The first step towards the era of biopolymers: production of butadiene from bioethanol

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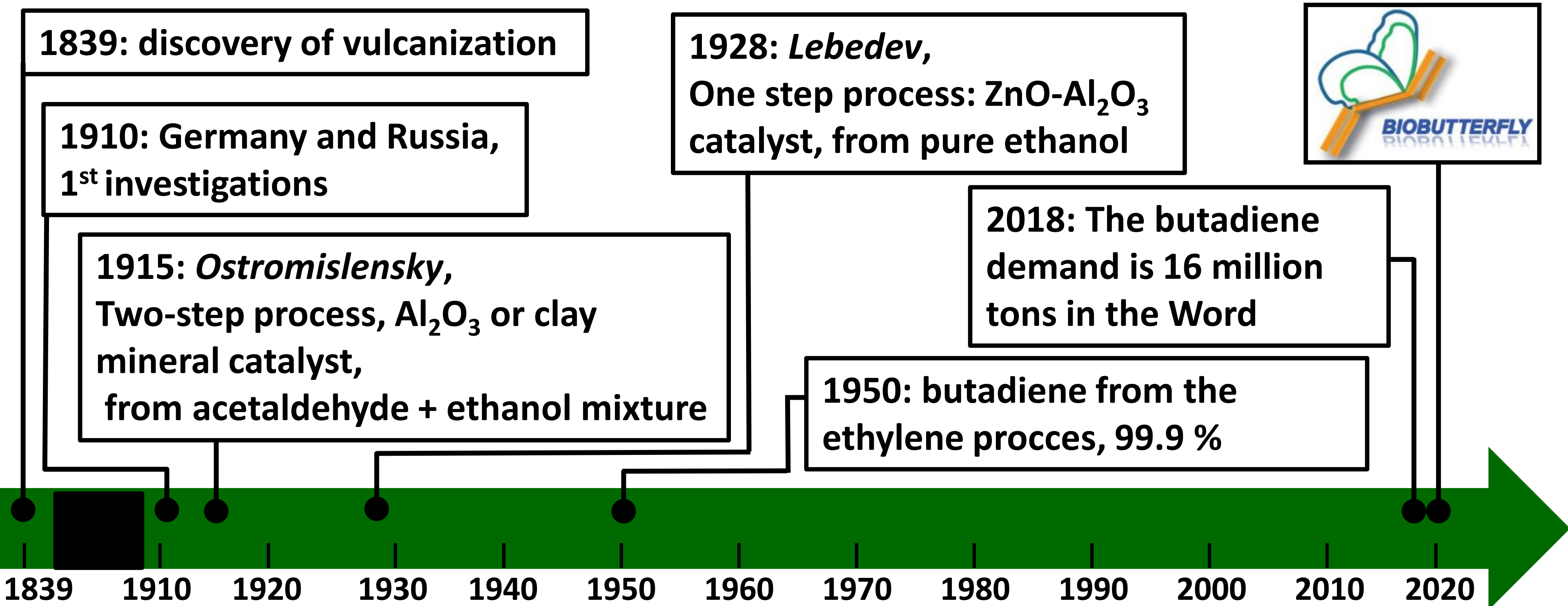
Research Centre for Natural Sciences

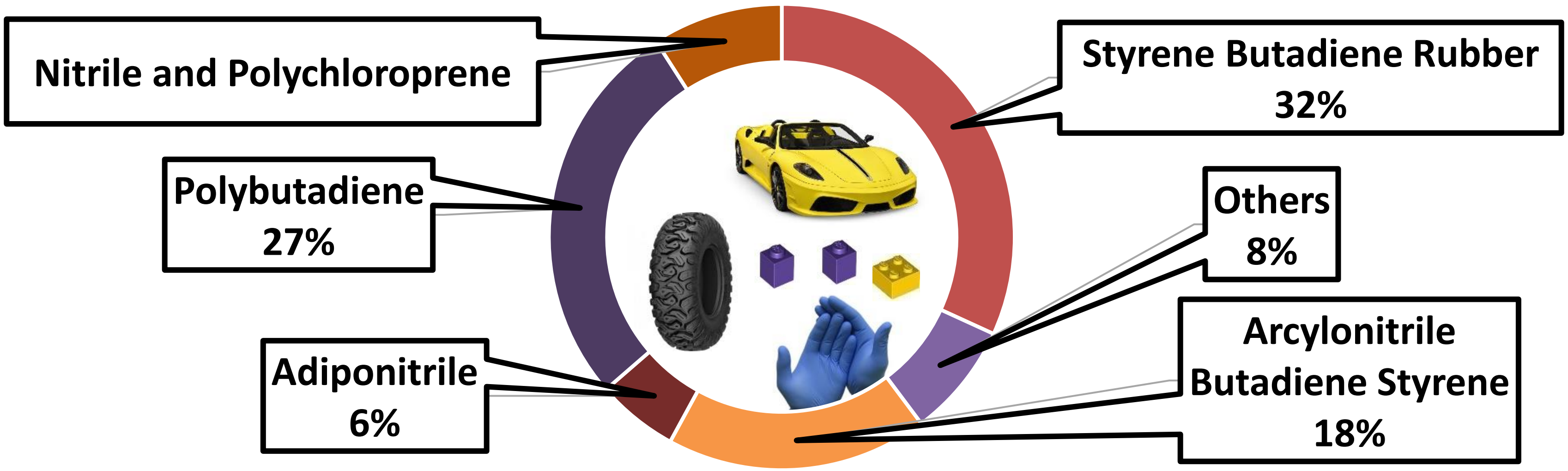
Project meeting
„Joint chemical laboratory for the service of bioeconomy in the Slovak-Hungarian border region"
Interreg, SKHU/1902/4.1/001/Bioeconomy

Faculty of Chemical and Food Technology STU in Bratislava
Radlinského 9, 812 37 Bratislava, Slovak Republic

