

Fuel production by bioethanol coupling over magnesia-alumina mixed oxide catalysts

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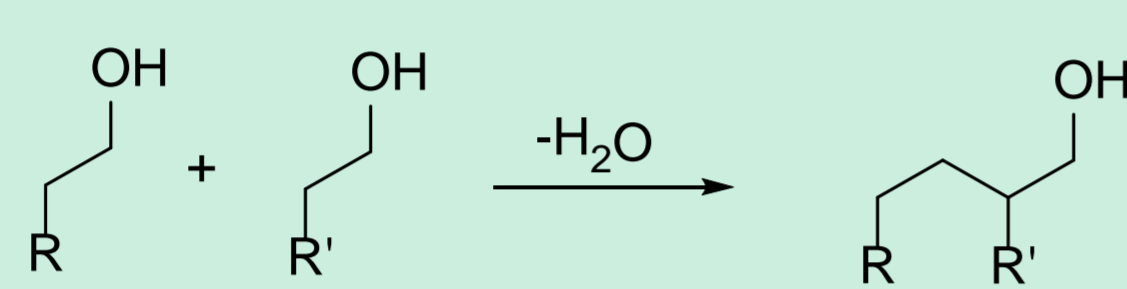


Introduction

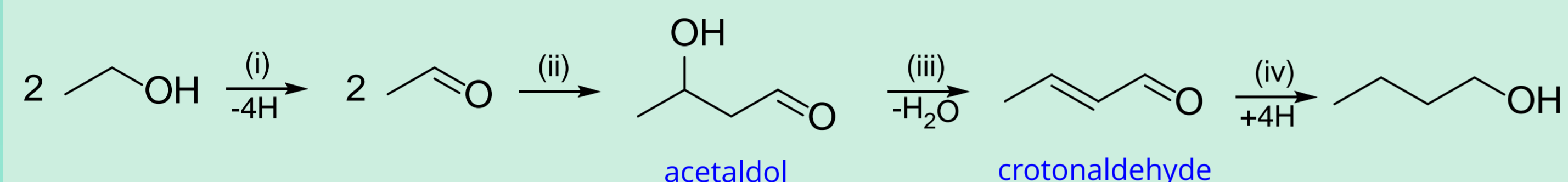
Conversion of bioethanol to biobutanol via **Guerbet coupling reaction** attracted significant interest of chemical industry, because 1-butanol can be used as renewable fuel or blending component of gasoline, moreover, it can be used also as precursor of other valuable chemicals.

The **Guerbet reaction** involves the coupling of two alcohol molecules to get a higher alcohol. According to the most accepted mechanism the coupling occurs via four steps: alcohol dehydrogenation to aldehyde, aldol addition, dehydration, and hydrogenation of the obtained unsaturated aldehyde or ketone [1]. It is hardly understood how the hydrogen, formed in step (i) is preserved and used in step (iv). If the catalyst contains metal component, active in hydrogenation and dehydrogenation, it can be believed that the metal promotes the hydrogen transfer reactions from the beginning till the end of transformation series. Interestingly, the reaction proceeds also in absence of hydrogen carrier metal in the catalyst. Therefore, an alternative mechanism was suggested, in which ethanol was assumed to be the hydrogen donor. For the complexity of the process, the catalyst must contain optimal balance of different catalytic functions for dehydrogenation/hydrogenation, aldol addition and dehydration reaction steps. In the present work, MgO-Al₂O₃ mixed oxide catalysts, having acid-base properties were studied in the ethanol coupling reaction. In order to promote the hydrogen transfer reaction steps a metal component (Pd, Pt, Ru, or Ni) was introduced into the mixed oxide catalyst.

