Gas-phase hydrodeoxygenation of lignin-derived guaiacol and phenol on Ni catalysts using neat and phosphorous-modified γ-alumina supports

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Introduction

Lignocellulose is the major non-food component of biomass comprising three fractions such as cellulose, hemicellulose and lignin. Decomposition/depolymerizations of lignin results in lower molecular weight polymers and phenolic monomers. Guaiacol (GUA) is the most abundant product obtained from lignin, contains both major functional groups of lignin-derived phenolics, such as hydroxyl (–OH) and methoxy (–O–CH$_3$). Catalytic hydrodeoxygenation (HDO) of GUA is a potential route to the value-added products [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 cyclohexanol (CHL). These oxygenates are 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 and polymers [2,3]. In the present study γ-Al$_2$O$_3$ and phosphorous-modified γ-Al$_2$O$_3$-supported Ni catalysts were investigated in HDO of GUA using a fixed-bed flow-through microreactor.

[1] Bioresource Techology 2015, 178, 108; [2] Fuel 2015, 150, 175; [3] Applied Catalysis B: Environmental 2021, 285, 119826
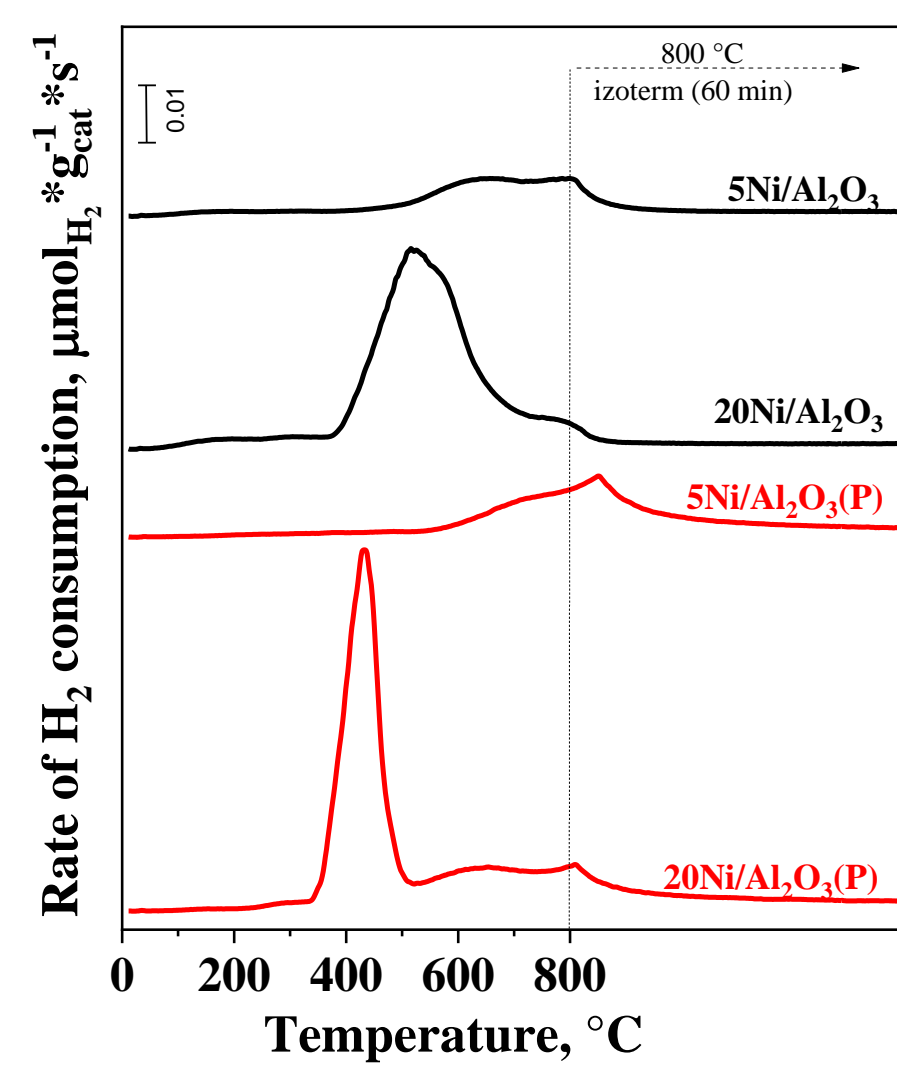
Catalysts preparation and characterization

