Catalytic conversion of ethanol to butadiene over $MgO-SiO_2$ catalysts: effects of texture, structural heterogeneity and metal-oxide promoters on the catalytic activity

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National Research, Development and Innovation Office
Hungary

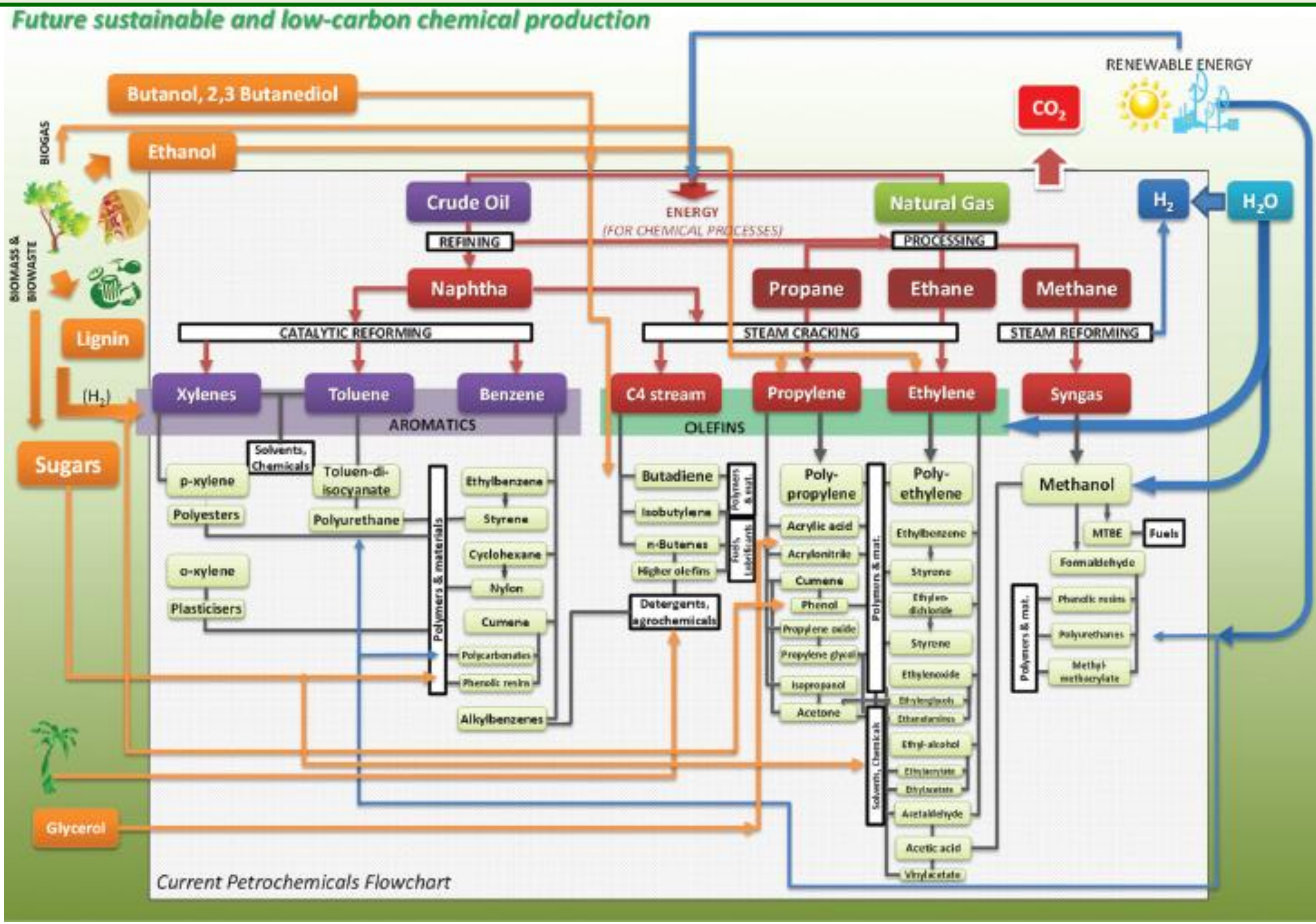
PROGRAM FINANCED FROM THE NRDI FUND

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences

Budapest, Hungary

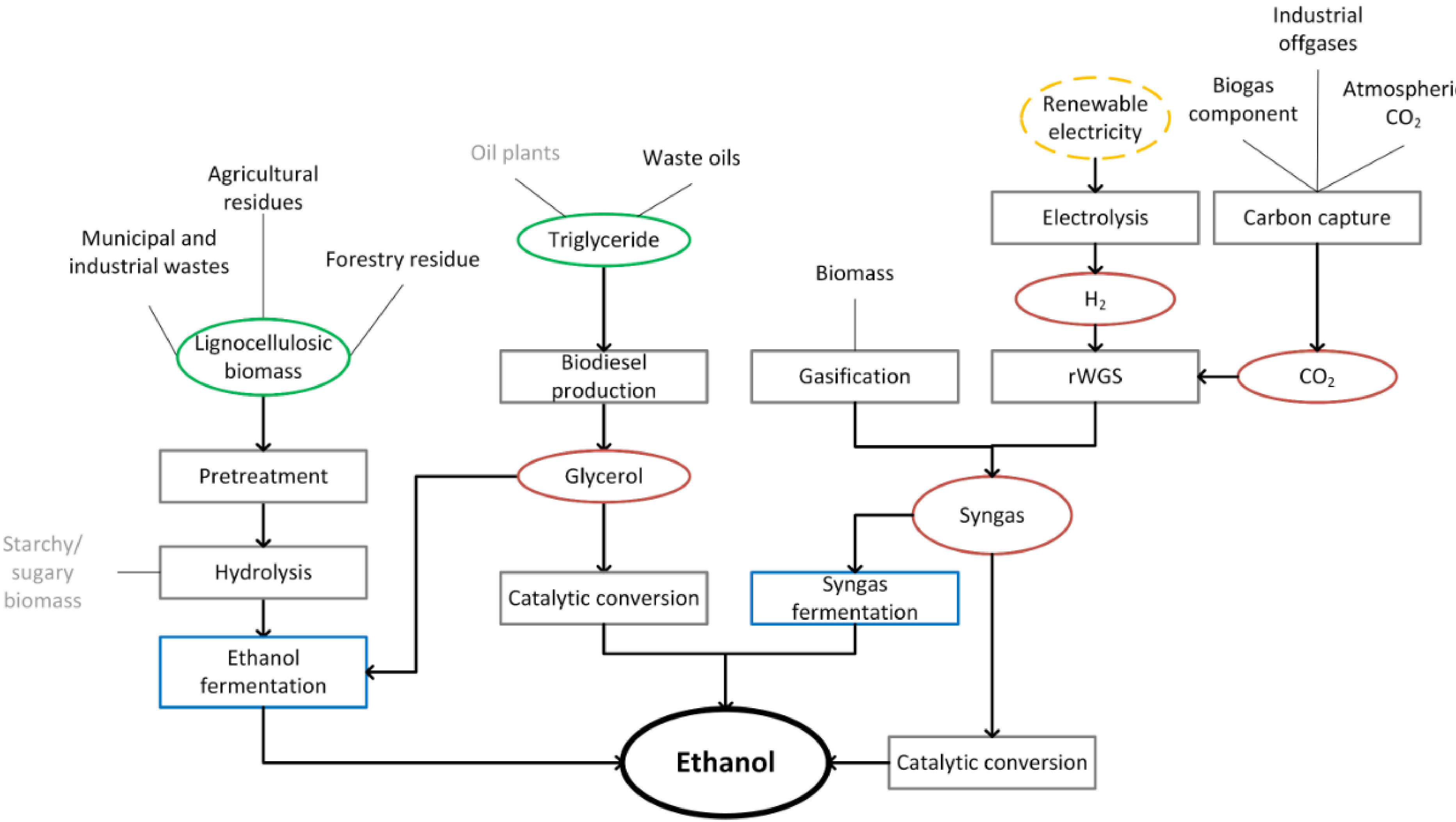
28 November, 2023

New scenario for a sustainable chemical production based on the reuse of CO_2 and of biomass



ChemSusChem2014,7, 1274 – 1282.

Pathways towards renewable ethanol



Biofuel Bioprod. Biorefin. **2020**, 14, 845–878.

Historical review I.

1839: discovery of vulcanization

2-methyl-1,3-butadiene

1918-1938: Ukraine, Russia, Kazakh dandelion (rubber root)

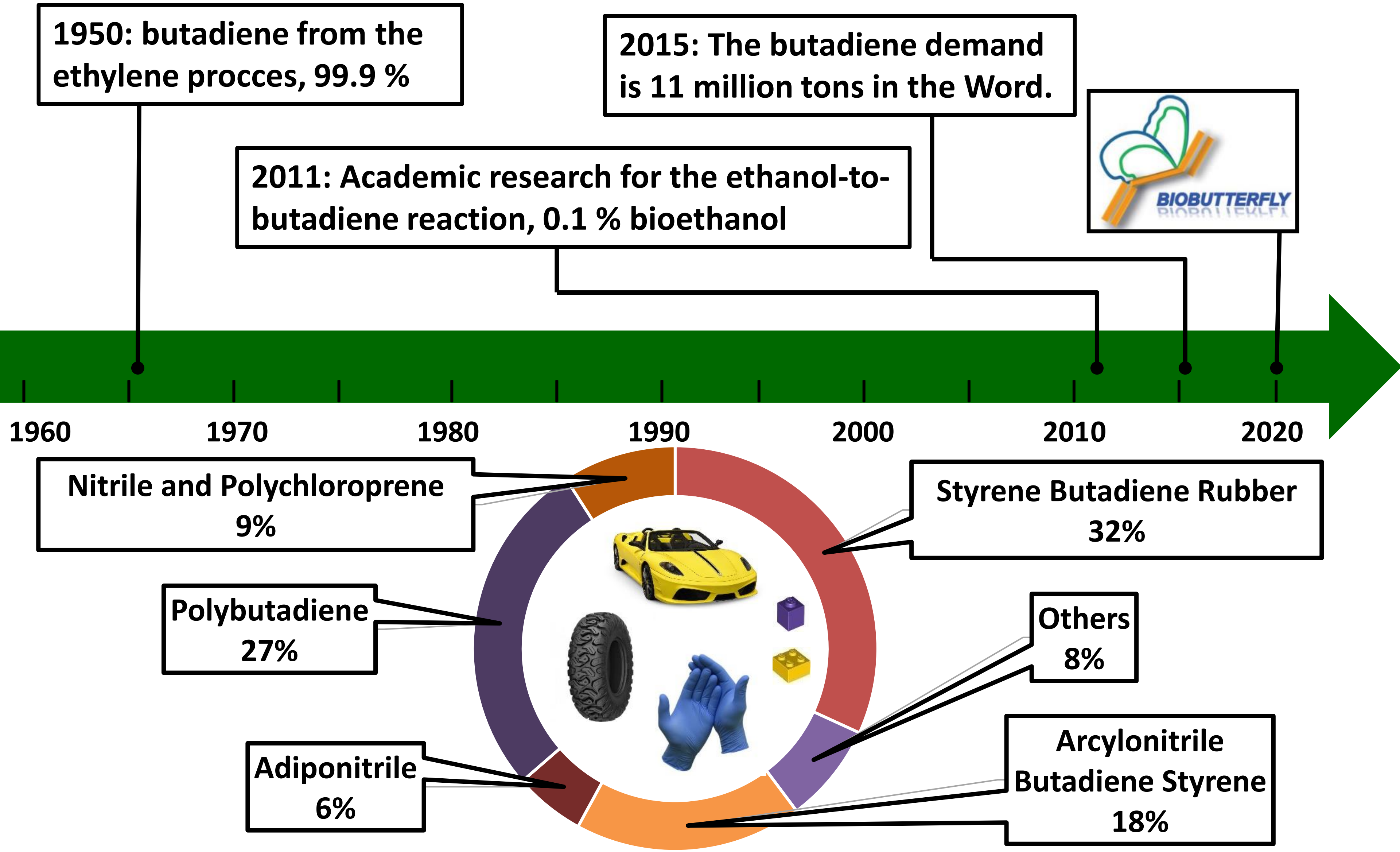
1830 1840 1850 1860 1870 1880 1890 1900 1910 1920 1930 1940