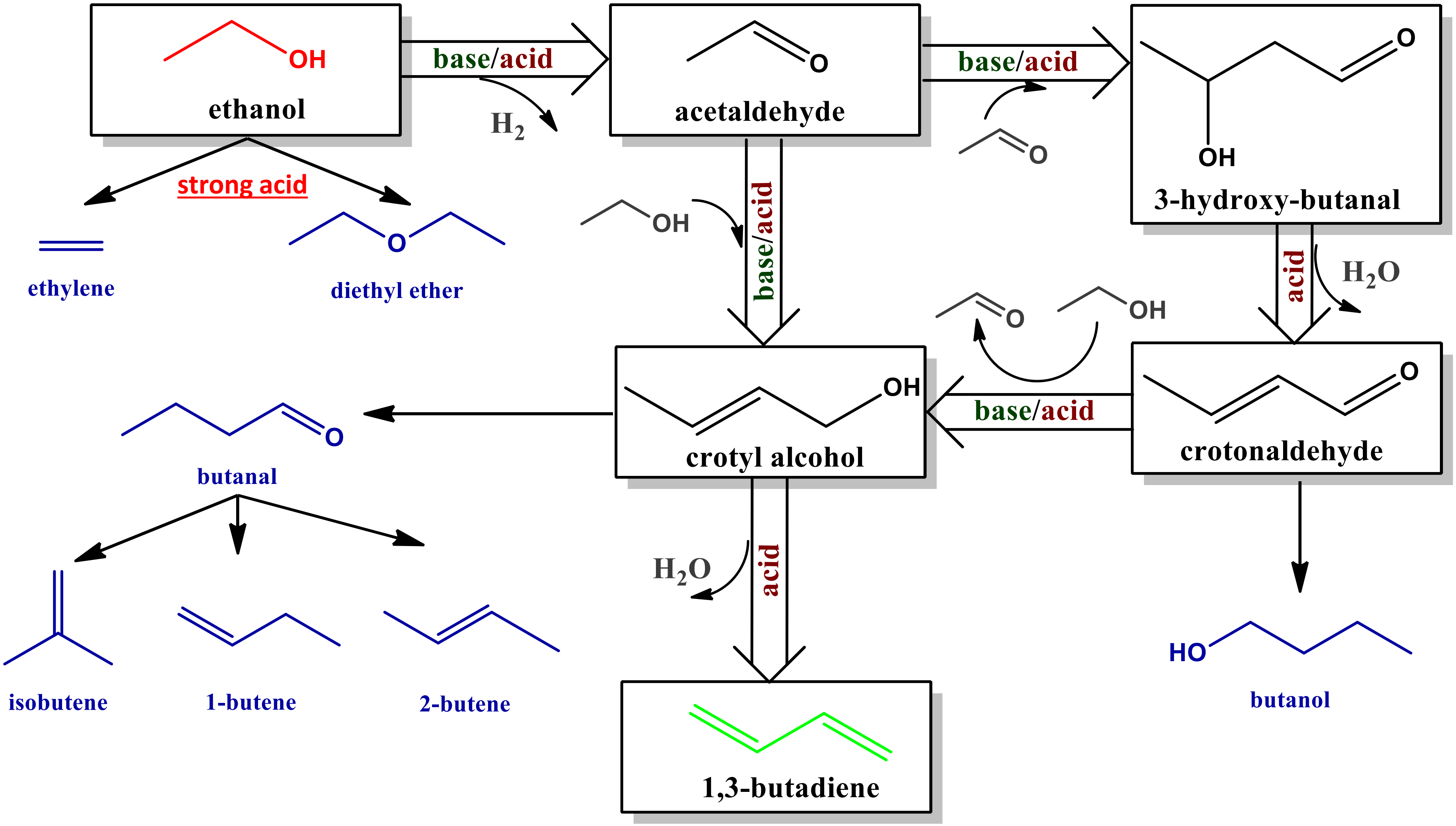
28th September, 2022

Historical review





Theories of the ethanol to butadiene reaction pathway



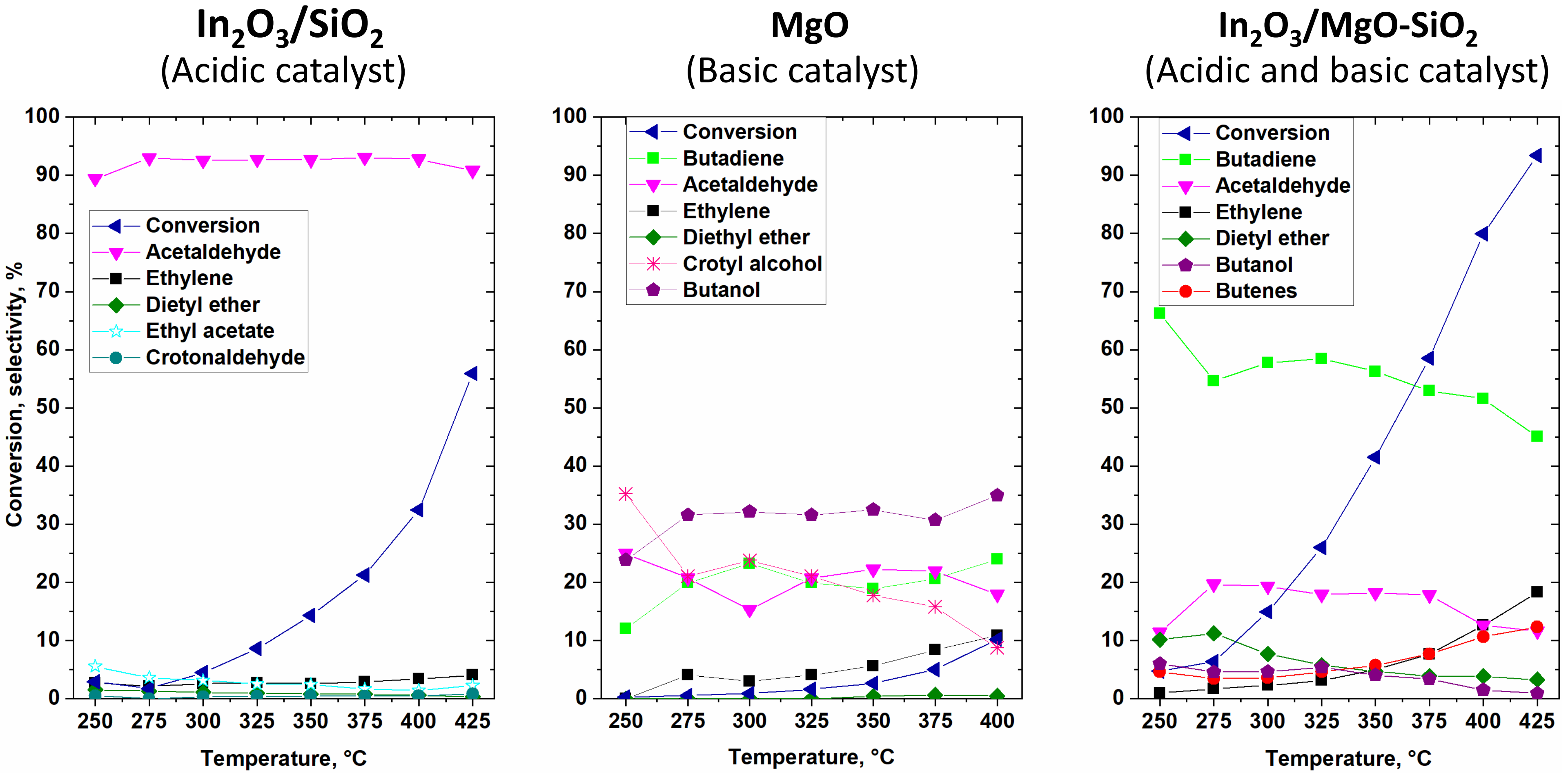
Catalytic test reactions

- Fixed-bed, continuous-flow reactor at atmospheric pressure
- On-line GC, two FID (PLOT-Fused Silica Al_2O_3/KCl – hydrocarbons; HP-PLOT-U - oxygenates) and TCD detector
- The GC was calibrated for reactant and all products separately
- Selectivities were calculated on carbon basis (number of carbon atoms in selected product divided by the summarized number of carbon atoms in all product molecules)
- Identical conversion levels were achieved over the different catalysts by changing the weight hourly space velocity (WHSV) of the ethanol

The role of acidic and basic sites in ethanol-butadiene reaction

- Catalysts:

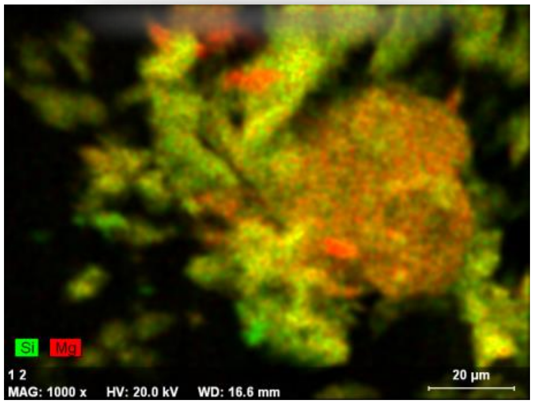
  Al_2O_3, Titania, Hydroxyapatite, Zirconia, β-zeolite, MgO, SiO_2, MCM-48, TUD-1, **$MgO-SiO_2$**