X-ray diffraction (XRD)
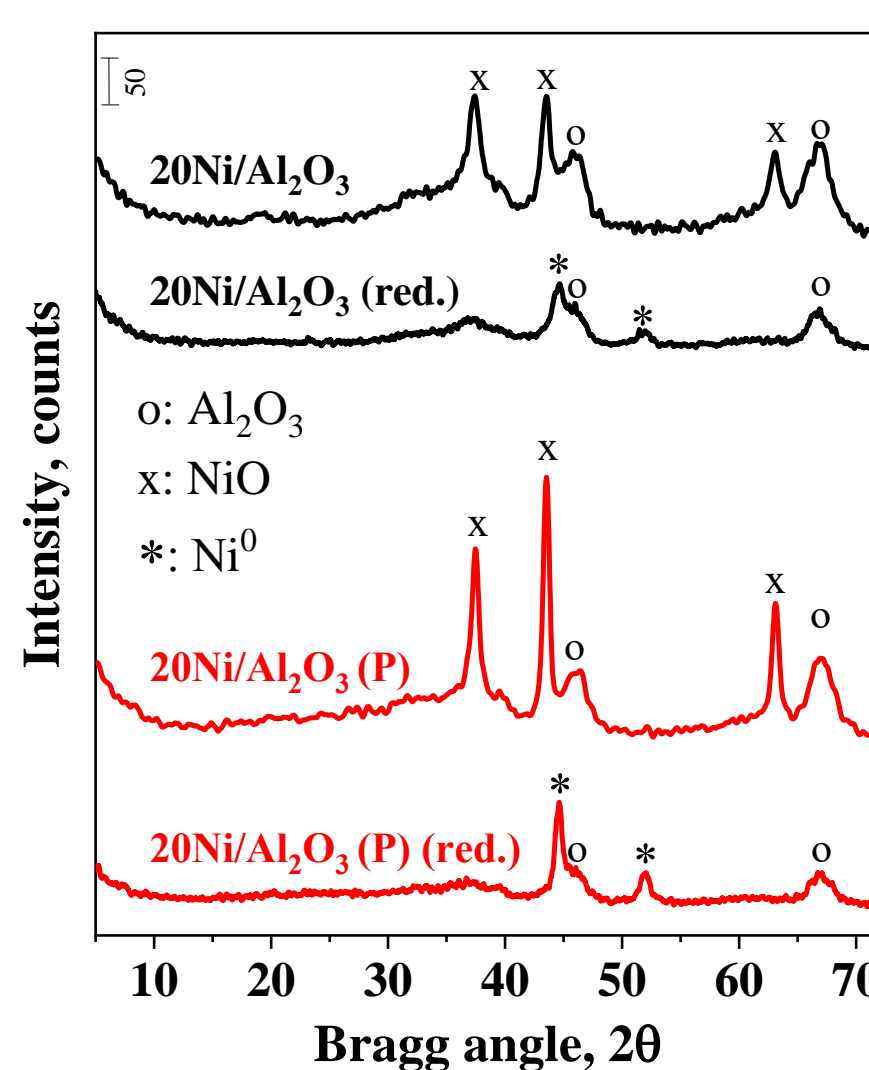
o: Al$_2$O$_3$
x: NiO
*: Ni^0

➤ γ-Al$_2$O$_3$ is the only detectable phase of catalysts with low metal loading (crystallites are well dispersed; not shown).

➤ The XRD pattern of 20Ni/Al$_2$O$_3$ and 20Ni/Al$_2$O$_3$(P) catalysts show the reflections of NiO and Ni^0.

### Temperature-programmed reduction (H$_2$-TPR)

➤ The catalysts were in situ reduced at 450 °C in the reactor before catalytic run.

➤ The degree of reduction at 450 °C:
5Ni/Al$_2$O$_3$ ~ 4.5 % of Ni (H/Ni=0.09)
5Ni/Al$_2$O$_3$ (P) ~ 0.5% (H/Ni=0.01)
20Ni/Al$_2$O$_3$ ~ 68 % (H/Ni=1.37)
20Ni/Al$_2$O$_3$ (P) ~ 65 % (H/Ni=1.3)

Metal and P content; Specific surface area (SSA)

| Supports and catalysts	Metal content wt%	P content wt%	SSA m²/g	Average diameter, nm NiO	Average diameter, nm Ni
Al$_2$O$_3$	-	-	196	-	-
5Ni/Al$_2$O$_3$	5.21	-	192	<5	<5
20Ni/Al$_2$O$_3$	~20	-	190	30	16
Al$_2$O$_3$(P)	-	4.85	167	-	-
5Ni/Al$_2$O$_3$(P)	5.06	4.82	165	<5	<5
20Ni/Al$_2$O$_3$(P)	~20	4.82	131	30	19