1910: Germany and Russia,
1st investigations

1928: *Lebedev*,
One step process: $ZnO\text{-}Al_2O_3$ catalyst,
from pure ethanol

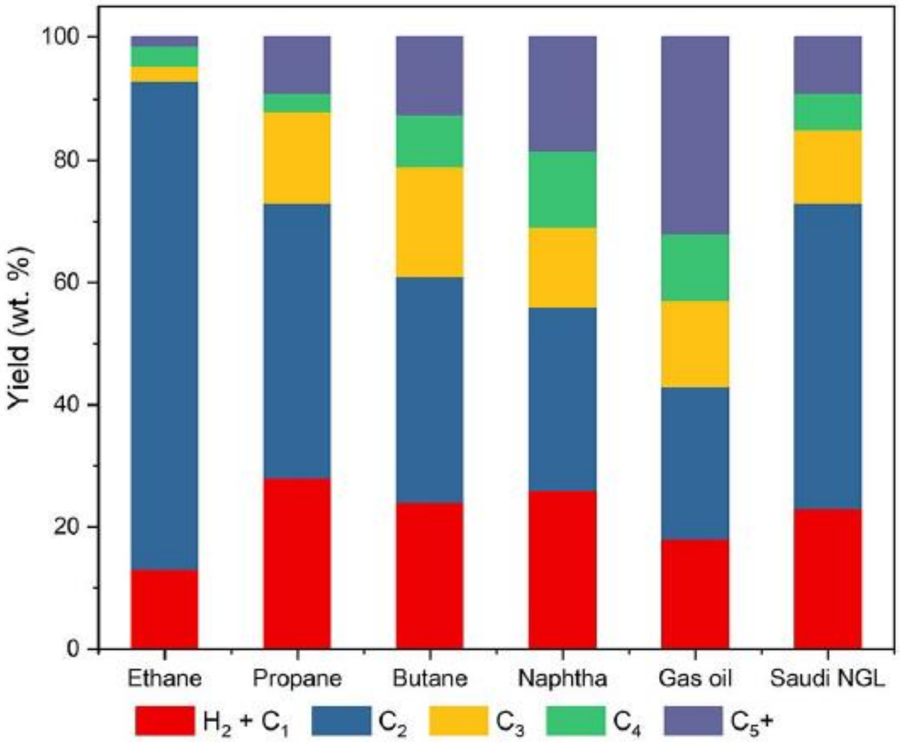
1915: *Ostromislensky*,
Two-step process, Al_2O_3 or clay mineral catalyst,
from acetaldehyde + ethanol mixture

Historical review II.

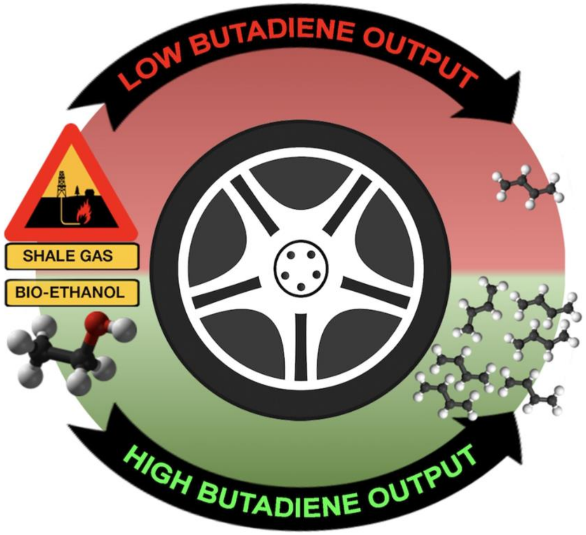


Ethanol to butadiene as an alternative technology

Yield of C_4 fraction from different feedstocks



The advantage of ethanol over shale gas



The BioButterfy Plant

Chem Asian J. 2020, 15, 4199–4214

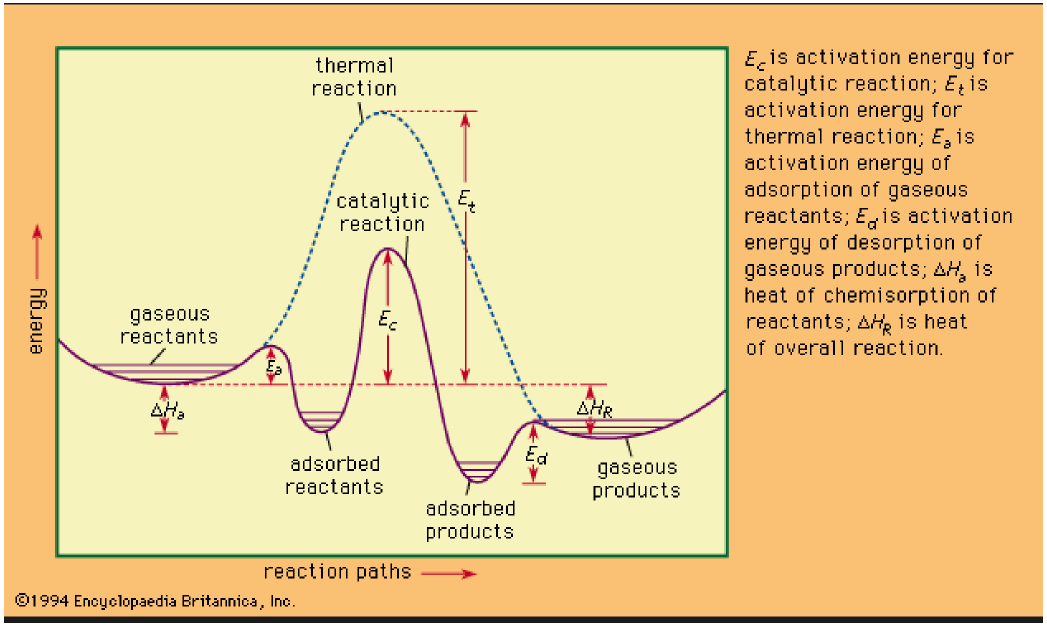
The BioButterfly project

Michelin, IFP Energies nouvelles and Axens constructed an industrial prototype for mass production between 20 and 30 tonnes/year.

This is the last phase before industrial implementation of the process (100,000 tonnes/year)

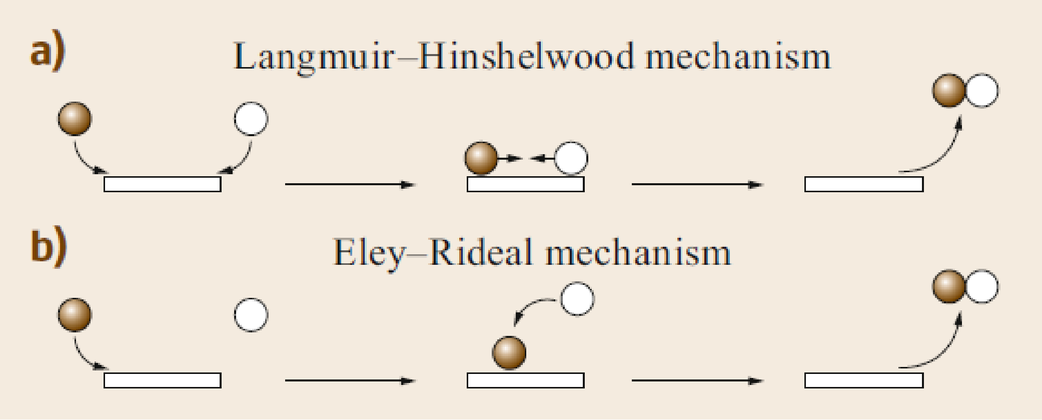
Heterogeneous catalysis and surface reactions

Potential energy profile of heterogeneous catalytic reactions



Schematics of the possible mechanisms of the heterogeneous reactions

The brown and white balls represent the two reactants



Springer Handbook of Surface Science pp 905–928

Definition of acid and base

Definition by Brønsted: an acid (AH) donates a proton and a base (B^-) accepts a proton.

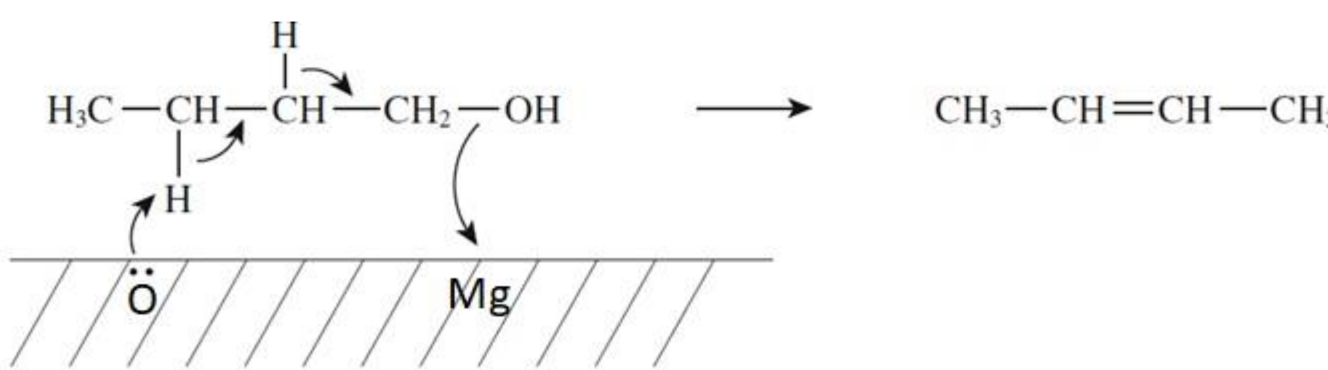
$$AH + B^- \longrightarrow A^- + BH$$

Definition by Lewis: a base (:B) donates a lone pair and an acid (A) accepts a lone pair.