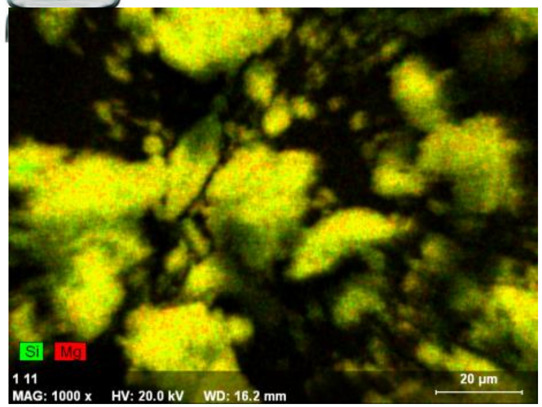
1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

Talk like catalysts

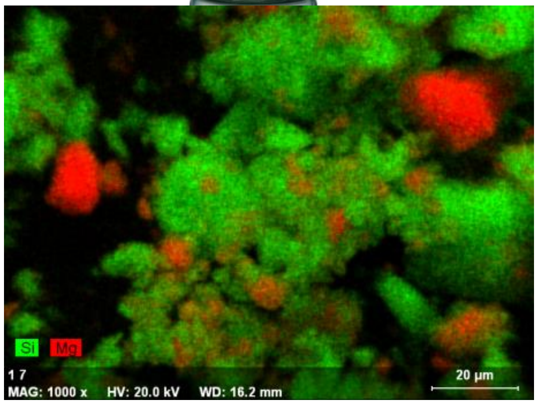
1. Natural talc=Talc $Mg_3Si_4O_{10}(OH)_2$



2. Coprecipitated sample =CP



3. Wet-kneaded sample=WK



Sample ID	Characterisation		Basic properties			Acidic properties	
	Si/Mg[a]	SSA[b] m^2/g	CO_2 TPD µmol/g	$CDCl_3$-FT-IR Weak sites RT, 2250 cm^{-1}	$CDCl_3$-FT-IR Strong sites RT, 2235 cm^{-1}	NH_3 TPD µmol/g	Pyridine FT-IR 200°C, 1448 cm^{-1}
Talc	1.46	9	7.7	0.07	-	17.12	-
CP	1.44	208	10.5	0.09	-	412.01	0.15
WK	1.61	250	94.5	0.15	0.74	461.11	0.35

a: ICP-OES analysis Theoretical Si/Mg ratio 1.54, b: BET method

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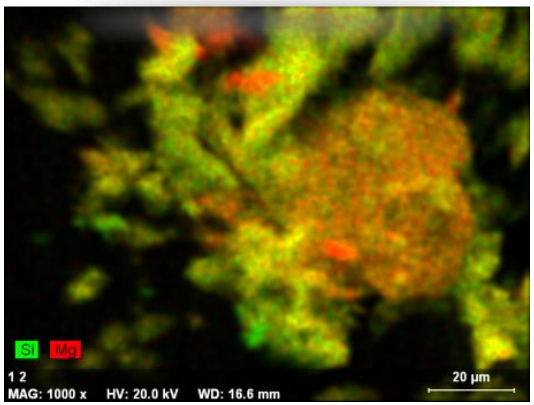

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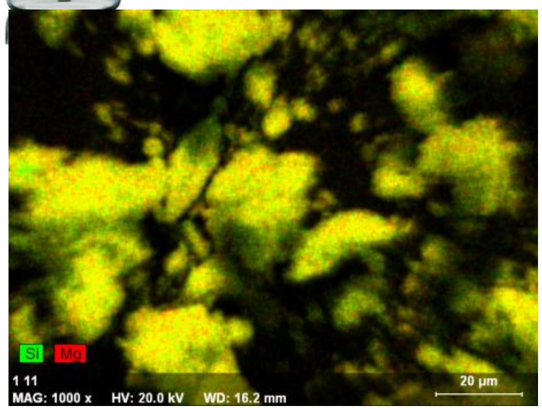
TEOS



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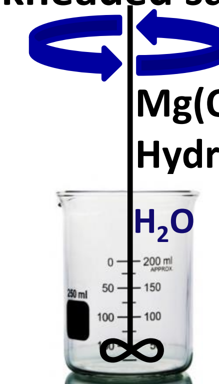
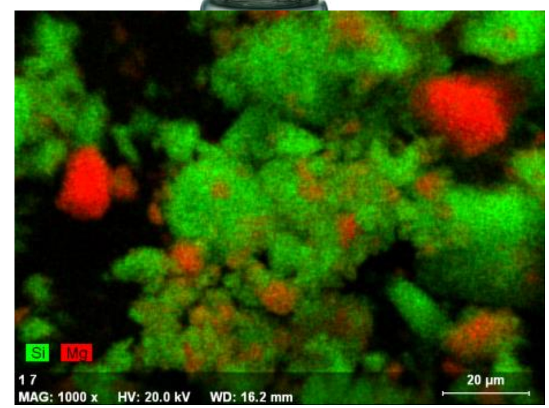


$Mg(OH)_2$
Hydrolized TEOS



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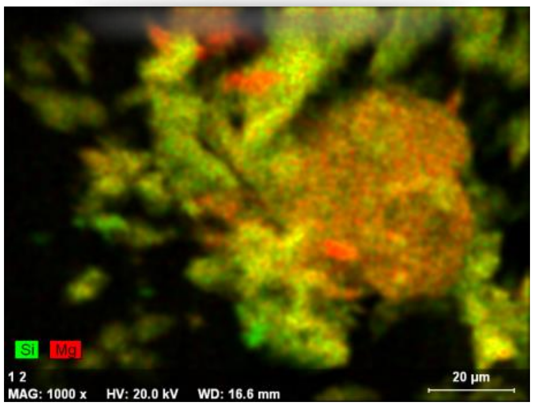

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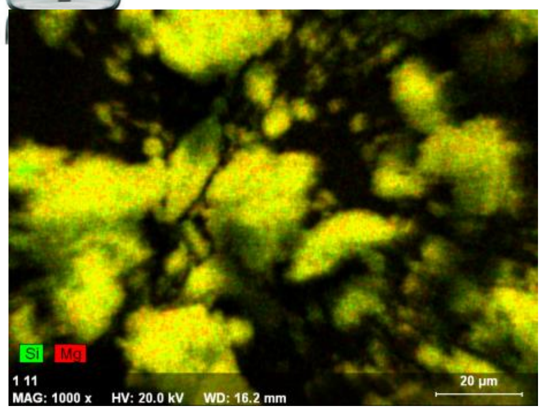

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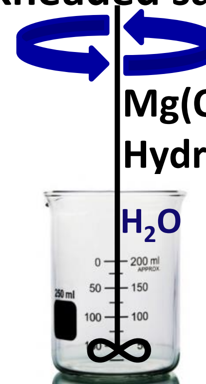