➤ Commercial γ-Al$_2$O$_3$ and phosphorous (P)-modified γ-Al$_2$O$_3$ were used as support.
➤ The phosphorous (P) modification was done with H$_3$PO$_4$ solution.
➤ The SSA decreased upon P-modification.
➤ The 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
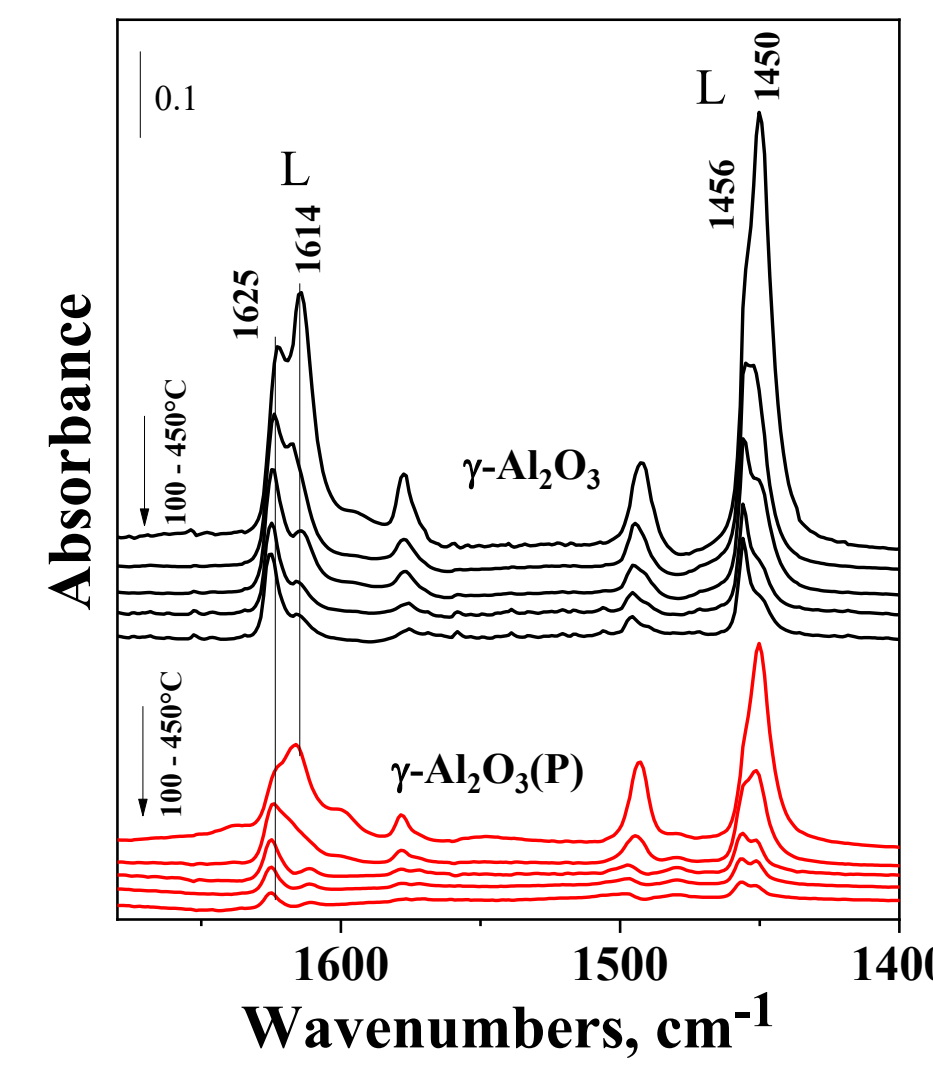
➤ On Al$_2$O$_3$ (P) support the intensity of bands is lower, indicating its lower Lewis acidity.
➤ Phosphorus modification reduces the Lewis acidity of the alumina support.
➤ Monomeric and polymeric phosphate species are formed.
