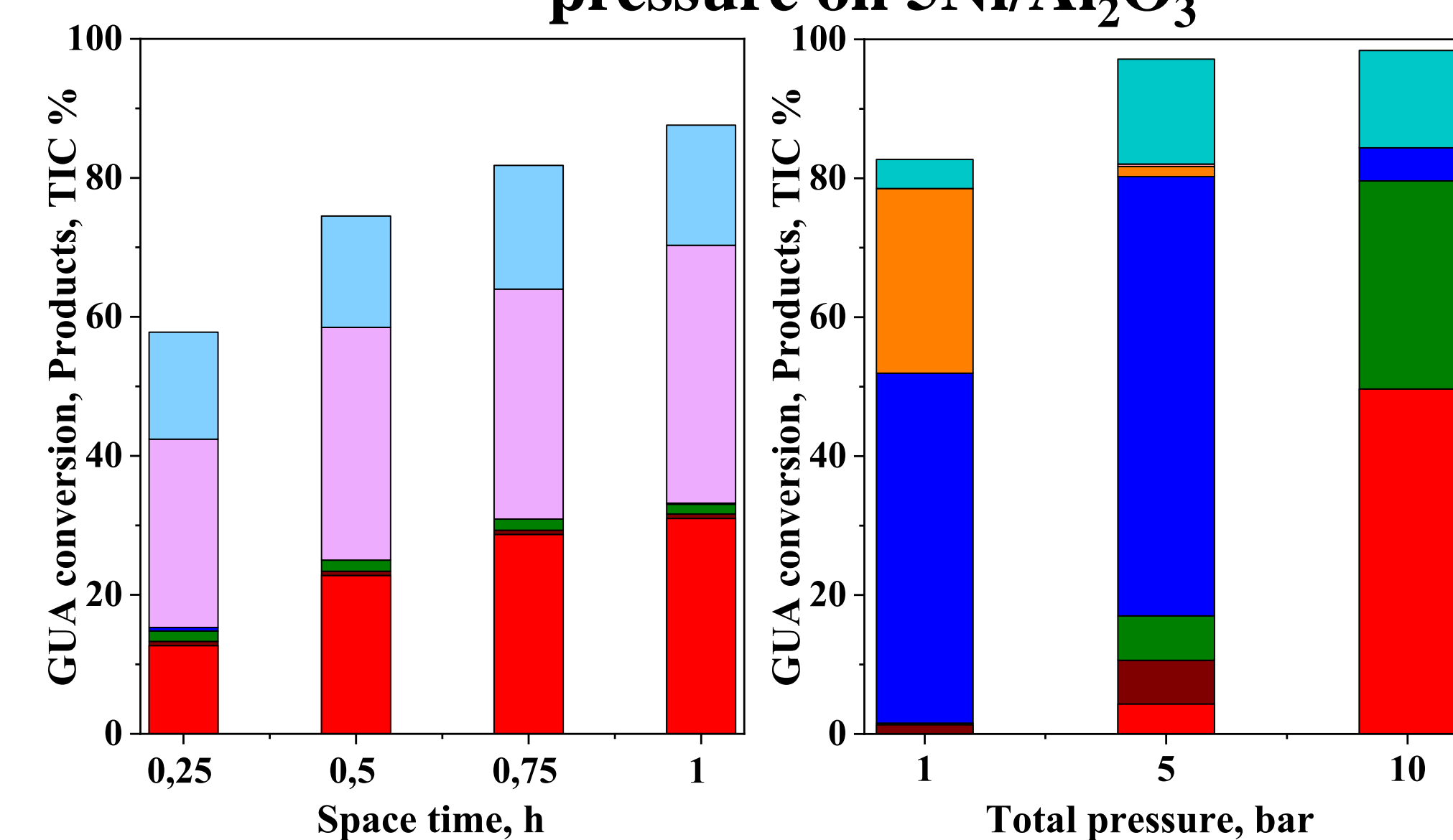
Stability



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

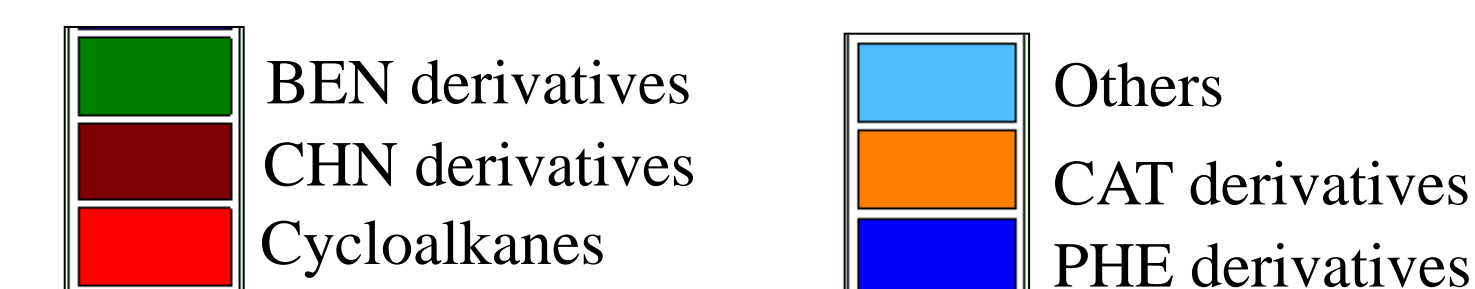
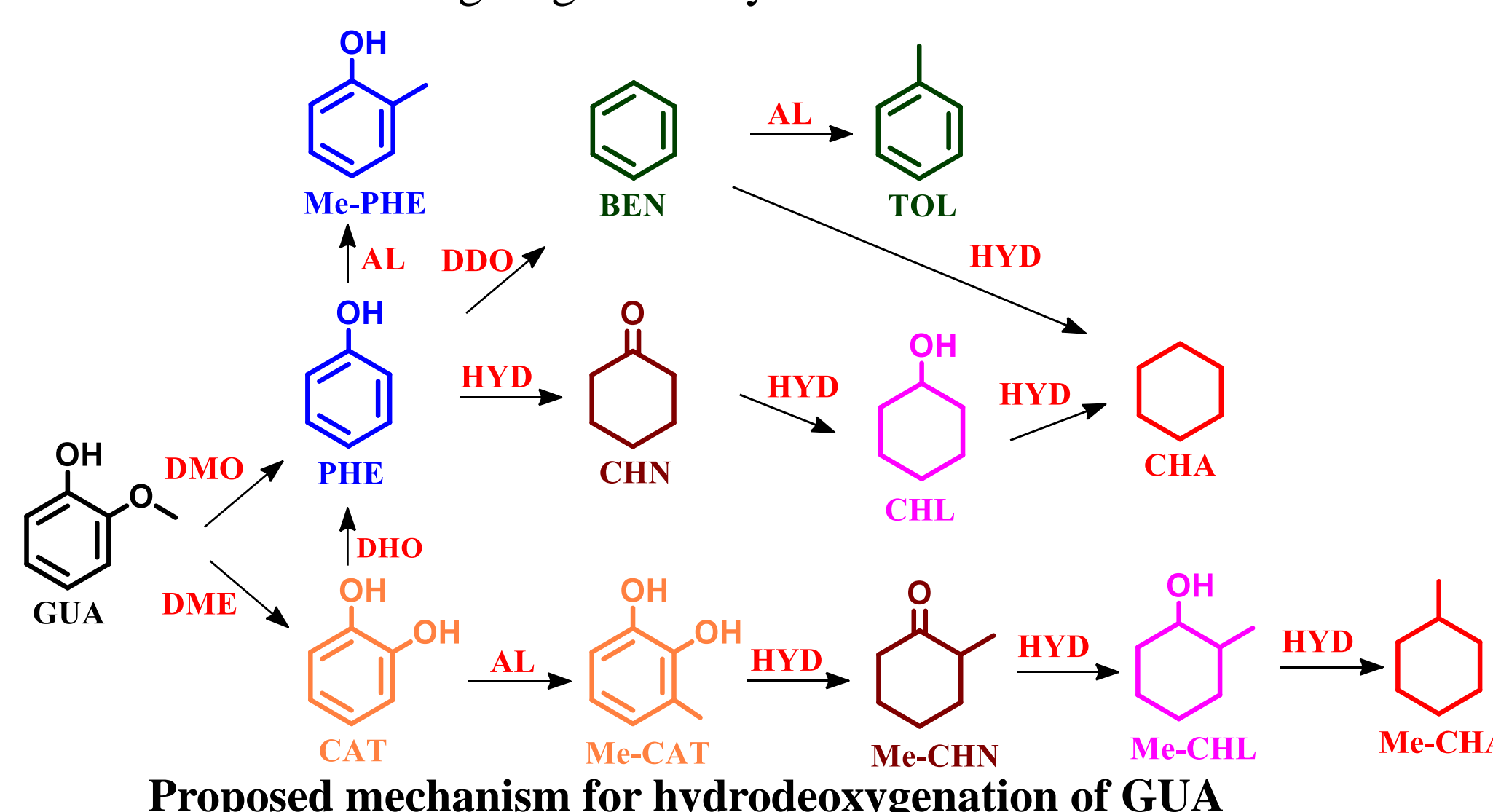
- Demethylation (DME) and transalkylation (AL) are the main reactions over Al₂O₃ and Al₂O₃ (P) supports.
- CHN and cycloalkanes are the main products on Pd/Al₂O₃.
- O-free compounds were mainly formed on Ni/Al₂O₃.
- Aromatics (phenols, catechols) were formed on P modified catalysts.
- 5Ni/Al₂O₃ and 20Ni/Al₂O₃ catalysts were stable; their activity did not change significantly with TOS.

Effect of space time and total pressure on 5Ni/Al₂O₃



225 °C, 10 bar, H₂/GUA=20 300 °C, 1 g_{cat}/g_{GUA} *h, H₂/GUA=20

- At lower space time phenol and benzene 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. At 5 bar total pressure phenols, at atmospheric pressure phenols and catechols were the main products.
- With total pressure more hydrogenated products were formed.



DME: Demethylation;
DMO: Demethoxylation
DDO: Direct deoxygenation;
AL: Alkylation
HYD: Hydrogenation, or hydrogenation and subsequent elimination of oxygen

Conclusions

- The sequential steps of GUA hydroconversion can be controlled by using noble and non-noble metal and modifying the alumina support.
- Demethylation of GUA on Al₂O₃ and phosphorous modified Al₂O₃(P) supports leads to catechol formation.
- Pd/Al₂O₃ catalyst shows high activity and selectivity in GUA HDO to cyclohexanones.
- Ni/Al₂O₃ catalyzed hydroconversion of GUA to O-free compounds like cyclohexane.
- At lower temperature and space time cyclohexanols were formed in large amounts.
- Pd and Ni supported on phosphorus-modified alumina behave similarly, they are selective to aromatics.
- Pd/Al₂O₃(P) and Ni/Al₂O₃(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)

Acknowledgment

The authors thank the Ministry of Innovation and Technology for its support from the National Research, Development and Innovation Fund within the framework of the 2019-2.1.13-TÉT_IN program (Project No.: 2019-2.1.13-TÉT_IN-2020-00043).