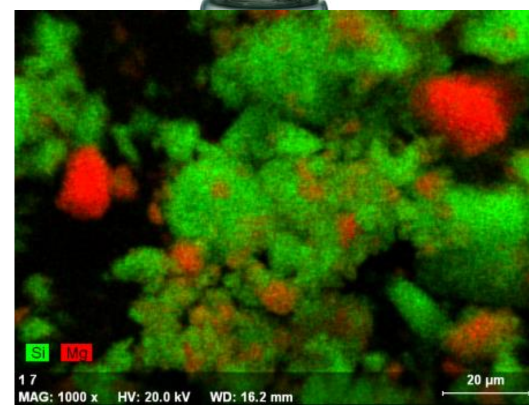

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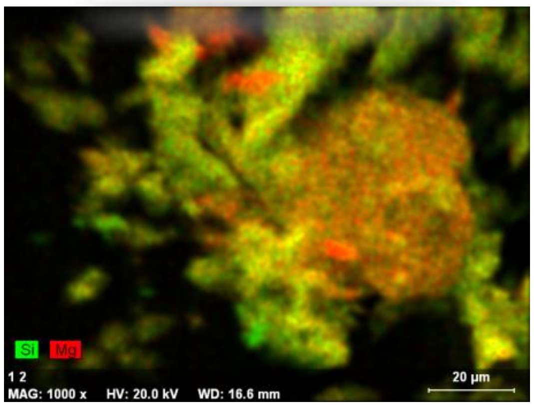

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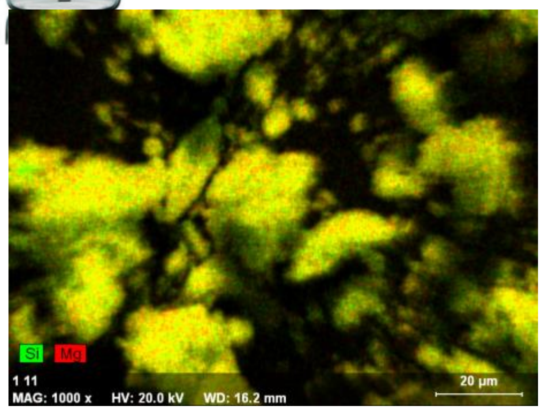

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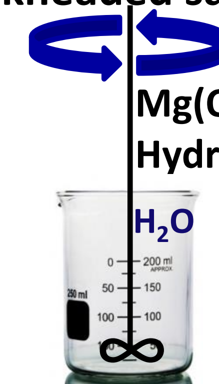

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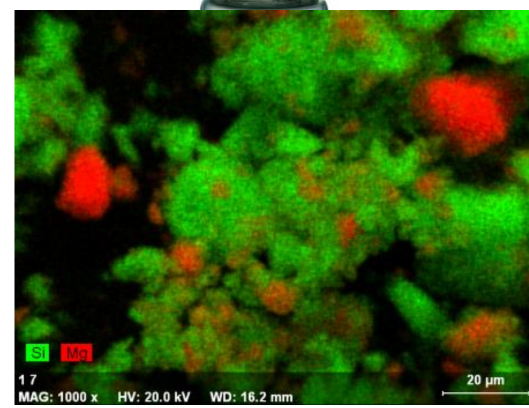

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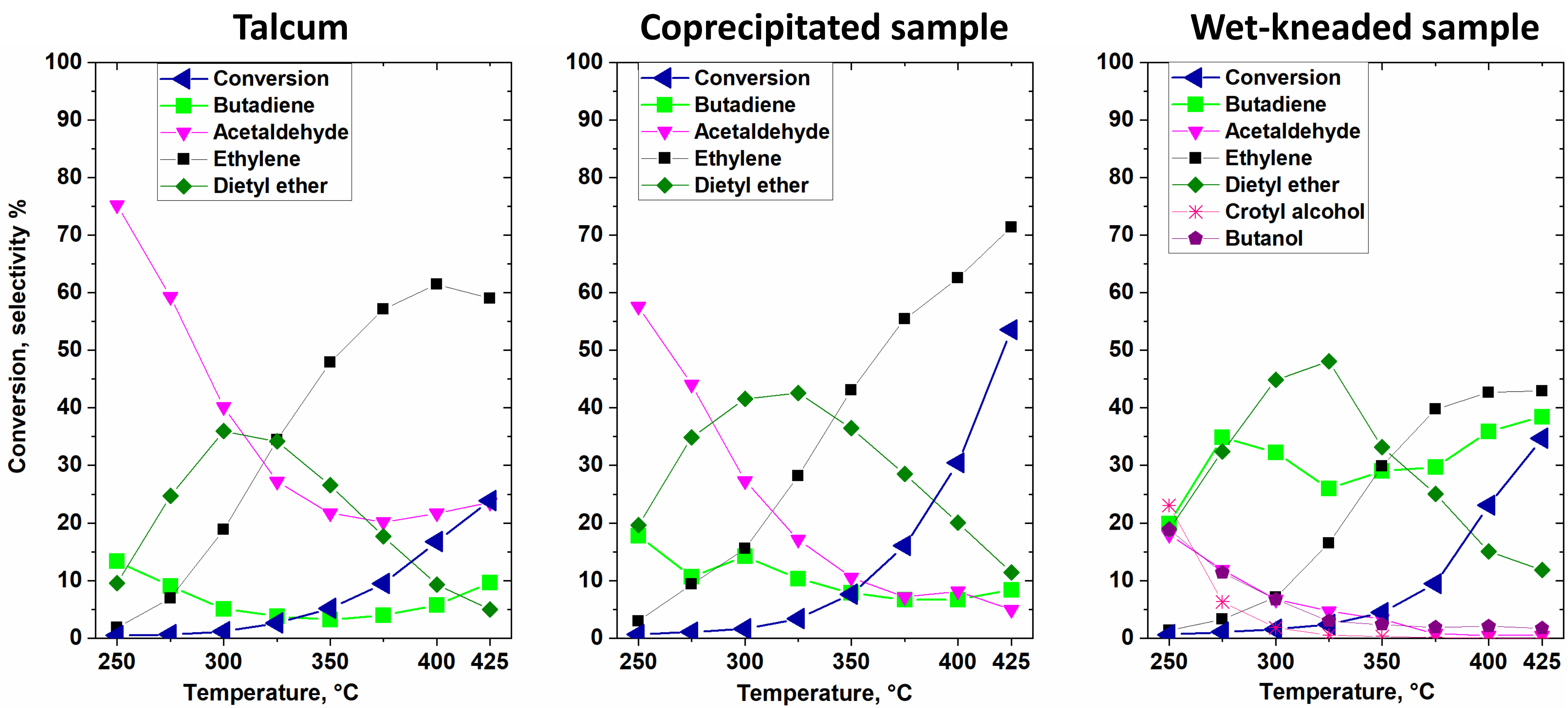
ETB conversion over talc like catalysts



1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

Conclusions

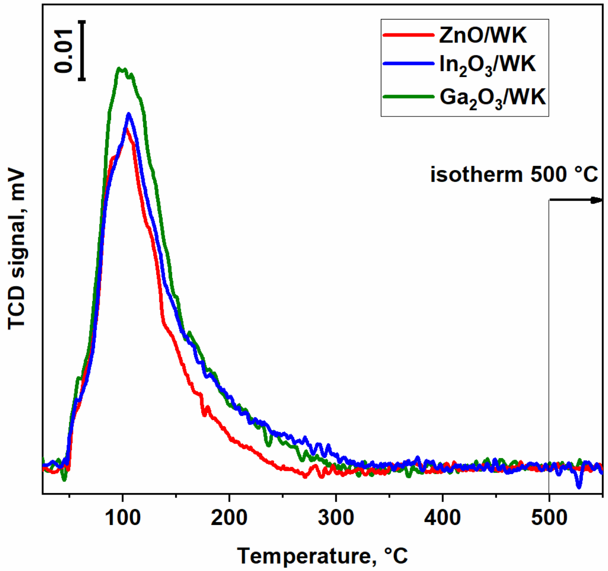
- ❑ Best catalytic activity: **WK sample**
    - High specific surface area (250 m^2/g)
    - Ideal Lewis-acidity
    - Stronger basic sites→ separeted MgO phase → efective C-C coupling