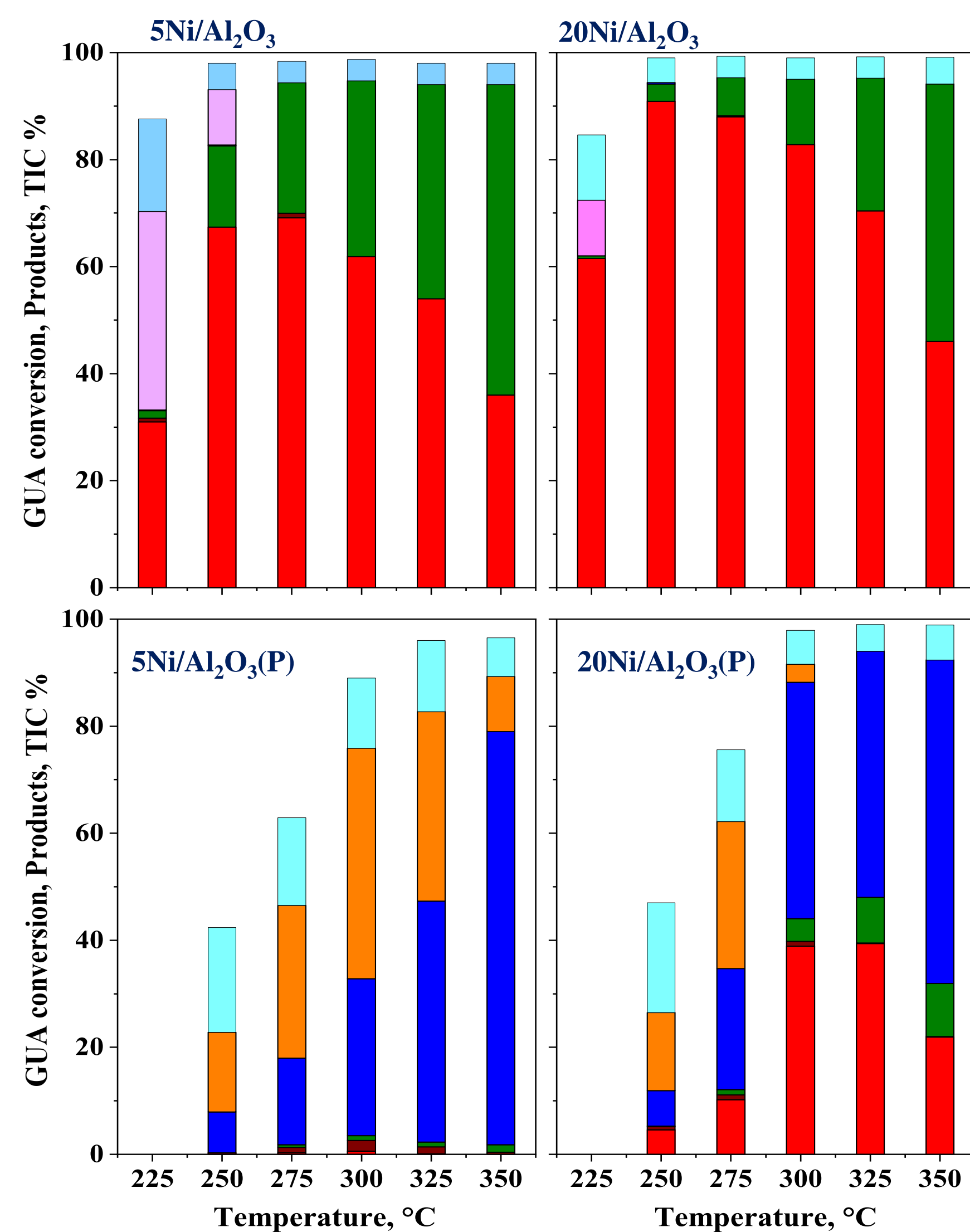
FT-IR spectra of adsorbed phenol
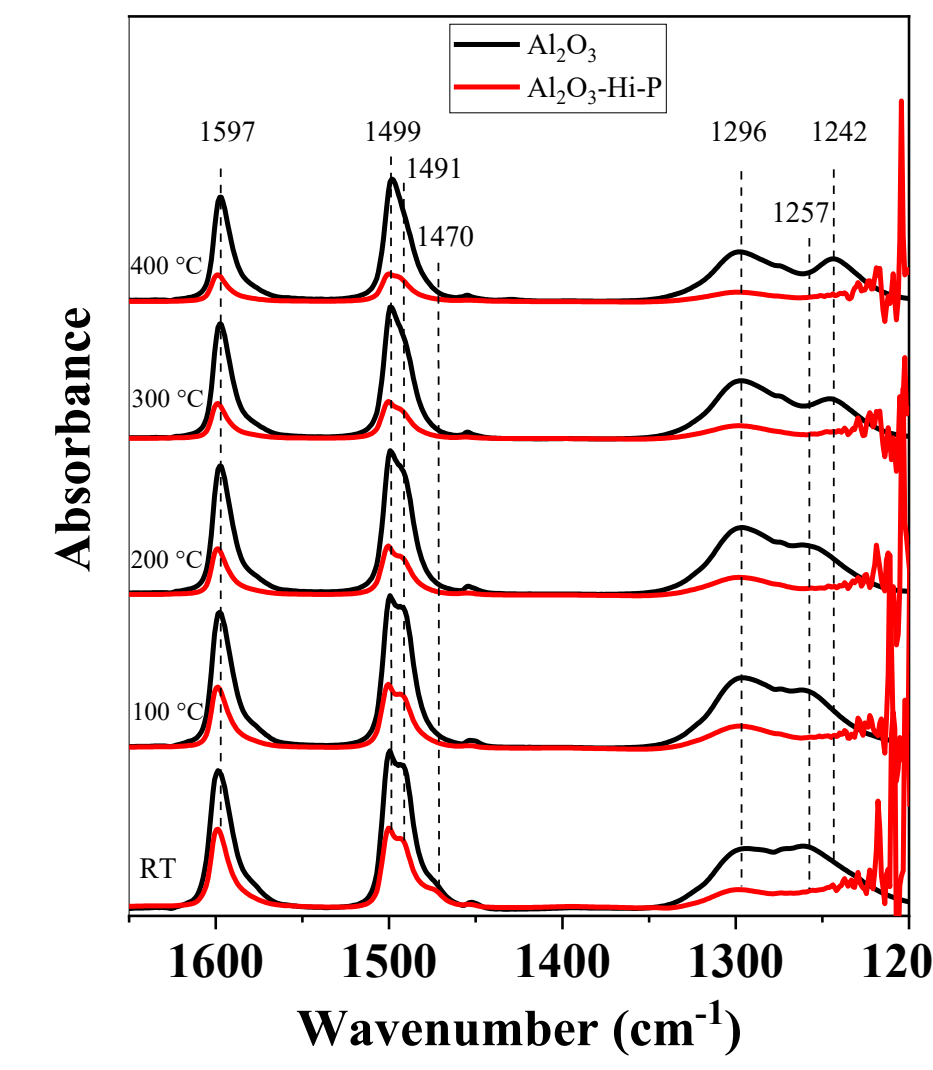
➤ Interaction of phenol with alumina leads to the formation of phenolate species (mono- and bi-dentate).
➤ Weak interaction was observed on the Al$_2$O$_3$(P) support.