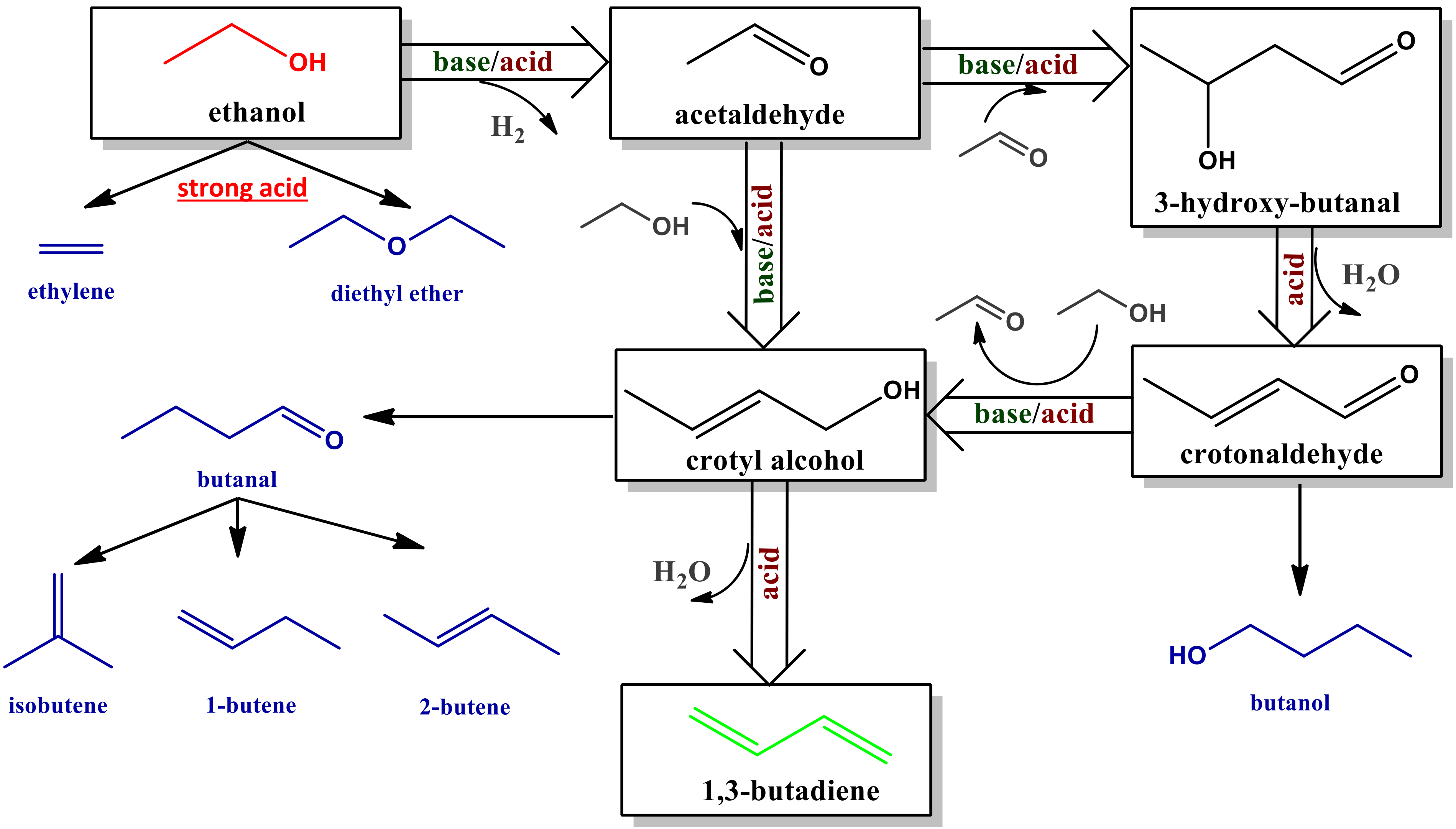
$$A + :B \longrightarrow A:B$$

Coopirative action of acidic and basic sites

Concerted mechanism in 1-butanol dehydration over MgO



Reaction mechanism of ethanol to butadiene transformation

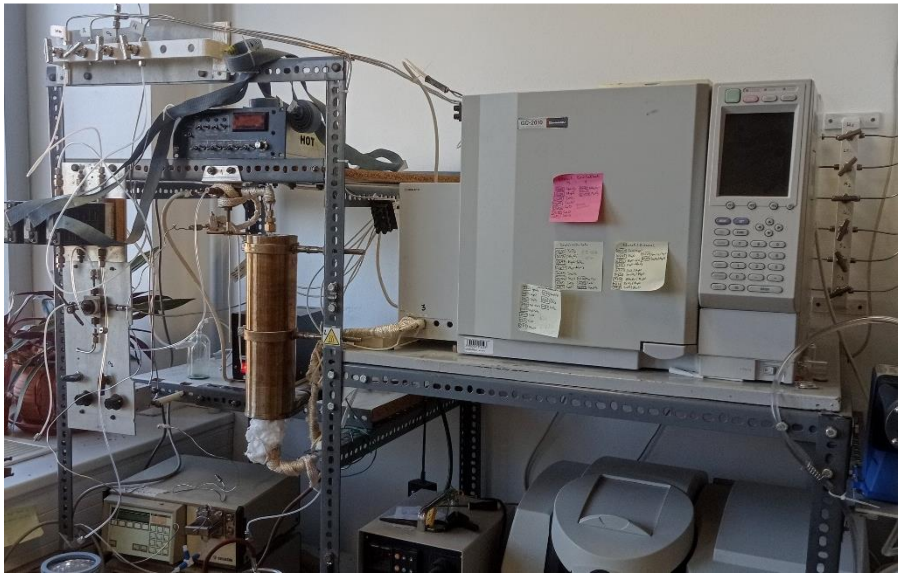


Catalytic test reactions

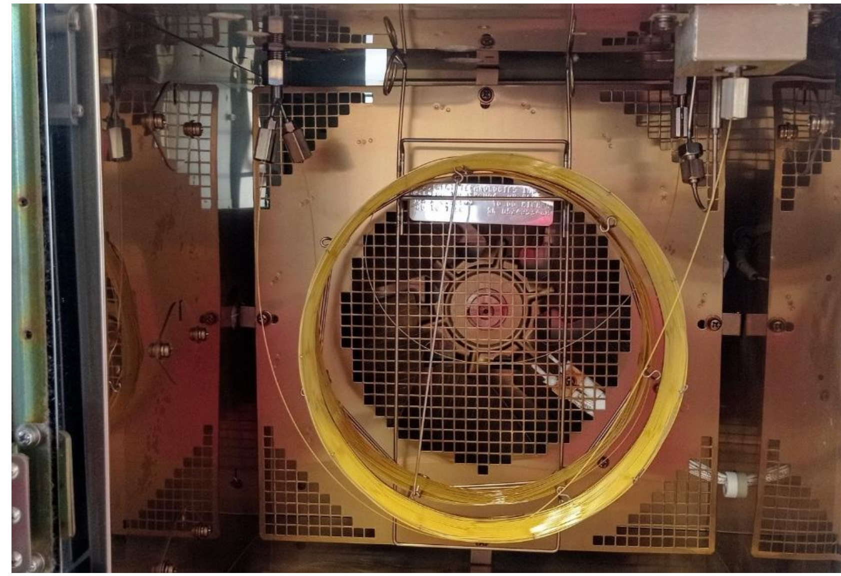
- Fixed-bed, continuous-flow reactor at atmospheric pressure
- On-line GC, two FID (PLOT-Fused Silica Al_2O_3/KCl – hydrocarbons; HP-PLOT-U - oxygenates) and TCD detector
- The GC was calibrated for reactant and all products separately
- Selectivities were calculated on carbon basis (number of carbon 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

System for catalytic test reactions

On-line GC



The two-column layout



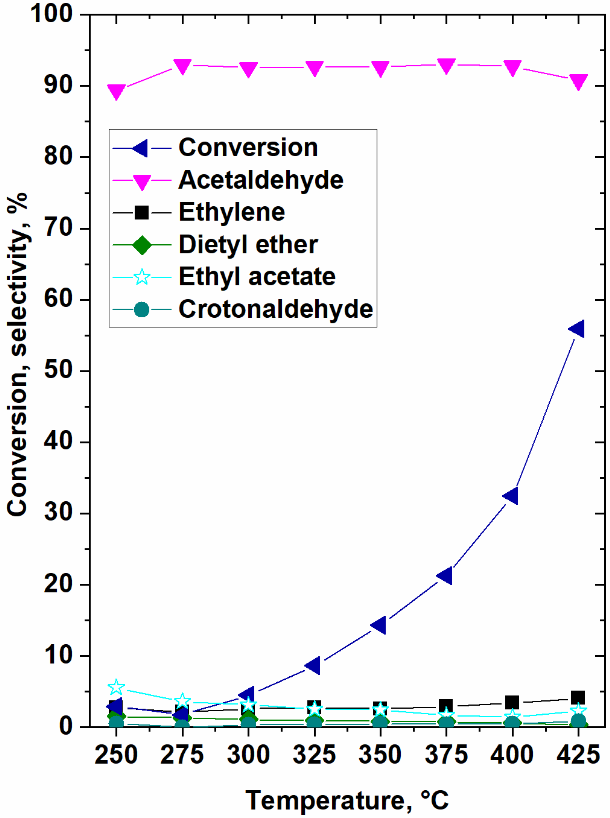
The flow-through quartz reactor (l = 30 mm, ⌀ = 10 mm)

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

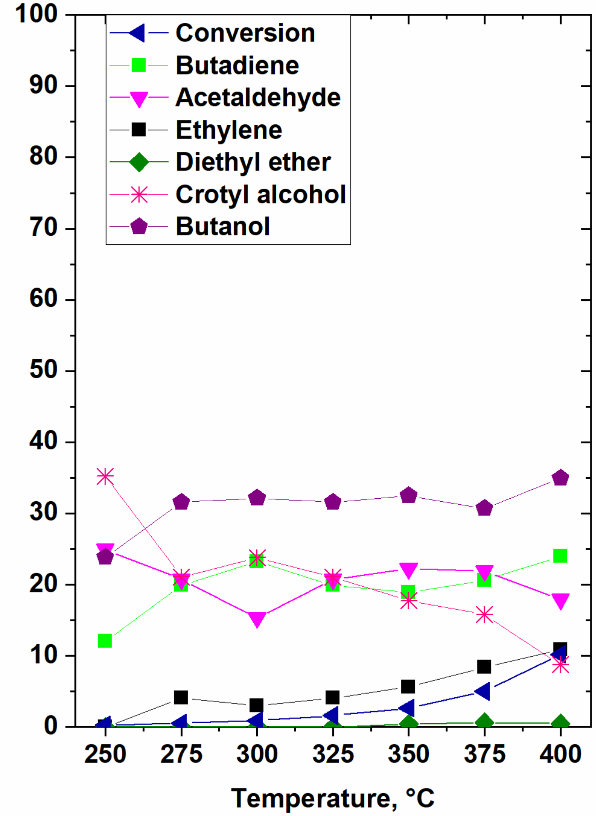
- Catalysts:

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

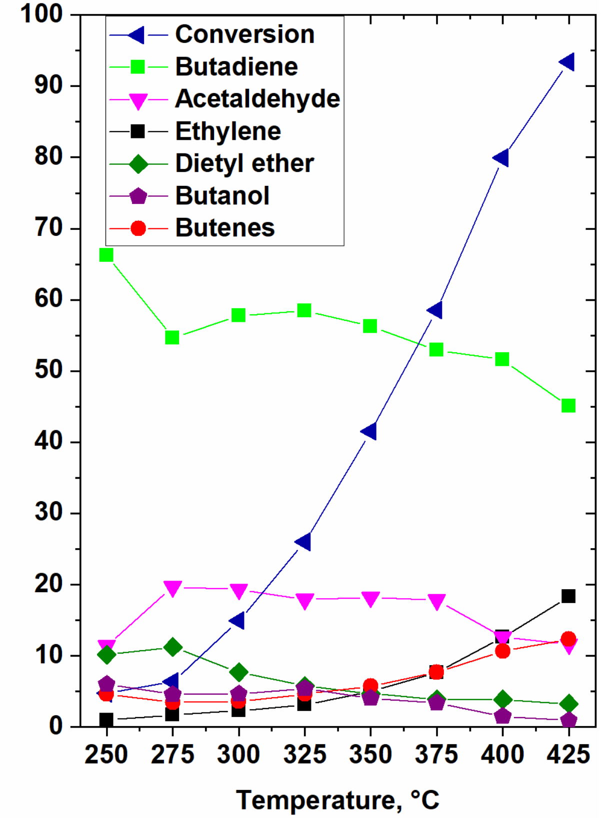
In_2O_3/SiO_2
(Acidic catalyst)



MgO
(Basic catalyst)



In_2O_3/MgO-SiO_2
(Acidic and basic catalyst)



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

Tested catalysts in the ethanol-butadiene reaction

I. Stage: talc like catalysts

1. **Natural talc** ($Mg_3Si_4O_{10}(OH)_2$)
2. **Coprecipitated sample**
3. **Wet-kneaded sample**
   - **1 wt% Ga_2O_3, In_2O_3 and ZnO**

Blanka Szabó, *Gyula Novodárszki, Zoltán Pászti, Attila Domján, József Valyon, Jenő Hancsók, Róbert Barthos:* ***MgO–SiO$_2$ Catalysts for the ethanol to butadiene reaction: The effect of Lewis acid promoters****, ChemCatChem, 12 (2020) 5686–5696*

II. Stage: high SSA-SiO_2-MgO catalysts group

1. **Wet-kneaded sample**: 30 % MgO-SBA-15 from $Mg(OH)_2$
2. **Incorporated sample:** 30 % MgO-SBA-15 from $Mg(OMet)_2$
   - **2,5,10 wt% In_2O_3,**