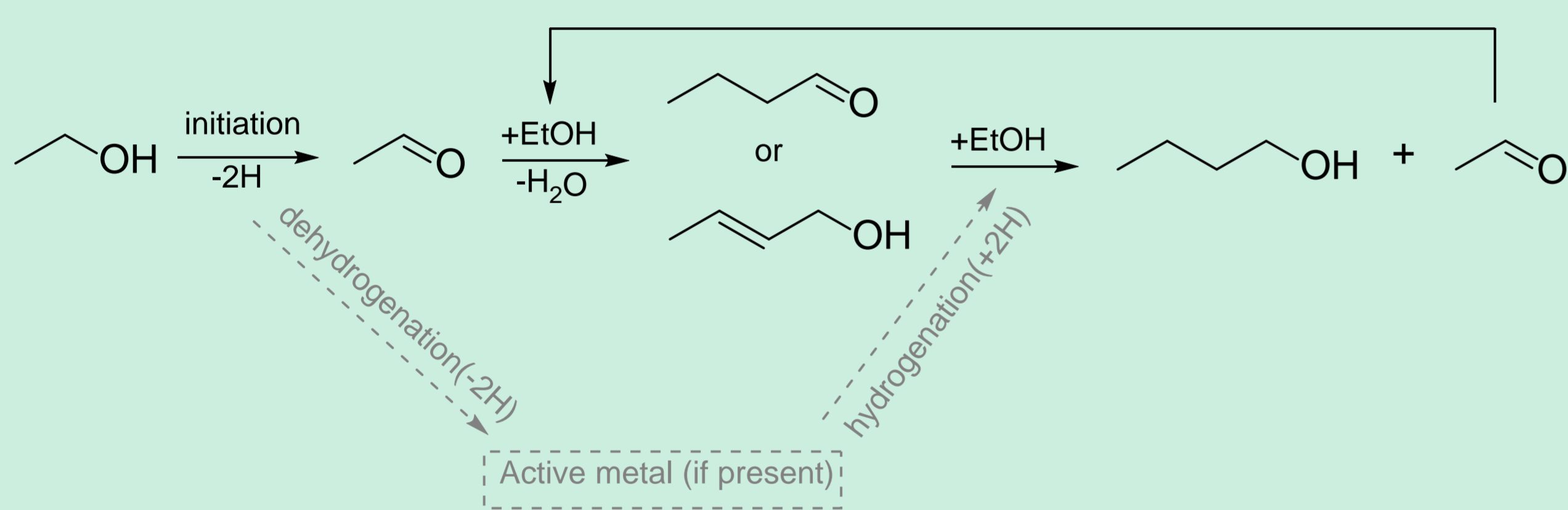
Guerbet coupling



Butanol formation via aldol condensation



Butanol formation via a chain mechanism



Experimental

Mg₂Al(OH)₆NO₃·nH₂O hydrotalcite precursor of the mixed oxide catalyst was prepared by co-precipitation from aqueous solution of magnesium- and aluminum nitrates with sodium hydroxide. The **MgO-Al₂O₃ mixed oxide catalyst** was obtained by calcining the hydrotalcite precursor at 550 °C. The metal containing derivatives were prepared by impregnating the hydrotalcite precursor with aqueous solution of Pd(II)-, Pt(II)-, Ru(II)-, or Ni(II)-salt. The thus obtained catalyst precursors were calcined then at 550 °C to get metal-containing Me/MgO-Al₂O₃ mixed oxide catalysts.

Catalytic measurements were carried out applying a high-pressure, fixed bed, flow-through reactor system [2] at 21 bar total pressure using H₂ or He carrier gas in the temperature range of 200-350 °C and at WHSV = 1 g_{EtOH} · g_{cat}⁻¹ · h⁻¹. Prior to CO chemisorption and catalytic measurements, the catalysts were pretreated in H₂ flow at atmospheric pressure at 500 °C for 1 h to reduce the metal.