Catalytic hydrodeoxygenation of guaiacol (GUA) and phenol (PHE)

Effect of temperature

➤ O-free compounds like cyclohexane (CHA) and Me-CHA were mainly formed over 5Ni/Al$_2$O$_3$ and 20Ni/Al$_2$O$_3$ at 250 – 300 ºC.
➤ 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.

### Proposed mechanism for hydrodeoxygenation of GUA

Stability

A: TOS = 5h (* = 1 h)
B: TOS = 35-40 h (# = 4 h)
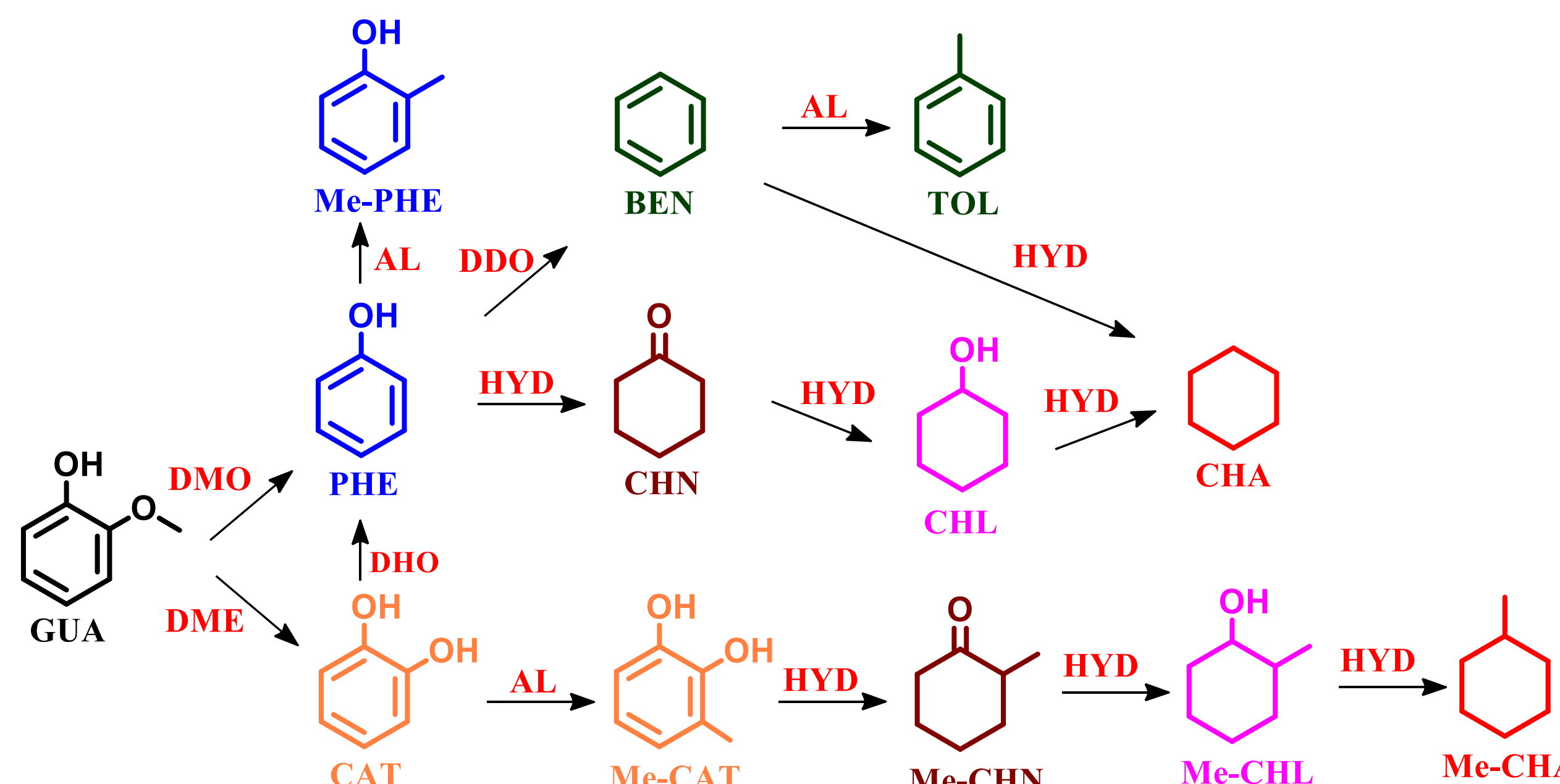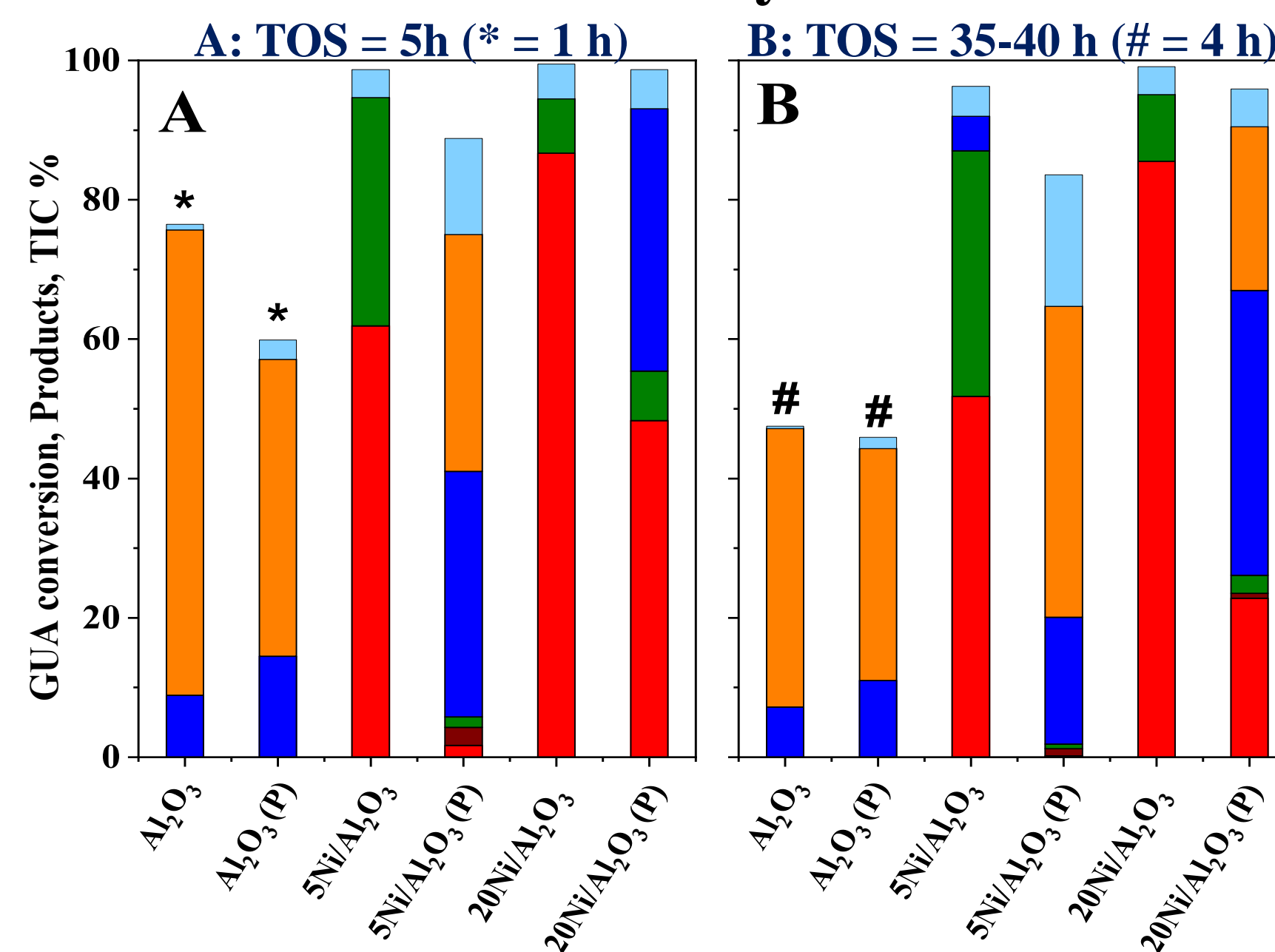
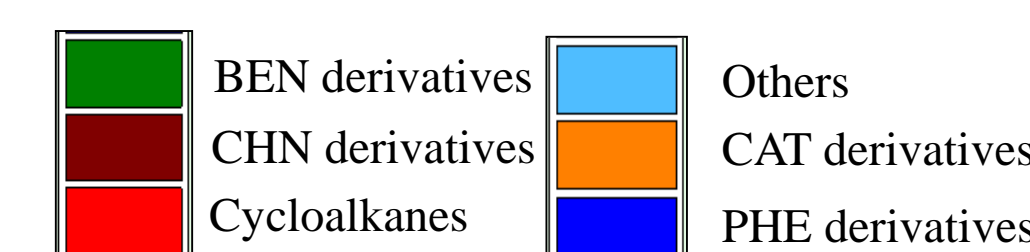Reaction conditions: 300 °C, 10 bar, 1 g$_{cat}$/g$_{GUA}$*h, H$_2$/GUA: 20