Blanka Szabó, *Gyula Novodárszkia, Zoltán May, József Valyon, Jenő Hancsók, Róbert Barthos:* ***Conversion of ethanol to butadiene over mesoporous In_2O_3 promoted MgO-SiO$_2$ catalysts****, Molecular Catalysis, 491 (2020) 110984*

III. Stage: high SSA MgO-SiO_2 catalysts group

1. Wet-kneaded family
- Low SSA MgO-SiO_2
- High SSA MgO-SiO_2

2. Silica-coated family
- Low SSA MgO-SiO_2
- High SSA MgO-SiO_2

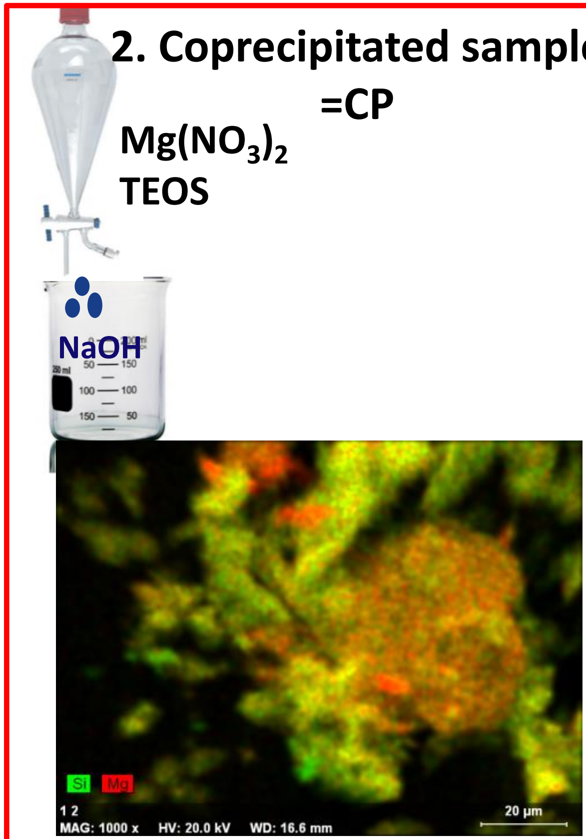
3. Internal hydrolyzed family
- Low SSA MgO-SiO_2
- High SSA MgO-SiO_2

Journal of Molecular Structure 1259 (2022) 132764 and React. Chem. Eng., 8 (2023) 718

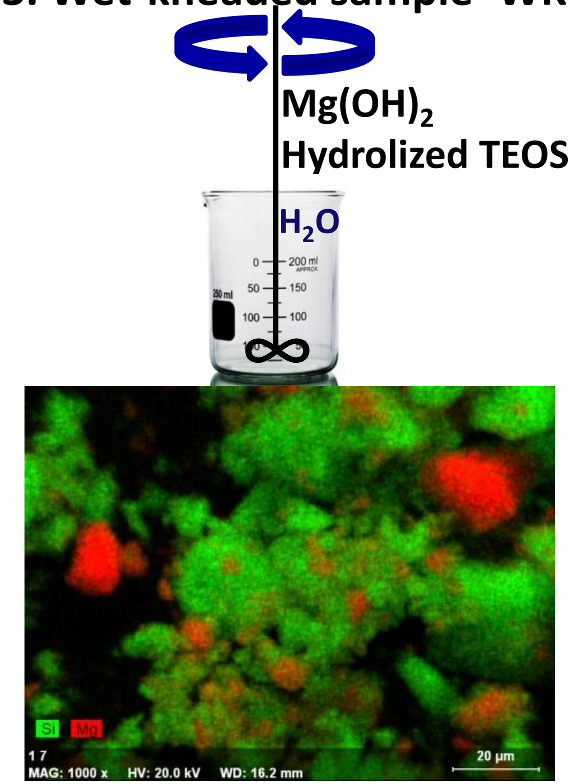
I. Stage: talc like catalysts

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	9.1	7.7	0.07	-	17.12	-
CP	1.44	207.5	10.5	0.09	-	412.01	0.15
WK	1.61	249.6	94.5	0.15	0.74	461.11	0.35

a: ICP-OES anal. Theoretical Si/Mg ratio 1.54
b: BET method

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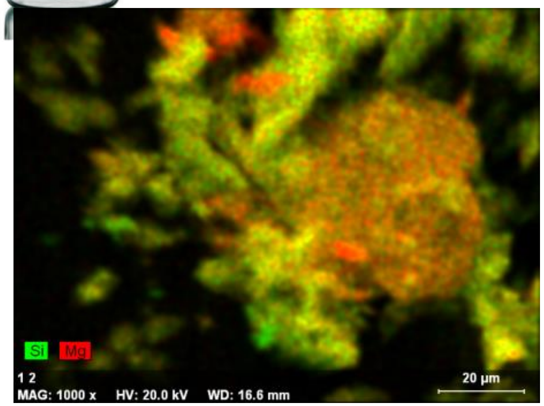

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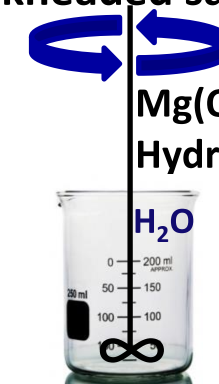

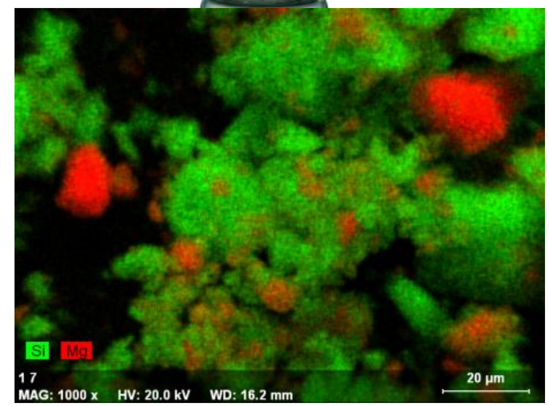

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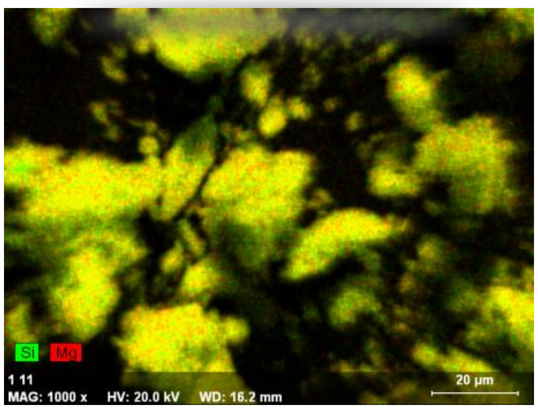
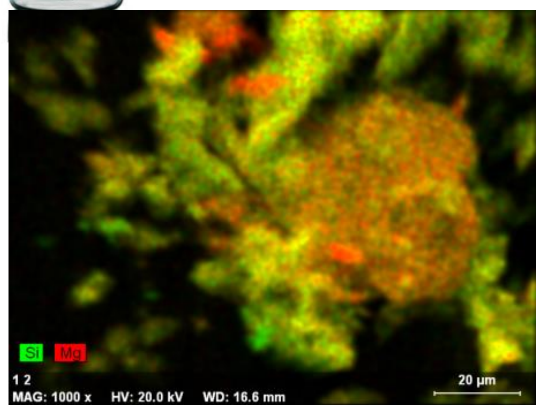


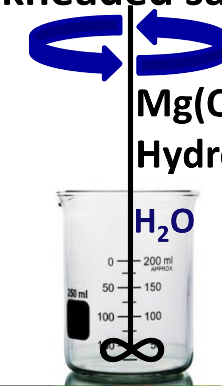
2. Coprecipitated sample =CP

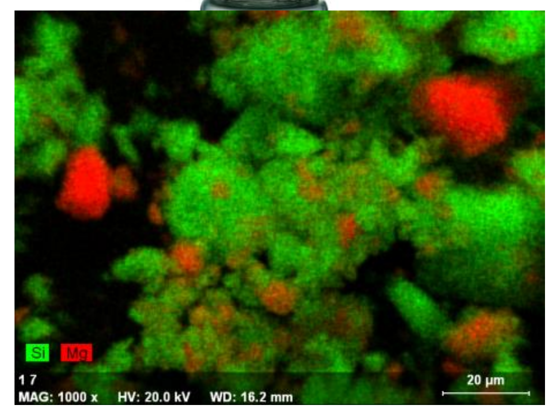
$Mg(NO_3)_2$
TEOS



3. Wet-kneaded sample=WK

$Mg(OH)_2$
Hydrolized TEOS





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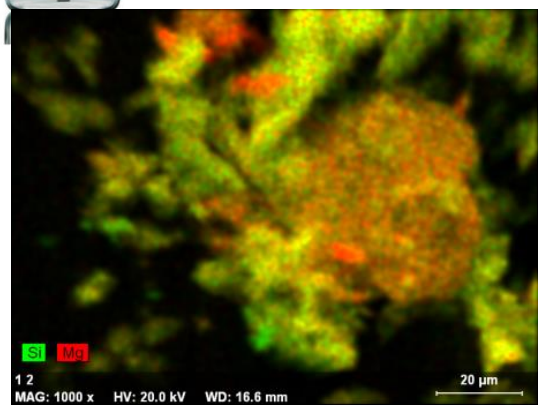

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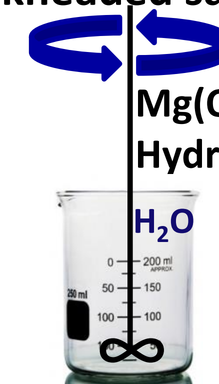
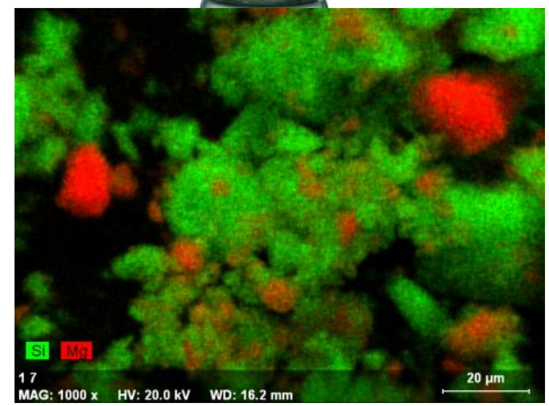
$Mg(OH)_2$
Hydrolized TEOS