Catalyst characterization

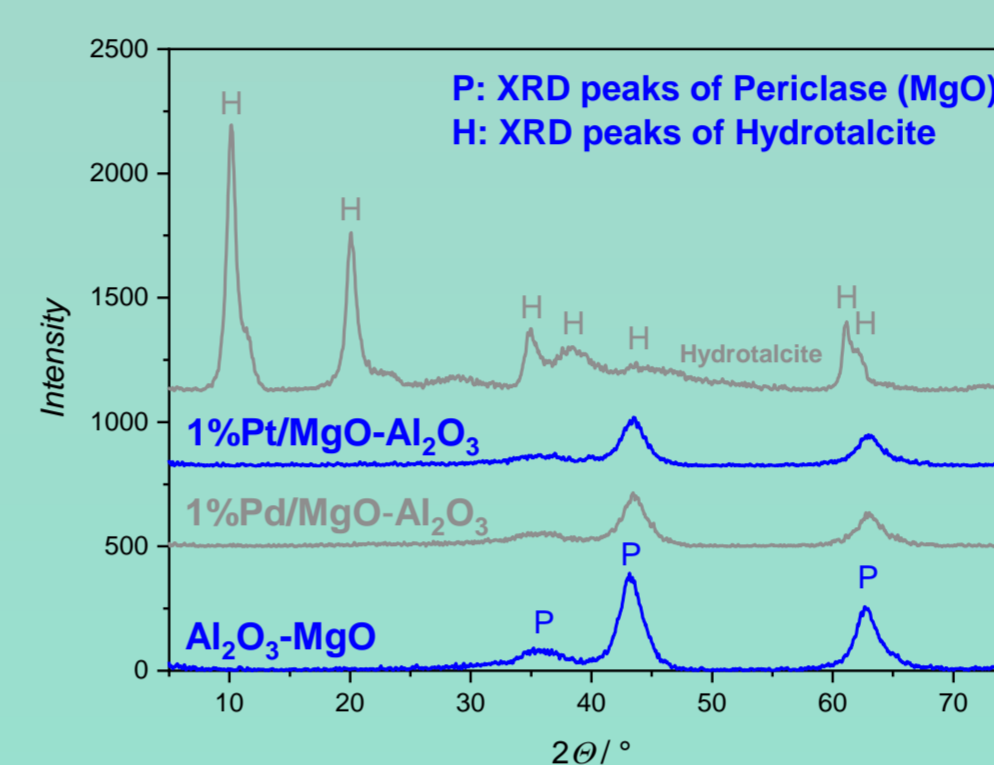
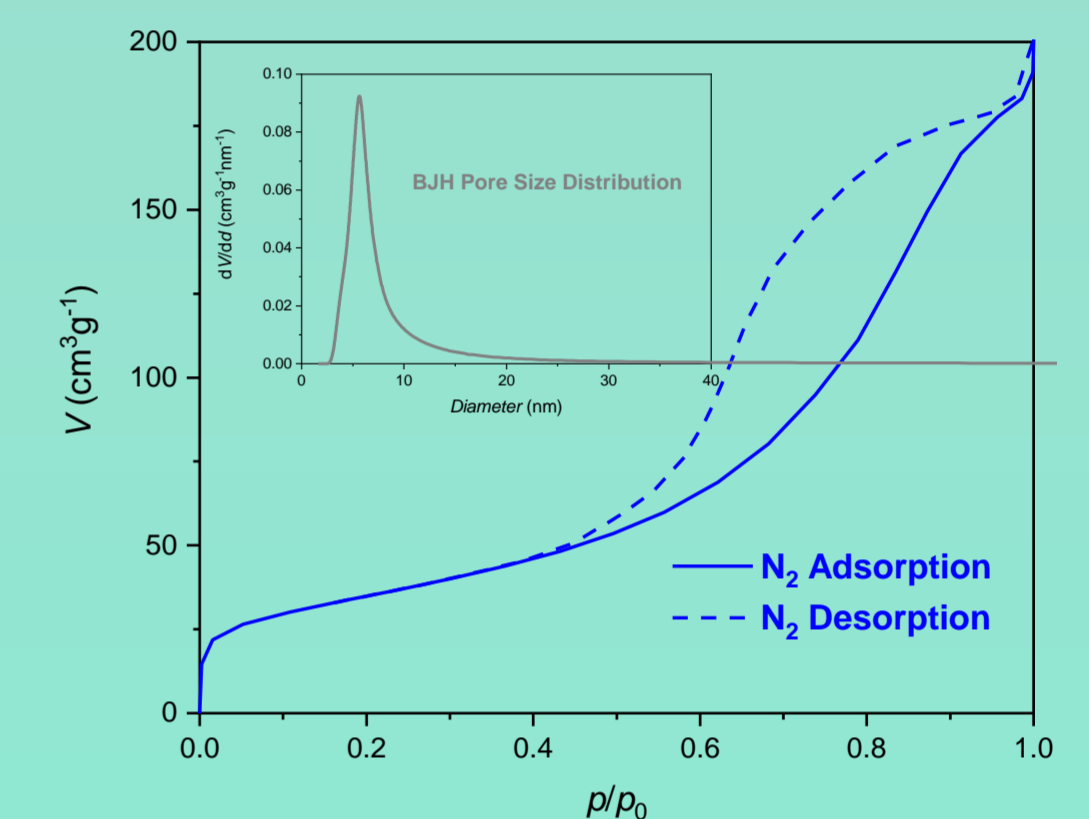