➤ Demethylation (DME) and transalkylation (AL) are the main reactions over Al$_2$O$_3$ and Al$_2$O$_3$ (P) supports.
➤ O-free compounds were mainly formed on Ni/Al$_2$O$_3$.
➤ Aromatics (phenols, catechols) were formed on P modified catalysts.
➤ 5Ni/Al$_2$O$_3$ and 20Ni/Al$_2$O$_3$ catalysts were stable; their activity did not change significantly with TOS.

Effect of space time to HDO of PHE
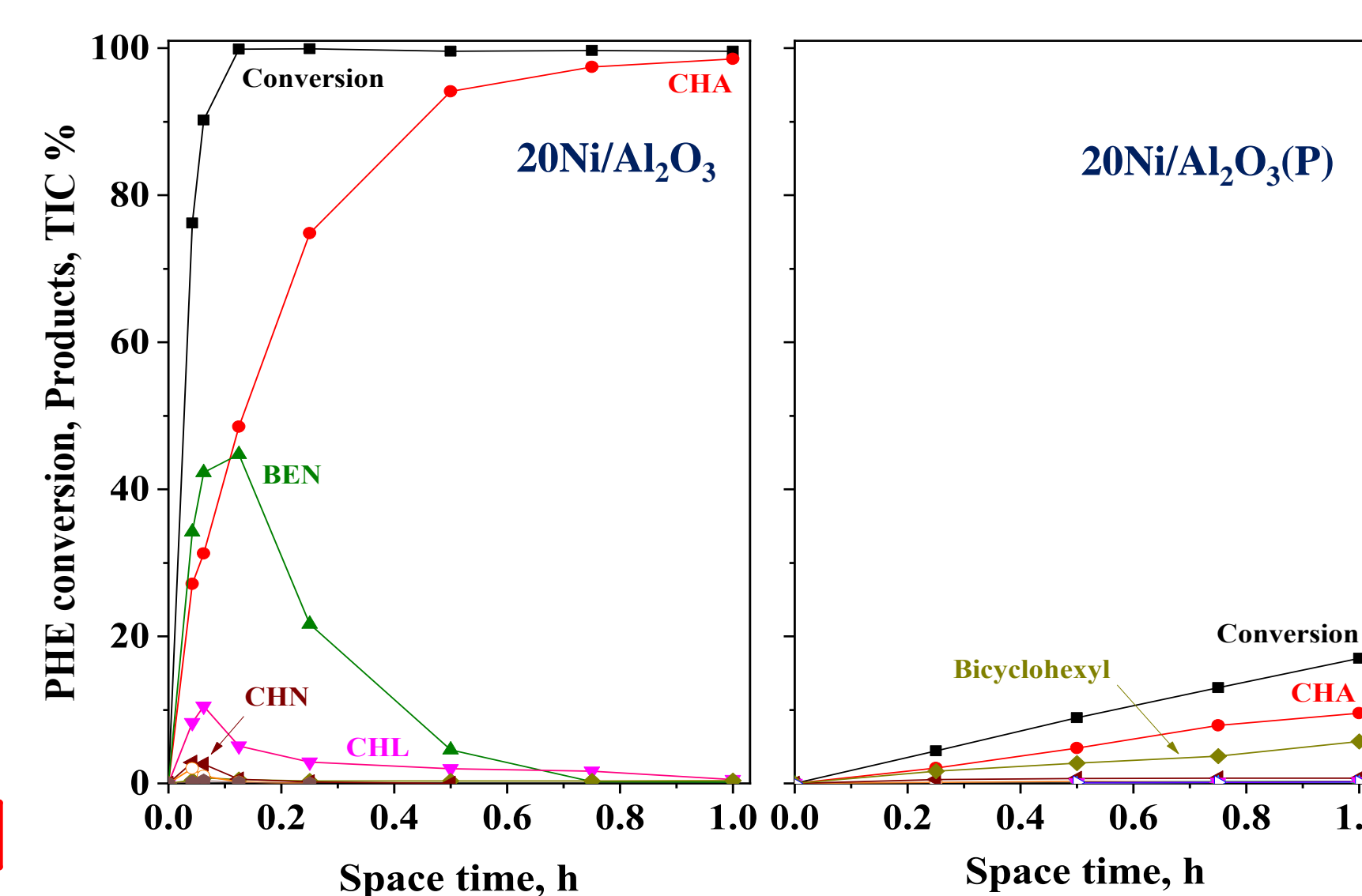
Reaction conditions: 200 °C, 1 bar, H$_2$/PHE: 16

➤ CHA were formed from PHE over 20Ni/Al$_2$O$_3$.
➤ At lower space time BEN intermediate appear in the product mixture.
➤ 20Ni/Al$_2$O$_3$(P) catalyst activity is lower due to weaker interaction between substrate molecules and phosphated support.
➤ These results are consistent with the results obtained from the FT-IR spectra of adsorbed phenol.

Legend:
- BEN derivatives (green)
- CHN derivatives (dark red)
- Cycloalkanes (red)
- Others (light blue)
- CAT derivatives (orange)
- PHE derivatives (blue)

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

Conclusions

➤ The sequential steps of GUA hydroconversion can be controlled by modifying the alumina support.
➤ Demethylation of GUA on Al$_2$O$_3$ and phosphorous modified Al$_2$O$_3$(P) supports leads to catechol formation.
➤ Ni/Al$_2$O$_3$ catalyzed hydroconversion of GUA to O-free compounds like cyclohexane.

➤ At lower temperature and space time cyclohexanols were formed in large amounts.
➤ With temperature the yield of benzenes increased.
➤ Ni/Al$_2$O$_3$(P) catalysts are selective to aromatics. These catalysts remain active in demethylation and demethoxylation, but lose their ability to hydrogenate the aromatic ring. Weak interaction of phenol intermediate was observed on the Al$_2$O$_3$(P) support.