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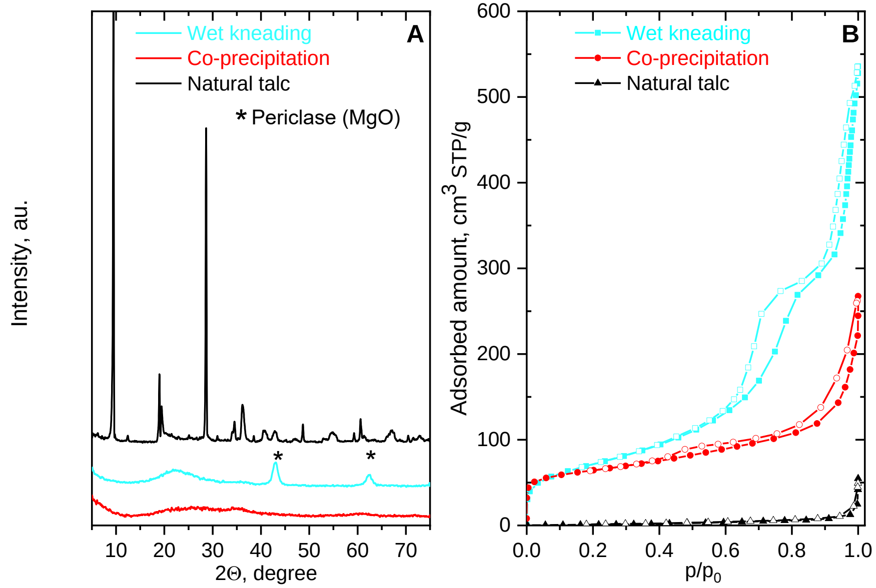
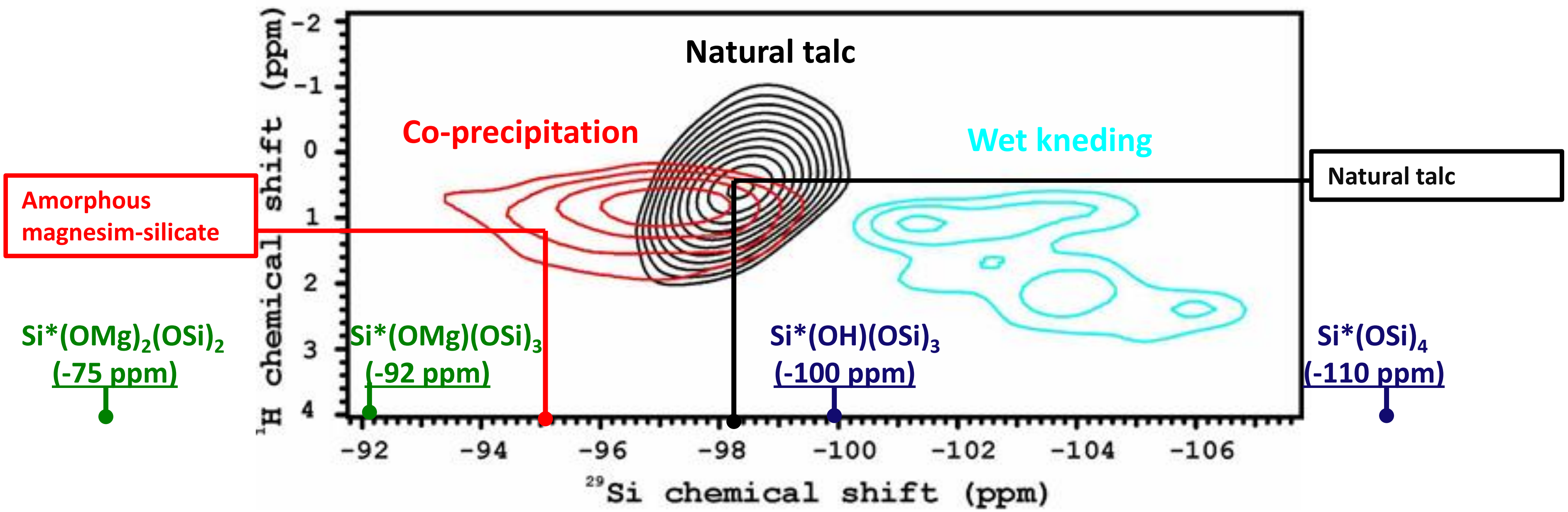
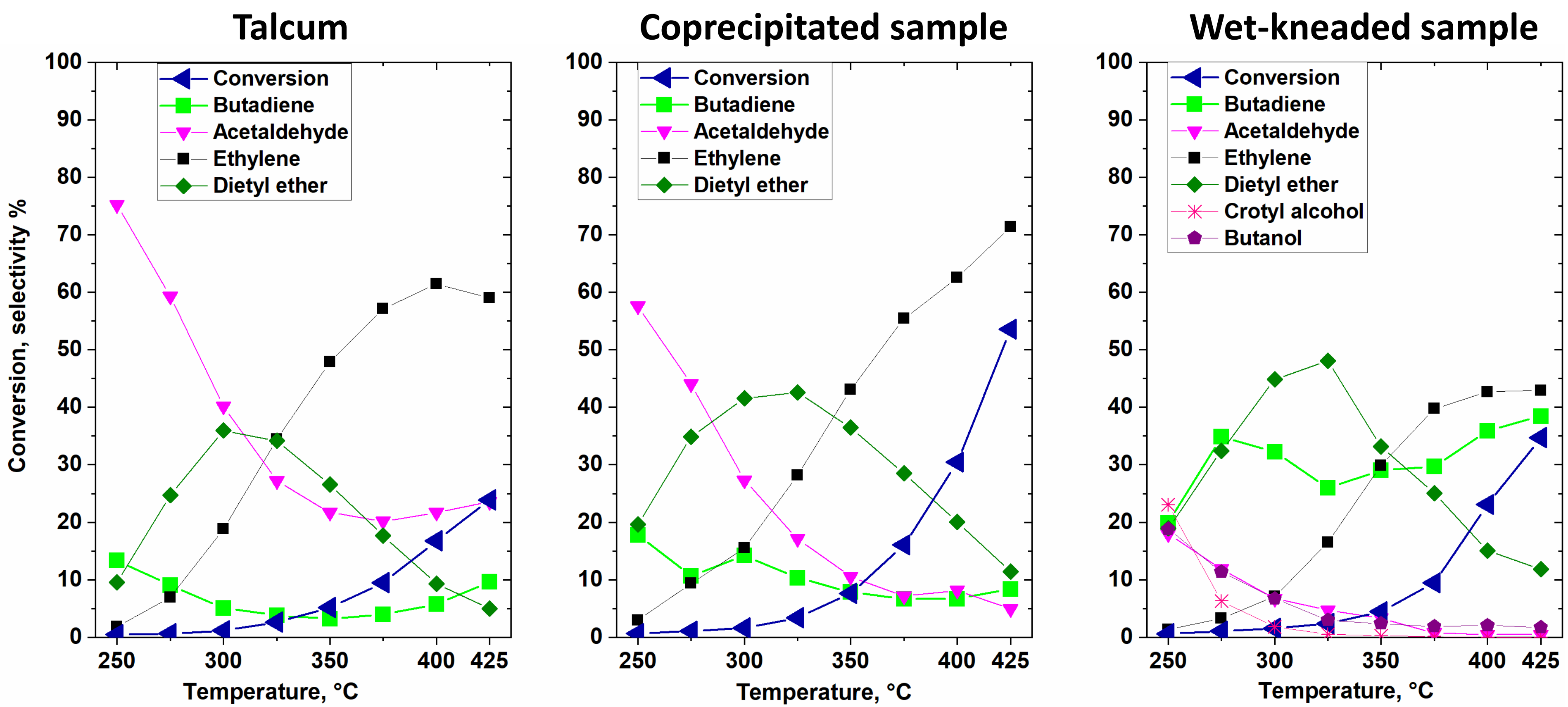
XRD patterns of the catalysts



NMR results



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

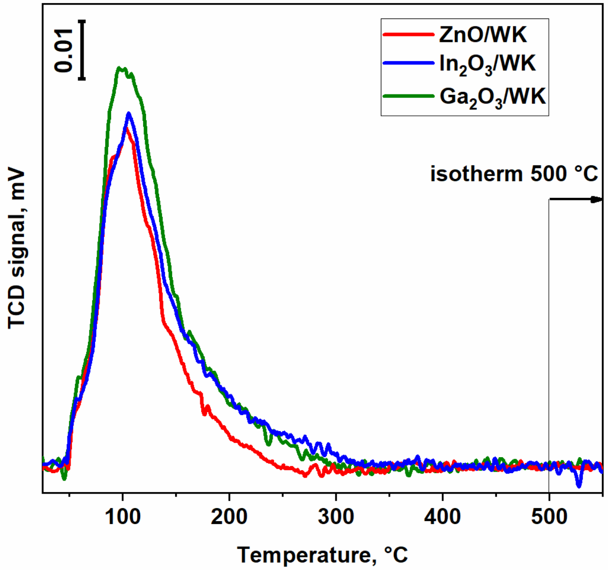
- ❑ Best catalytic activity: **WK sample.**
  - High specific surface area (250 m^2/g)
  - Ideal Lewis-acidity
  - Stronger basic sites→ separeted MgO phase → efective C-C coupling

The effect of metal oxides on the acid-base properties

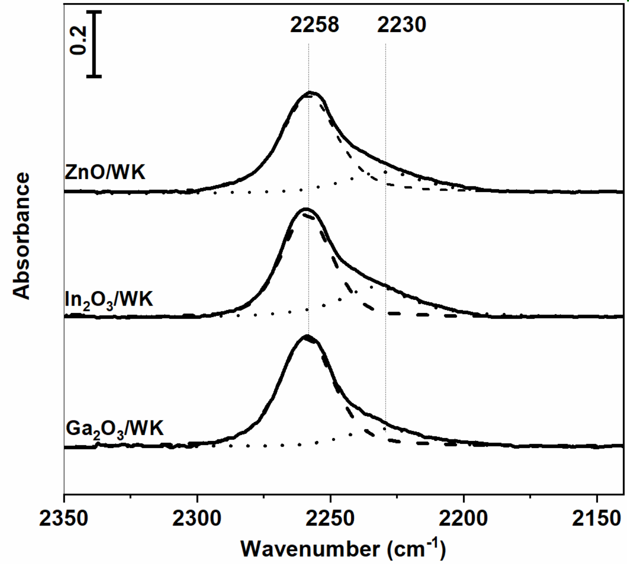
- 1 wt% of ZnO/ In_2O_3 /Ga_2O_3-WK

Basic properties:

CO_2 TPD

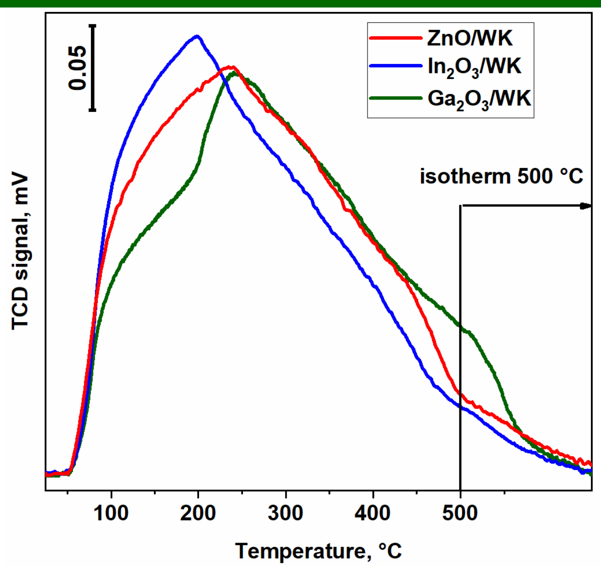


$CDCl_3$-FT-IR, RT

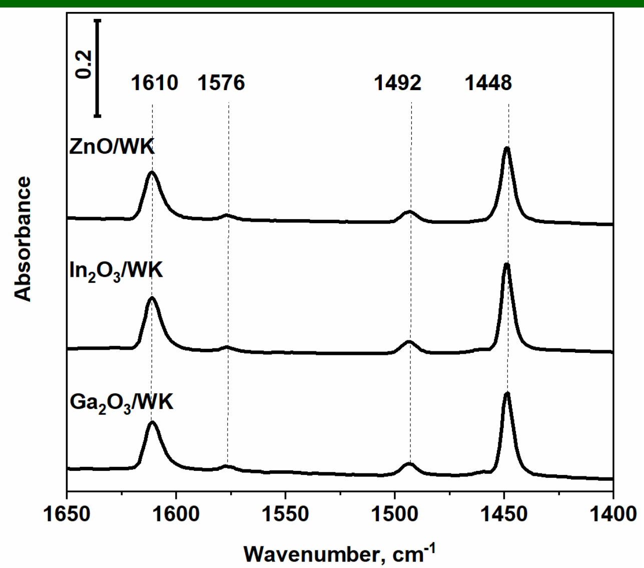


Acidic properties:

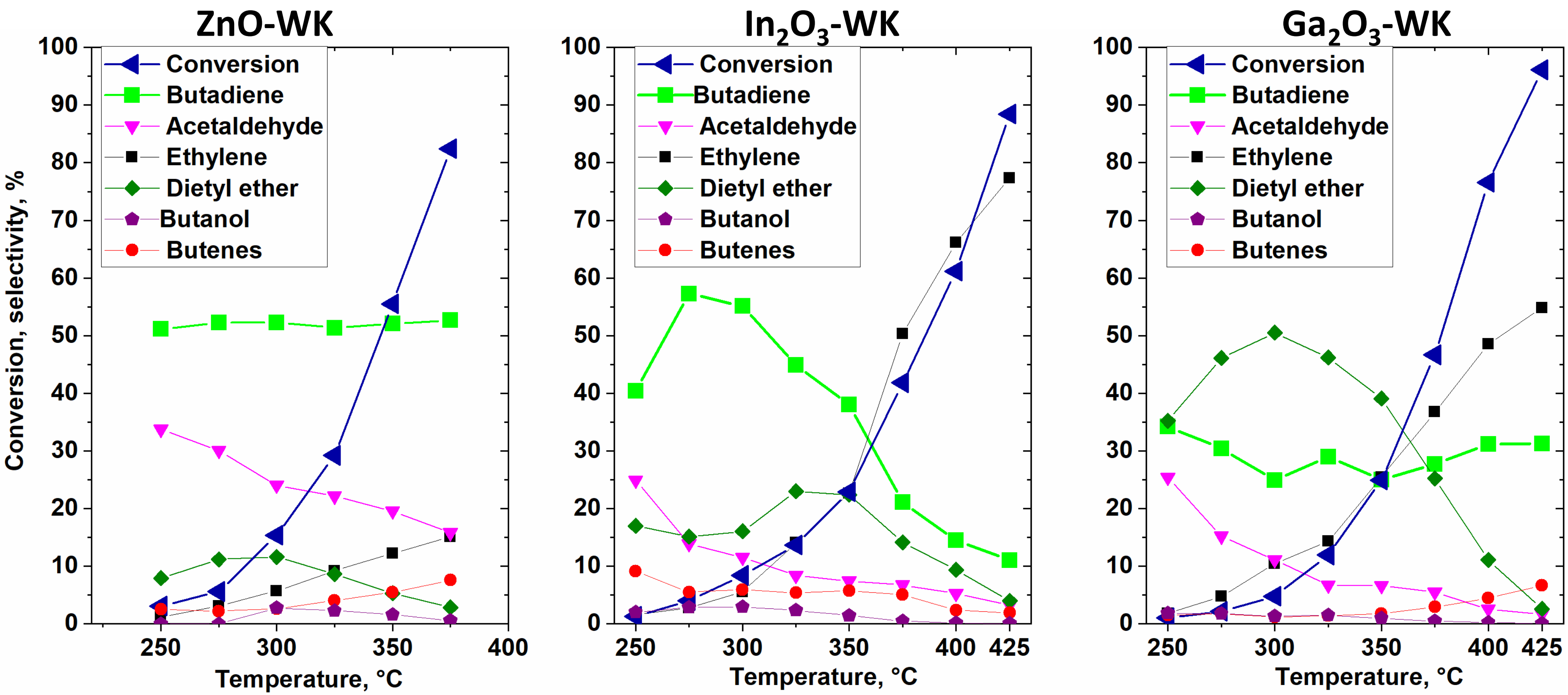
NH_3 TPD



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 acidity properties.
- ❑ Very similar basicity properties.
- ❑ The activity of the catalysts showed correlation with the chemical hardness of the metal-ions.
  Zn^{2+}(0.45) < In^{3+} (0.53) < Ga^{3+}(0.68)*

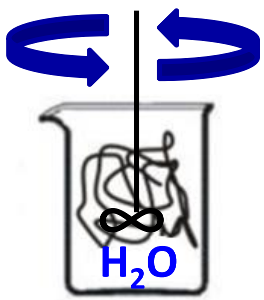
*Progress in Solid State Chemistry 39 (2011) 70

High SSA-SiO_2-MgO catalysts group

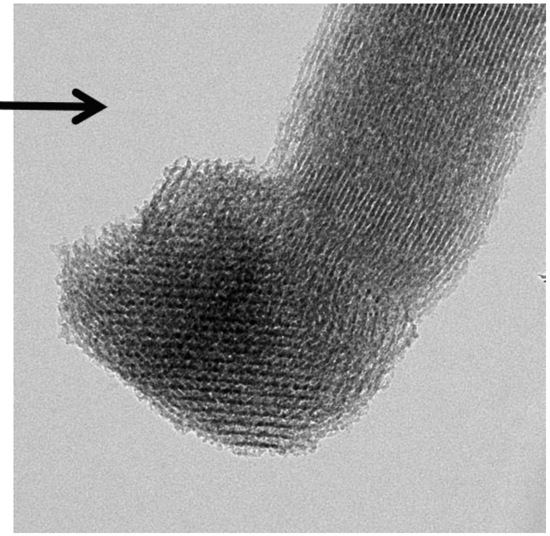
Wet-kneaded sample=WKSBA

1. Wet-kneading= WKSBA

$Mg(OH)_2$ + SBA-15



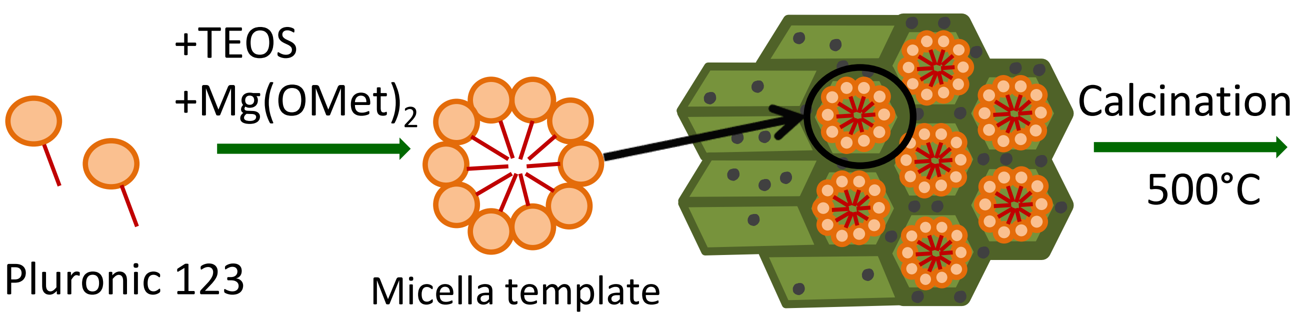
SSA: 356 m^2/g



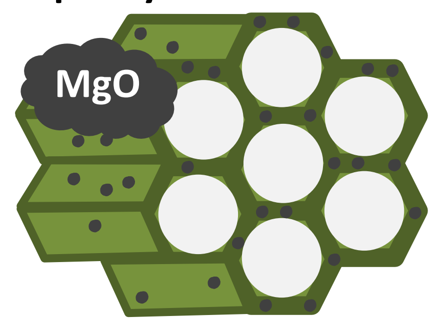
SBA-15

- ✓ Mesoporous SiO_2
- ✓ SSA: ~ 700 m^2/g
- ✓ Hexagonal pore system
- ✓ Thermal stability
- ✓ Hydrothermal stability

Incorporated sample=OPMET



2. One-pot synthesis= OPMET



30 wt% MgO-SBA-15
$Mg(OMet)_2$
SSA: 486 m^2/g

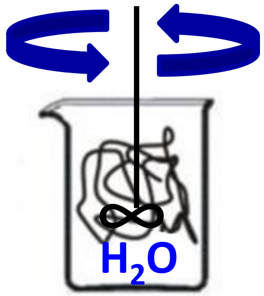
Pluronic 123: surfactant Pluronic 123Poly(ethylene glycol)-block-poly(propylene glycol)
TEOS: Tetraethyl orthosilicate

High SSA-SiO_2-MgO catalysts group

Wet-kneaded sample=WKSBA

1. Wet-kneading= In_2O_3/WKSBA

$Mg(OH)_2$ + SBA-15



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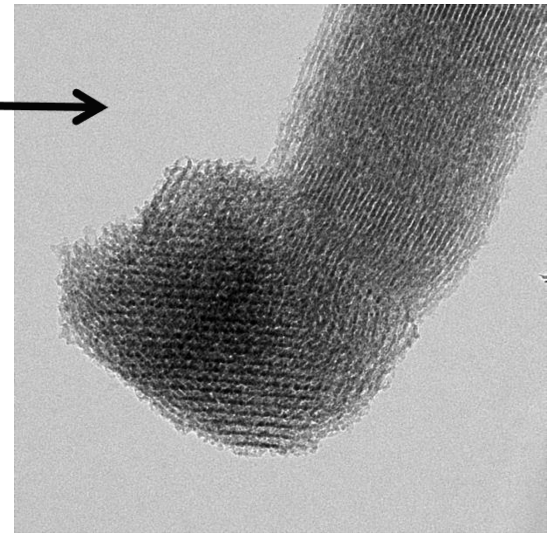

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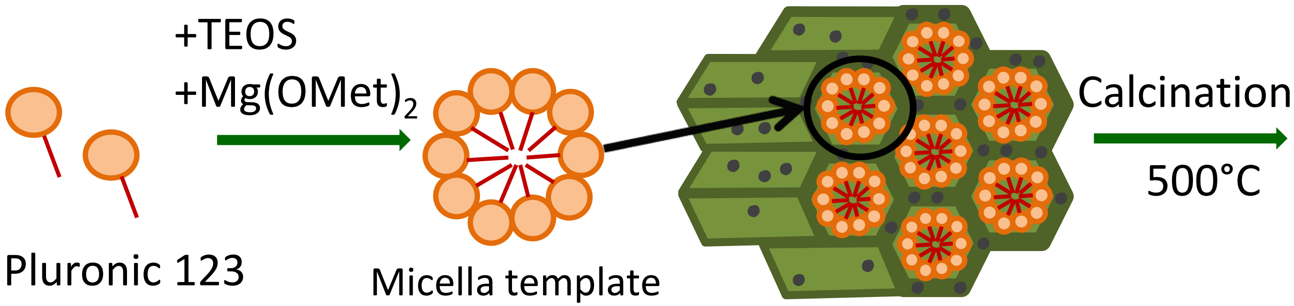

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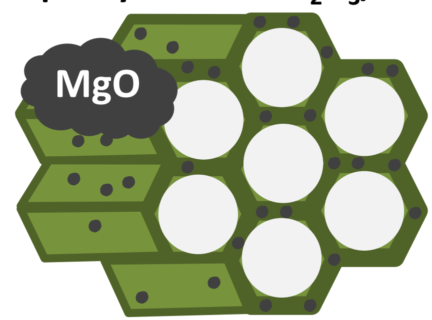