The effect of metal-oxides on the acid-base properties

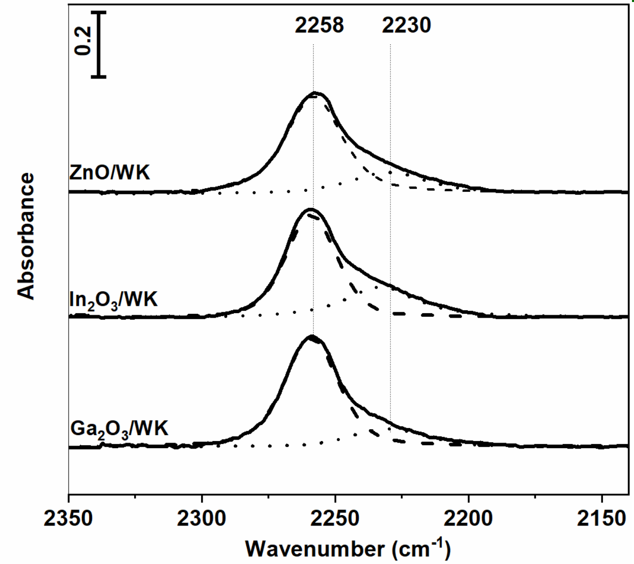
- 1 wt% of ZnO/ In_2O_3 /Ga_2O_3-WK

Basic properties:

CO_2 TPD

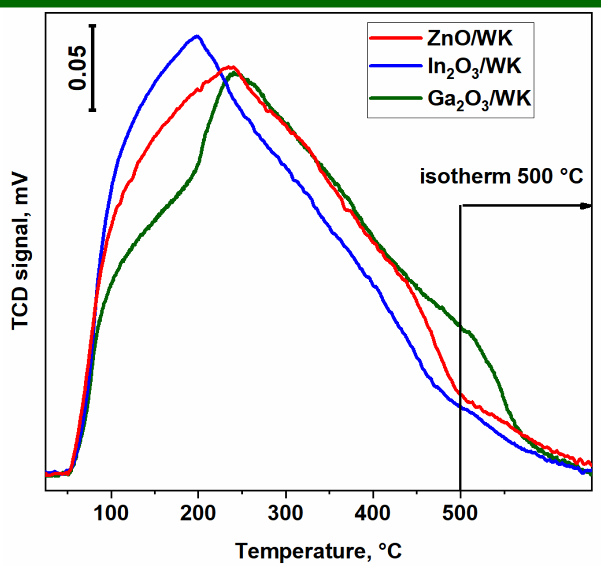


$CDCl_3$-FT-IR, RT

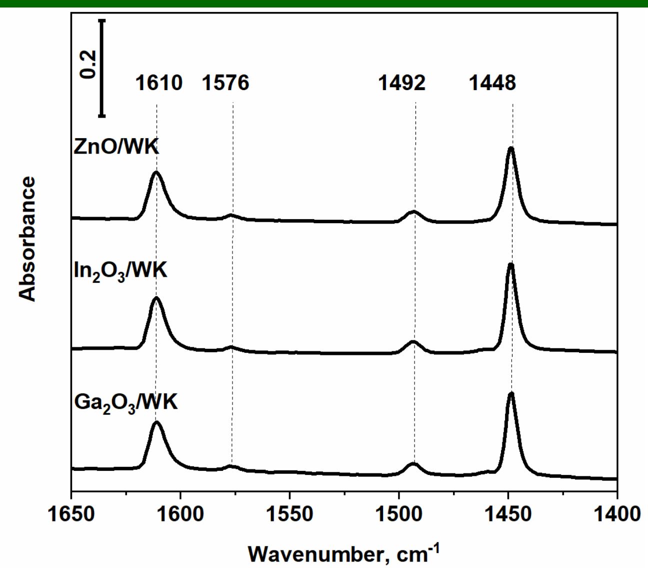


Acidic properties:

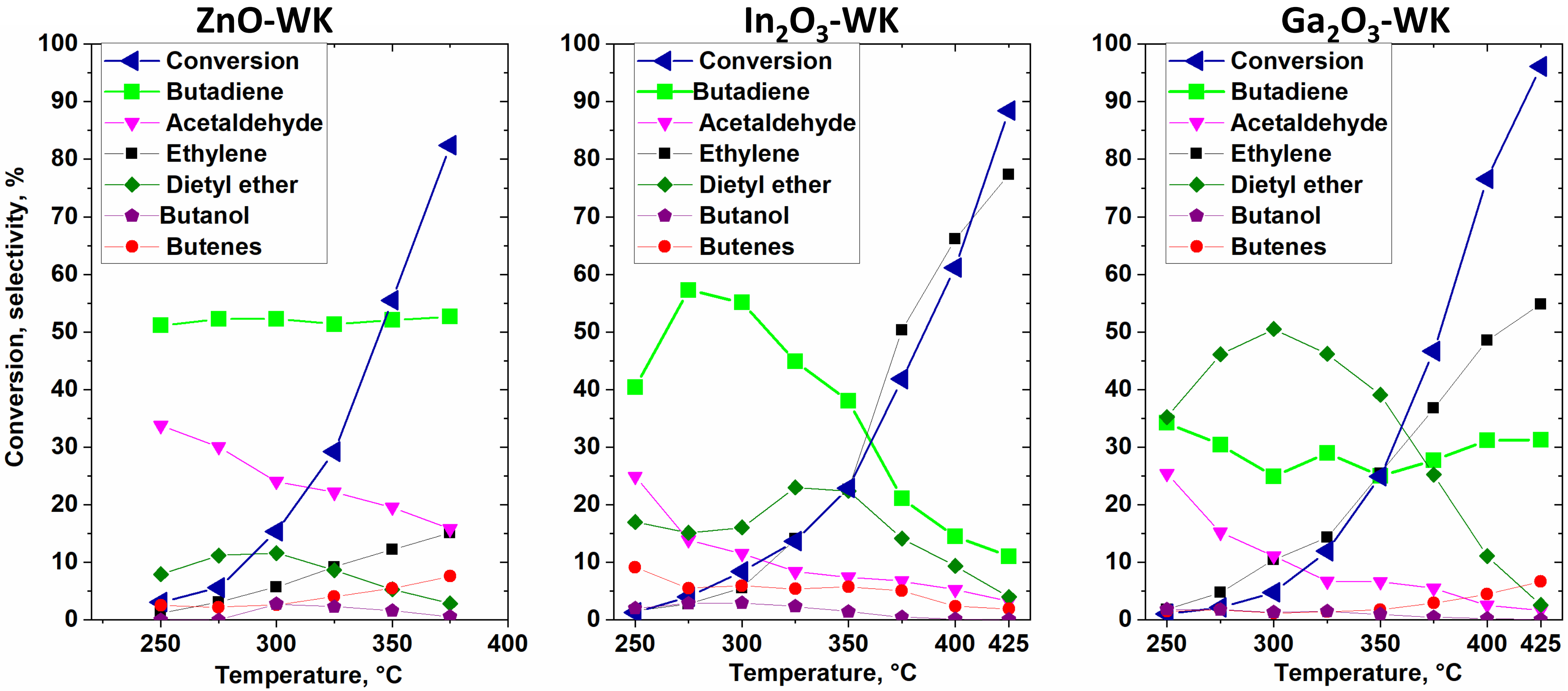
NH_3 TPD



Pyridine FT-IR, 200 °C



Effect of the metal-oxides



1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

Conclusions

- ❑ Very similar acidic properties.
- ❑ Very similar basic properties.
- ❑ The activity of the catalysts showed correlation with the chemical hardness of the metal-oxides.