Fig. 1 XRD patterns of hydrotalcite and MgO-Al₂O₃ catalyst calcined at 450 °C

XRD results of calcined catalysts suggest the formation of some MgO phase, whereas Pd or Pt metal particles (> 5 nm) could not be detected.

Fig. 2 N₂ adsorption/desorption isotherm and pore size distribution of the MgO-Al₂O₃ catalyst calcined at 450 °C

The BET surface area of the Me/MgO-Al₂O₃ catalysts was around 125 m²g⁻¹. The N₂ adsorption-desorption isotherms suggest a mesoporous structure with a relatively narrow pore size distribution.



Catalyst	Adsorbed CO	Metal dispersion
	μmol / g _{cat}	%
1%Pd/MgO-Al ₂ O ₃	19.33	20.6
1%Pt/MgO-Al ₂ O ₃	11.53	22.6
1%Ru/MgO-Al ₂ O ₃	3.35	3.4
1%Ni/MgO-Al ₂ O ₃ *	0.92	0.54
5%Ni/MgO-Al ₂ O ₃ **	6.27	0.74

* Prepared by solid state reaction ** Reduced at 600 °C

Table 1 Results of CO pulse chemisorption experiments

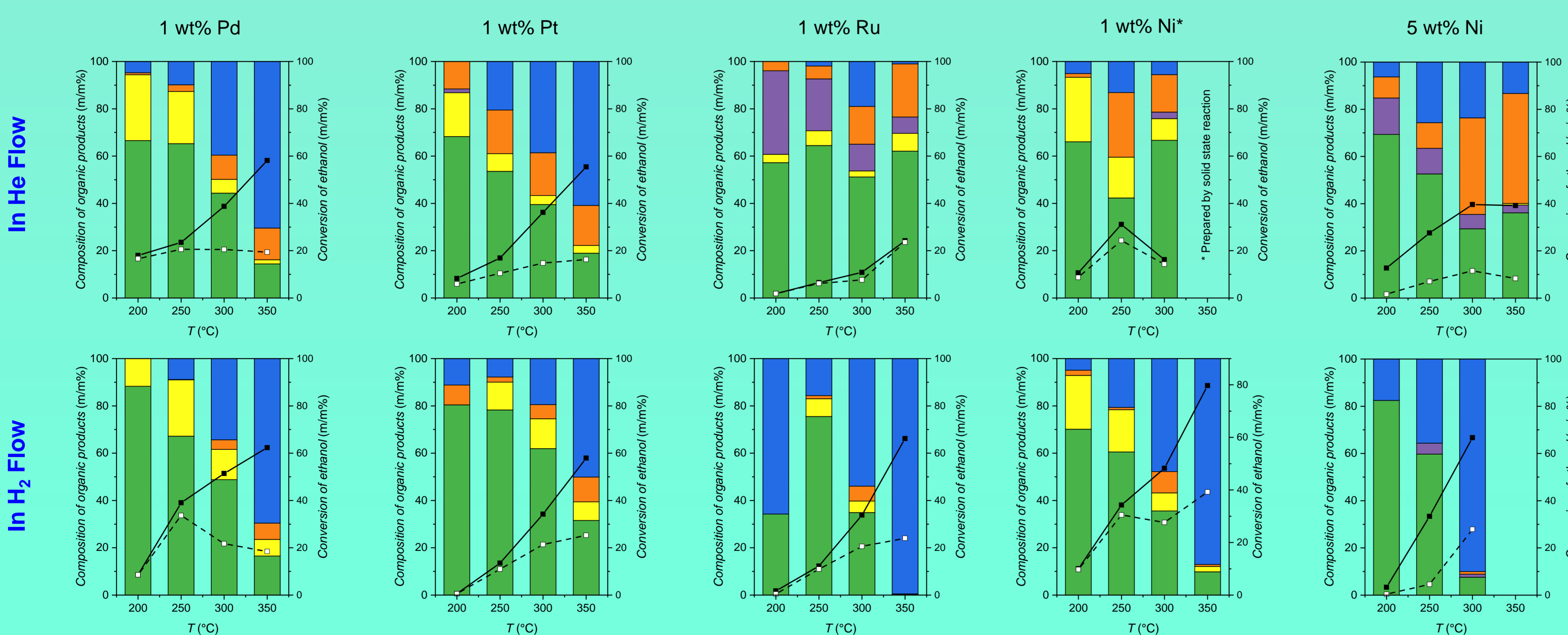


Fig.3 Effect of metals on the ethanol conversion and composition of organic products obtained on Me/MgO-Al₂O₃ catalysts. WHSV= 1 g_{EtOH} · g_{cat}⁻¹ · h⁻¹, p = 21 bar (in He or H₂ carrier gas). Dashed curves: yield of liquid phase products.

Detected byproducts

- **Alcohols:** mainly 1-hexanol
- **Other Oxygenates:**
 - **Ethers:** mainly diethyl ether and ethyl butyl ether
 - **Esters:** mainly ethyl acetate and ethyl butanoate
 - **Aldehydes and ketones:** mainly acetaldehyde and butanal
- **Alkanes:** mainly methane
- **CO, CO₂**

Conclusions