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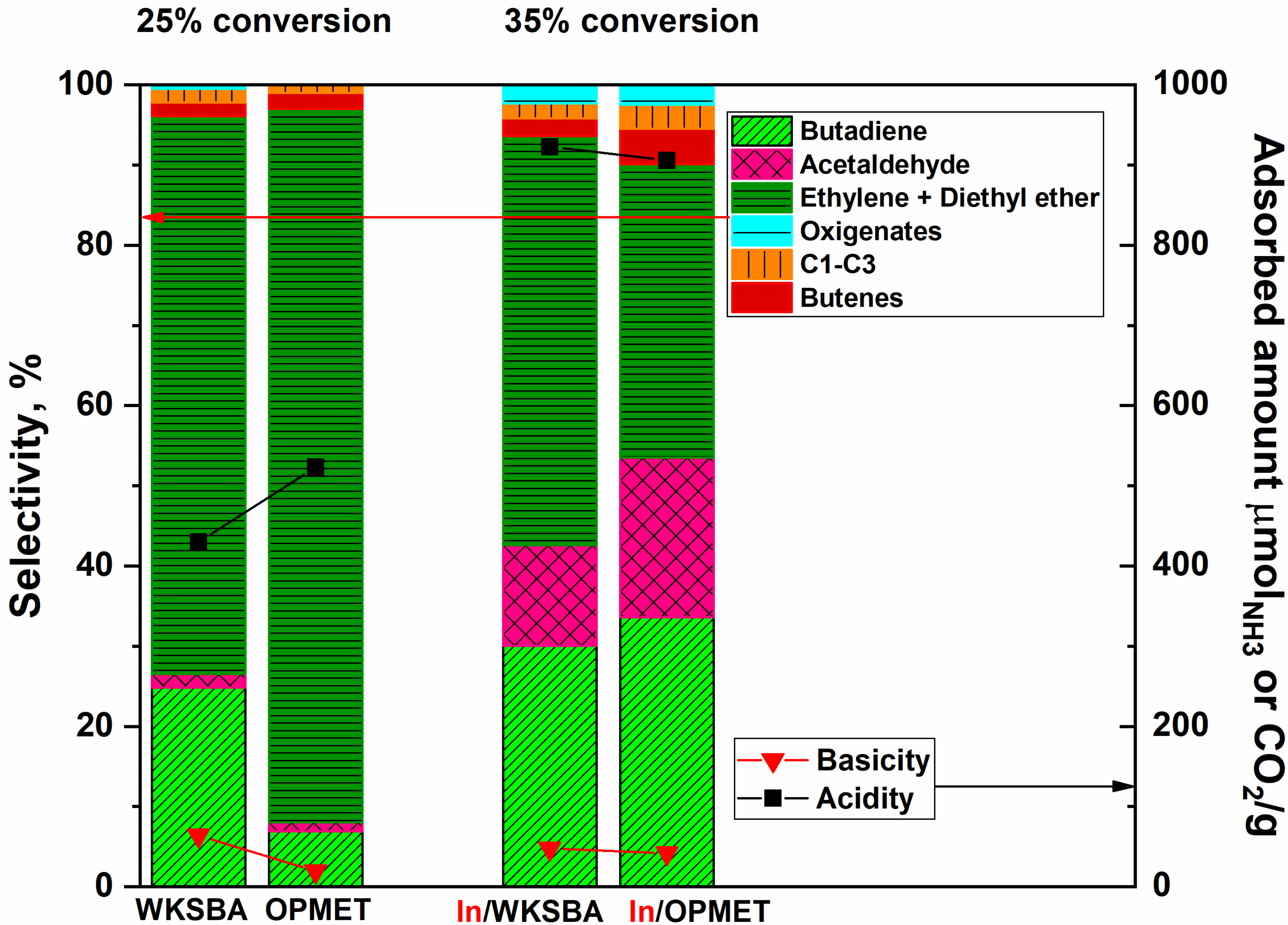
$Mg(OMet)_2$
SSA: 486 m^2/g

Pluronic 123: surfactant Pluronic 123Poly(ethylene glycol)-block-poly(propylene glycol)
TEOS: Tetraethyl orthosilicate

Effect of In_2O_3 on the distribution of the reaction products at 350°C over high SSA-SiO_2-MgO



High-SSA MgO-SiO_2 catalysts

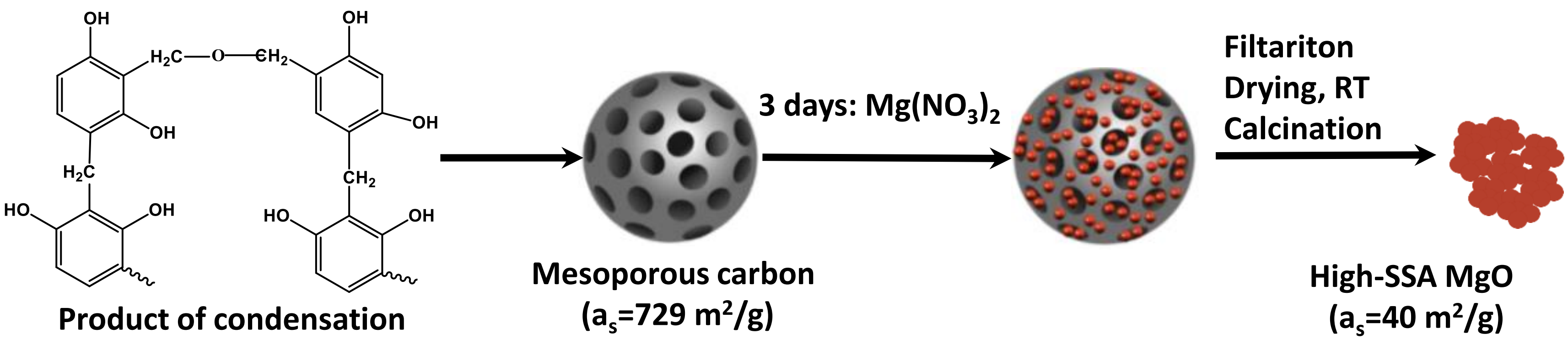
Catalyst groups

I. Internal hydrolyzed
- Low SSA MgO-SiO_2
- High SSA MgO-SiO_2

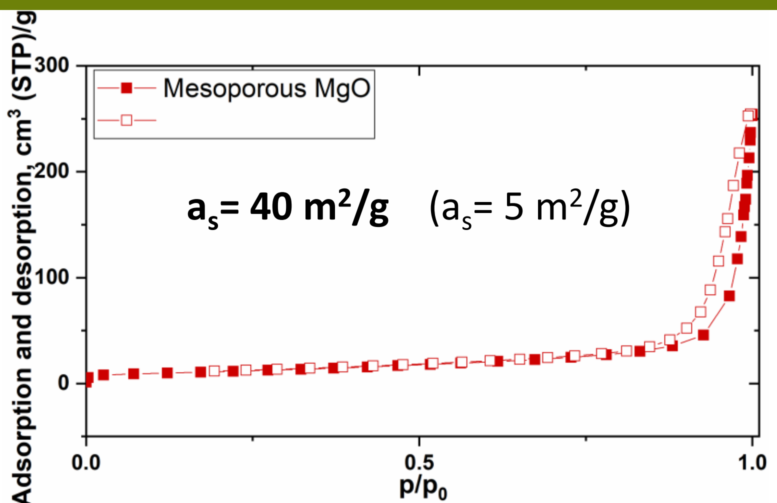
II. Wet-kneaded
- Low SSA MgO-SiO_2
- High SSA MgO-SiO_2

II. Silica-coated
- Low SSA MgO-SiO_2
- High SSA MgO-SiO_2

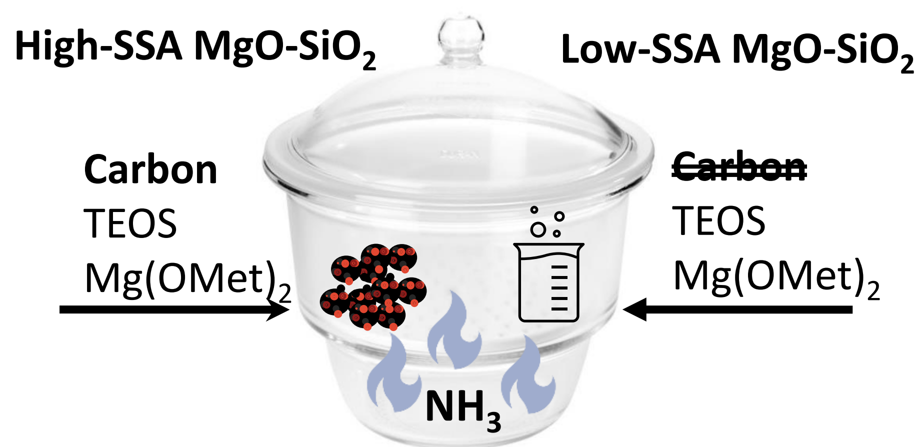
Mesoporous MgO synthesis

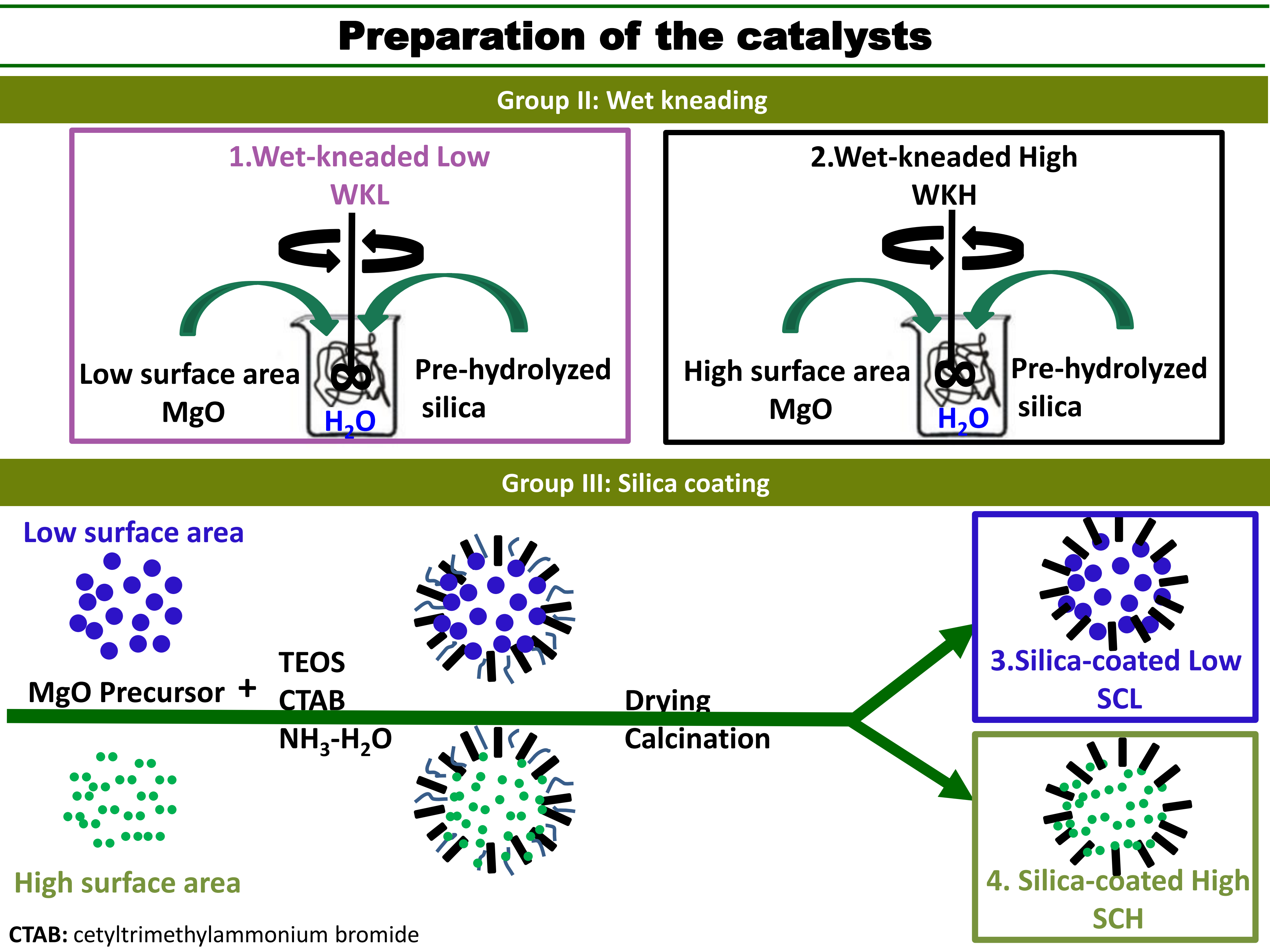


N_2 physisorption isotherm of the high -SSA MgO



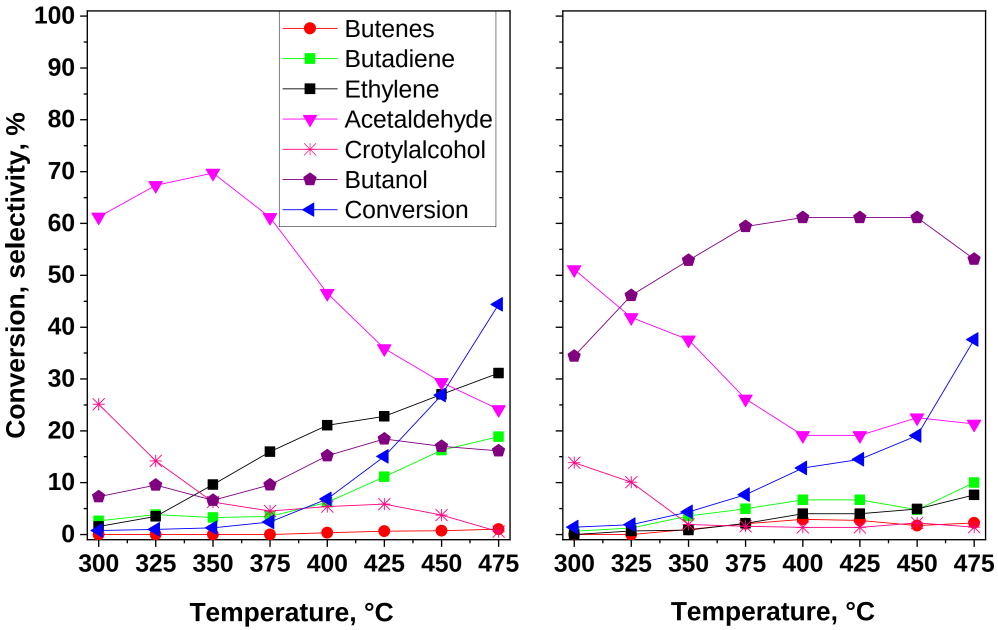
Internal hydrolyzed (Group I)