High-SSA MgO-SiO_2 catalysts

Catalyst groups

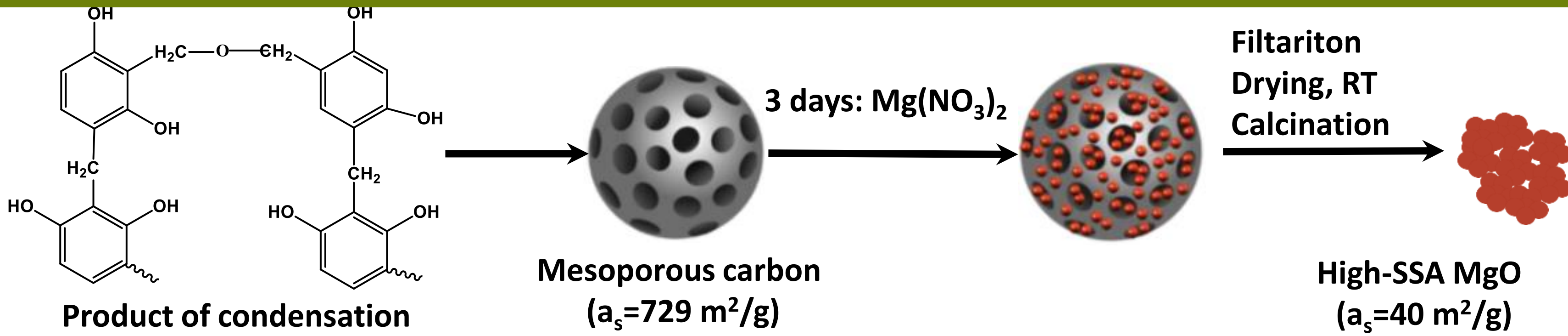
I. Silica-coated
- Low SSA MgO-SiO_2 (0.63)[a]
- High SSA MgO-SiO_2 (0.94)[a]

II. Wet-kneaded
- Low SSA MgO-SiO_2 (1.16)[a]
- High SSA MgO-SiO_2 (1.41)[a]

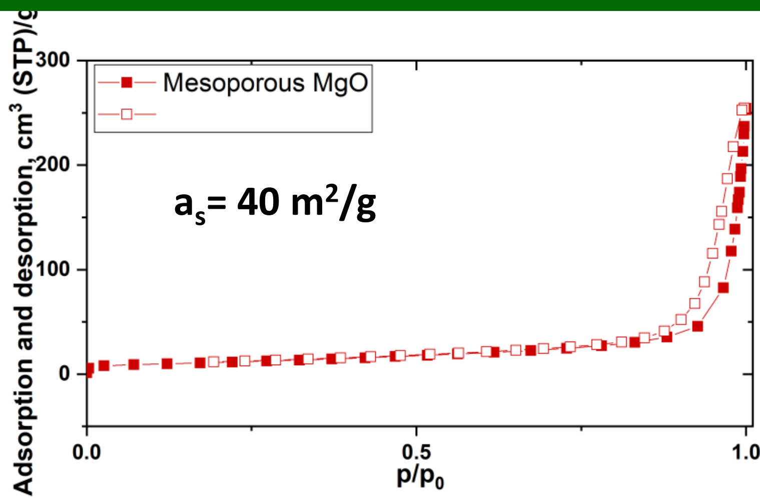
III. Internal hydrolyzed
- Low SSA MgO-SiO_2 (1.55)[a]
- High SSA MgO-SiO_2 (1.40)[a]

[a] *XPS analysis: Mg/Si, mol/mol*

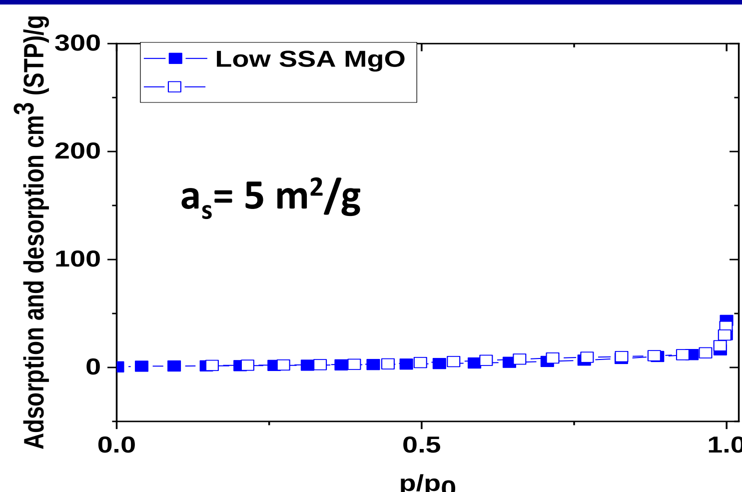
Mesoporous MgO synthesis



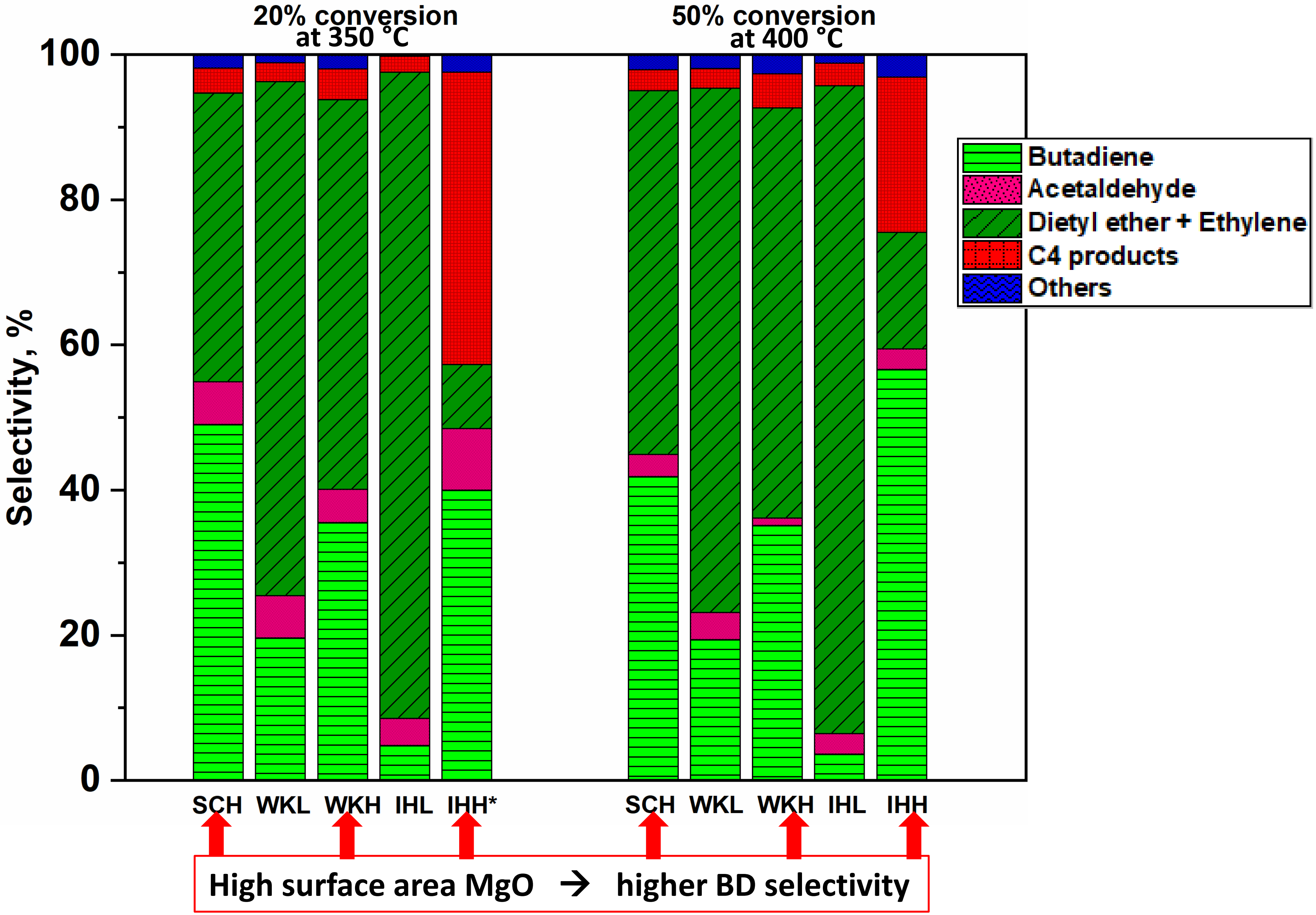
N_2 physisorption isotherm of the high -SSA MgO