- Introduction of a **metal modifier** significantly improved the activity (up to about 60% ethanol conversion) of the **MgO-Al₂O₃** catalyst in the whole applied temperature range (except over the Ru catalyst) **in inert atmosphere**, whereas the alcohol yields decreased in the high temperature range (≥300 °C) due to the acceleration of the undesired side reactions over the metallic sites, such as decarbonylation/decarboxylation and methane formation.
- **In presence of hydrogen**, conversion of ethanol was somewhat decreased on the metal containing catalysts at the lowest reaction temperature (200 °C). Hydrogen probably can hinder the initial dehydrogenation step of ethanol to acetaldehyde at low temperatures, where the dehydrogenation-hydrogenation equilibrium is more shifted towards hydrogenation. At high reaction temperature (≥300 °C) hydro-deoxygenation prevails leading to the formation of alkanes, mainly methane.
- **In inert atmosphere**, the alcohol selectivity significantly drops over the **Pd-** and **Pt-**containing catalysts at elevated temperatures, whereas the selectivity loss is considerably lower **in hydrogen** up to 300 °C. Results suggest that hydrogen can suppress reaction routes leading to the formation of other oxygenates (ethers, esters, aldehydes and ketones) and alkanes, especially methane.

References

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- [2] G. Onyestyák, S. Harnos, S. Klébert, M. Stölcová, A. Kaszonyi, D. Kalló, Appl. Catal. A Gen. 464–465 (2013) 313–321.

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