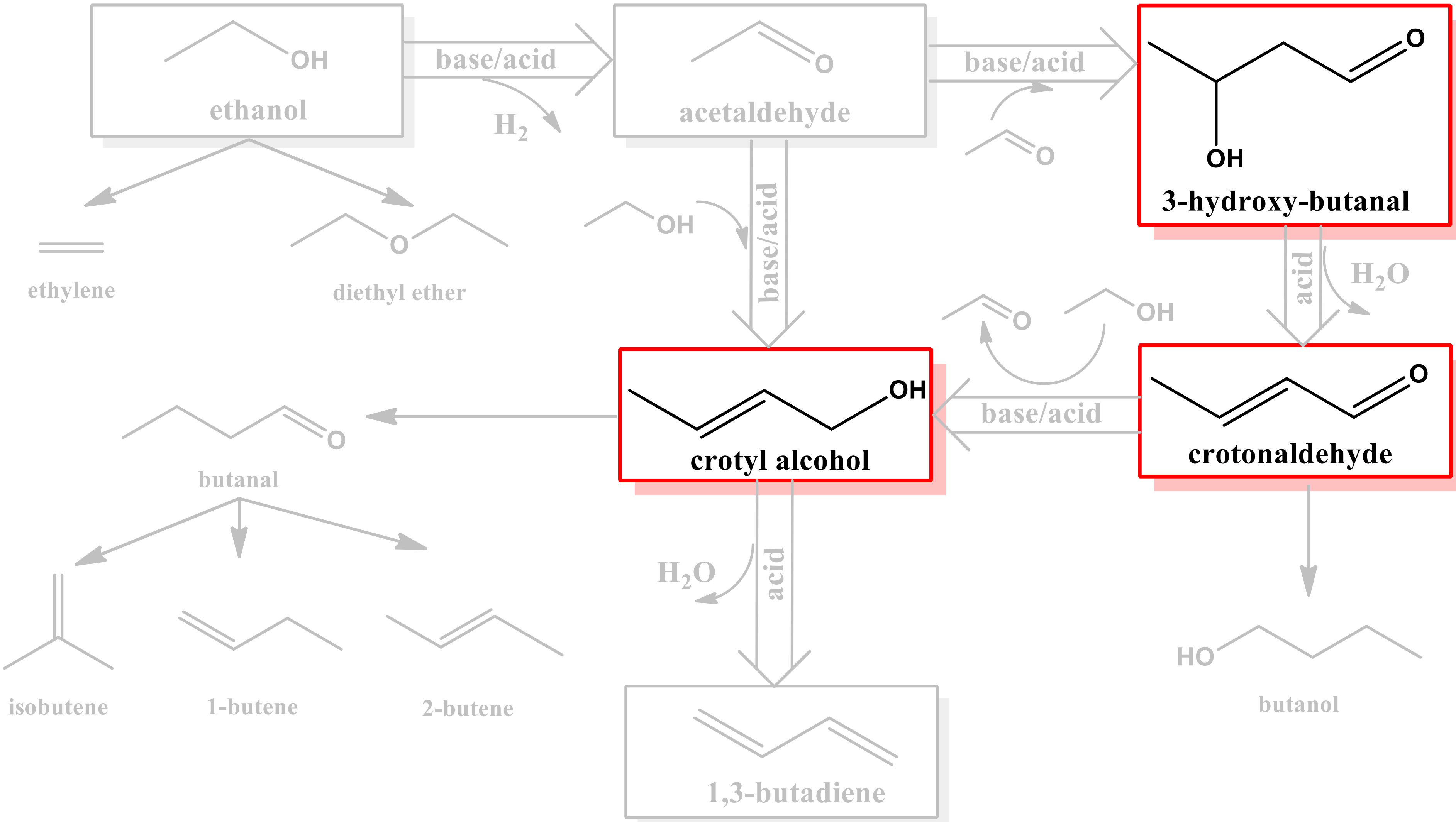
N_2 physisorption isotherm of the low -SSA MgO



Effect of the high SSA-MgO on the product distribution of the reaction products

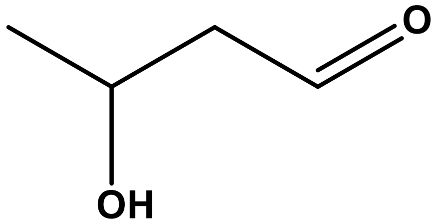


Reaction network



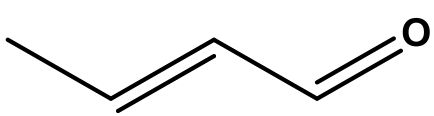
Conversion of the intermediates over MgO-SiO$_2$ catalysts

1. 3-hydroxy-butanal
   - Unstable → hard to detect



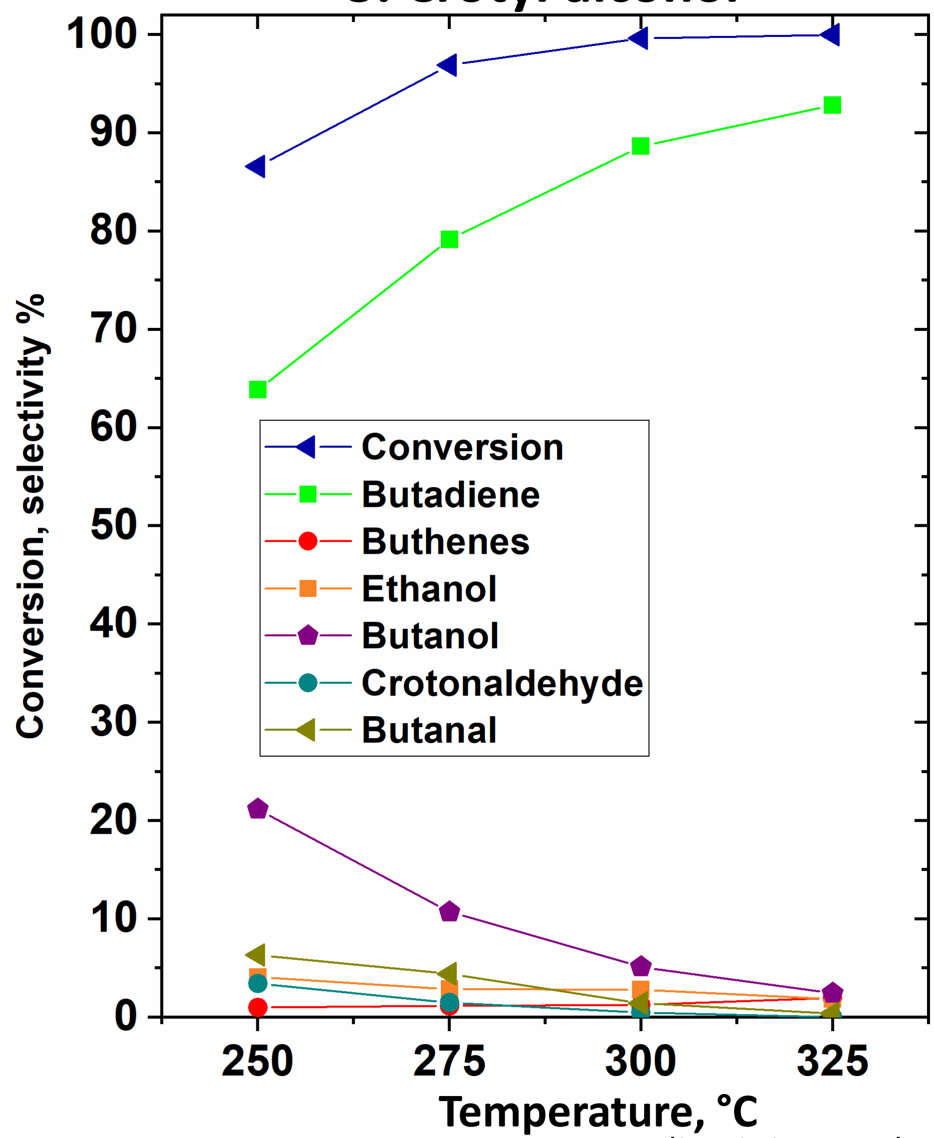
3-hydroxy-butanal

2. Crotonaldehyde
   - Polymerized products
   - Molecular H$_2$



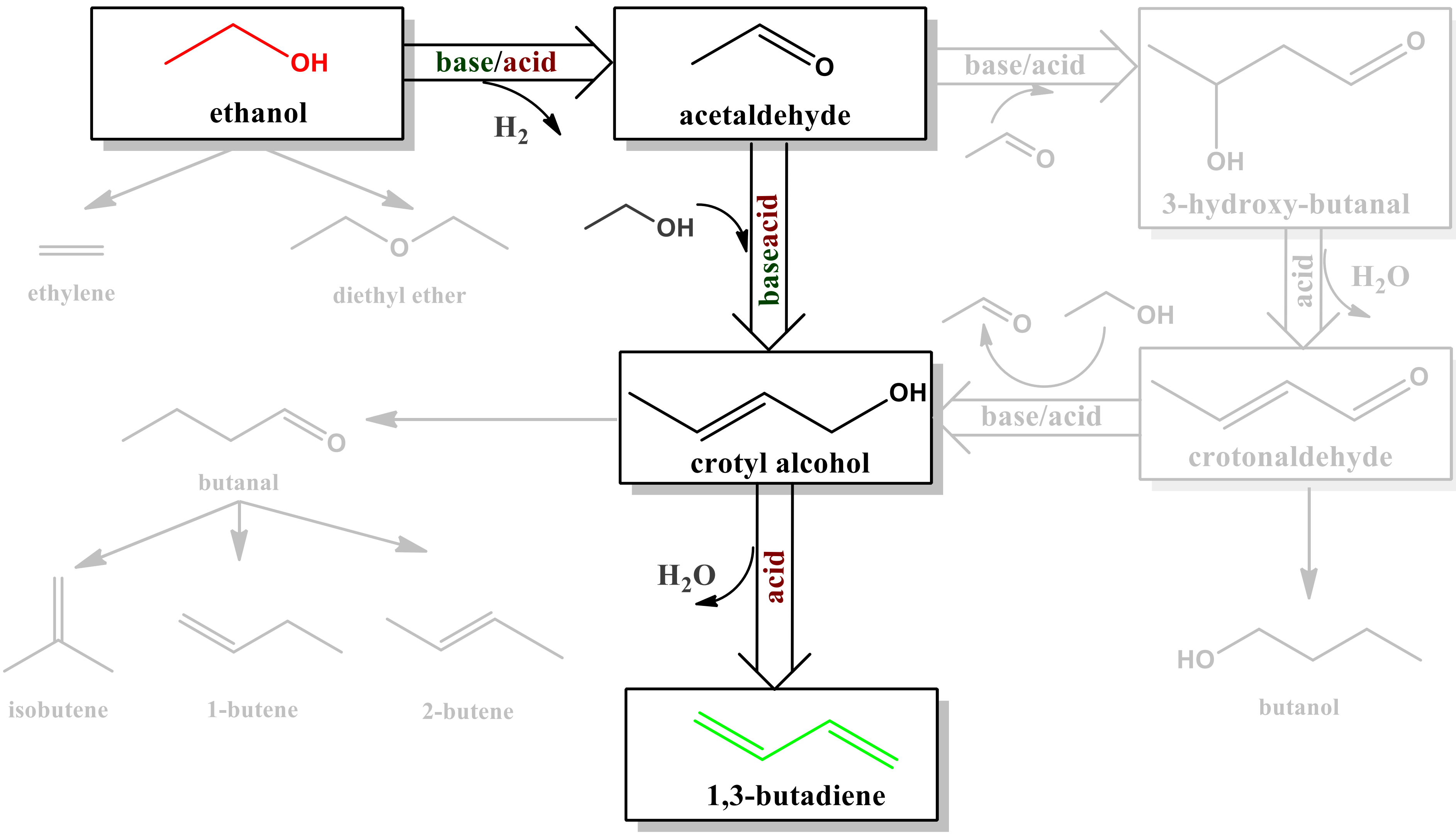
crotonaldehyde

3. Crotyl alcohol



1 g catalyst, 0.125 g crotyl alcohol/(g$_{cat}$*h), 30 ml/min (6.4 ml/min crotyl alcohol + 23.6 ml/min He)

Reaction network



SUMMARY

- Using new methods of catalyst synthesis (**In_2O_3**/WK, **In_2O_3/OPMET, WKH, SCH, IHH**) the butadiene yield could be increased.

- Addition of metal-oxides significantly increased the yield of butadiene, which was interpreted as accelerating the dehydrogenation reaction of ethanol.

- The metal oxide additive changed the acidity and basicity of the catalysts to the same level, however their catalyst activity were different, which was explained by the different chemical hardness of the oxides.

- The catalysts made of high surface area MgO gave significantly higher BD yields than the samples containing low surface area MgO.

- The higher BD yield obtained on samples made from mesoporous MgO are explained by the more favorable interaction of the catalyst components: the higher amount of MgO on the surface facilitates the coupling reaction, while the acidic sites are required for adequate dehydration activity.

- Based on our experiences we suggested the most likely reaction pathway (acetaldehyde intermediate **links to ethanol**).

Thank you for your kind attention!

Acknowledgement

European Regional Development Fund (Interreg, SKHU/1902/4.1/001/Bioeconomy)
www.skhu.eu

Interreg
Slovakia-Hungary

Building Partnership

www.ttk.hu/palyazatok/bioeconomy