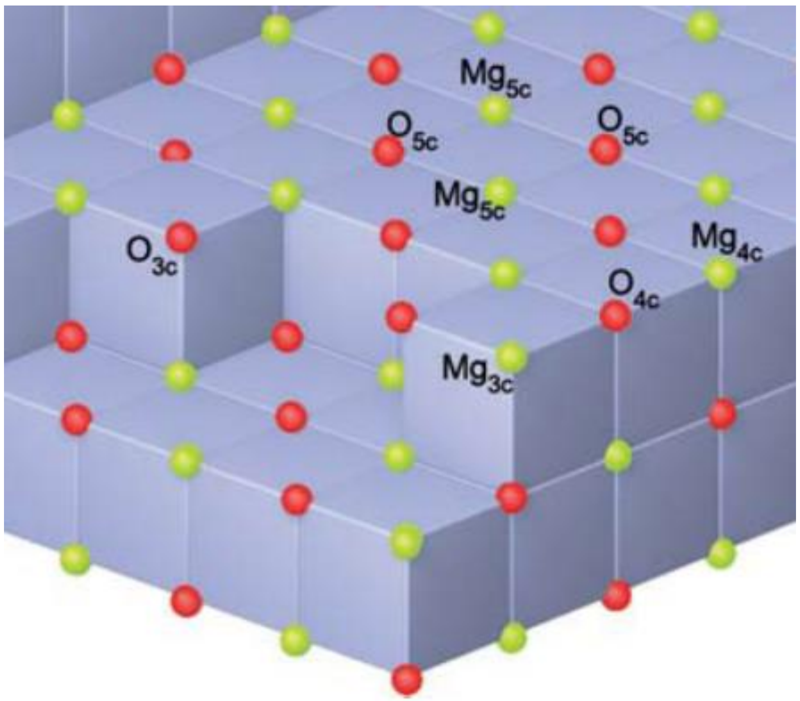

Preparation of the catalysts
Group II: Wet kneading
1.Wet-kneaded Low
WKL
Low surface area
MgO
H2O
Pre-hydrolyzed
silica
2.Wet-kneaded High
WKH
High surface area
MgO
H2O
Pre-hydrolyzed
silica
Group III: Silica coating
Low surface area
MgO Precursor +
TEOS
CTAB
NH3-H2O
High surface area
Drying
Calcination
3.Silica-coated Low
SCL
4. Silica-coated High
SCH
CTAB: cetyltrimethylammonium bromide

Effect of MgO morphology on catalytic activity

Low SSA MgO **High SSA MgO**



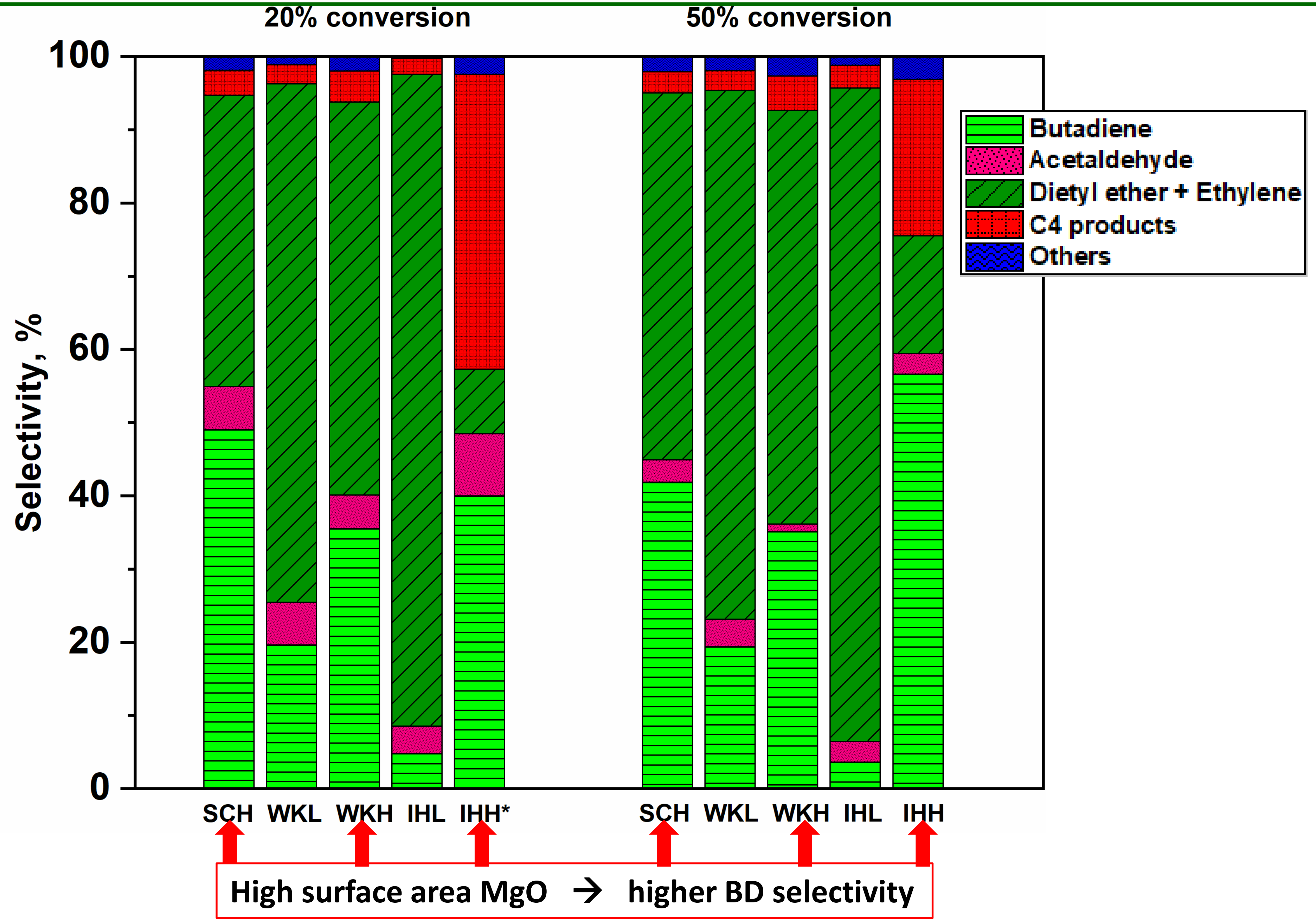
Scheme of a stepped MgO (1 0 0) surface



- Over LSSA MgO dehydrogenation and dehydration dominates
- Over HSSA MgO coupling is the main reaction

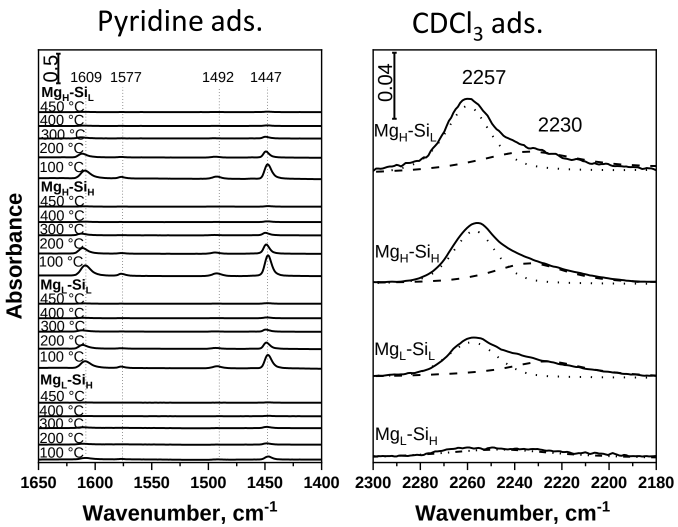
Terrace sites: O_{5c}, Mg_{5c}
Edge sites: O_{4c}, Mg_{4c}
Corner sites: O_{3c}, Mg_{3c}

Effect of the high SSA-MgO on the product distribution of the reaction products at 350 and 400 °C

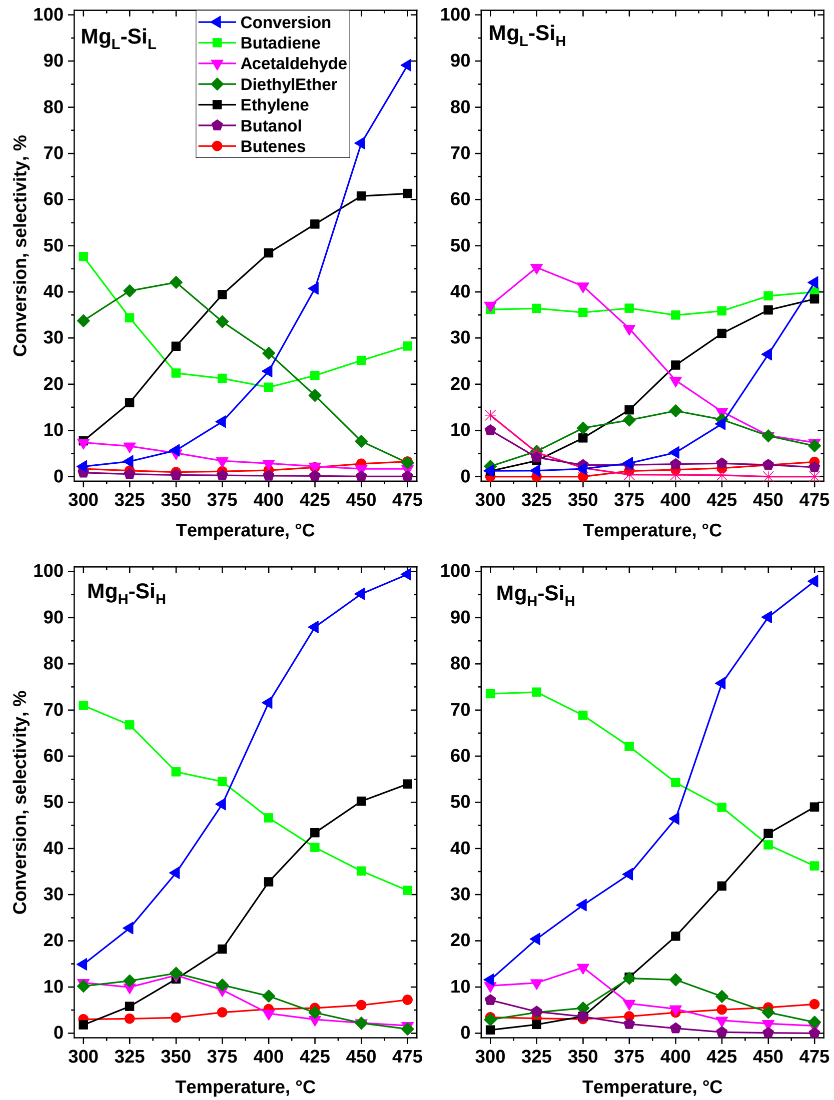


Effect of MgO and SiO_2 texture on product selectivity

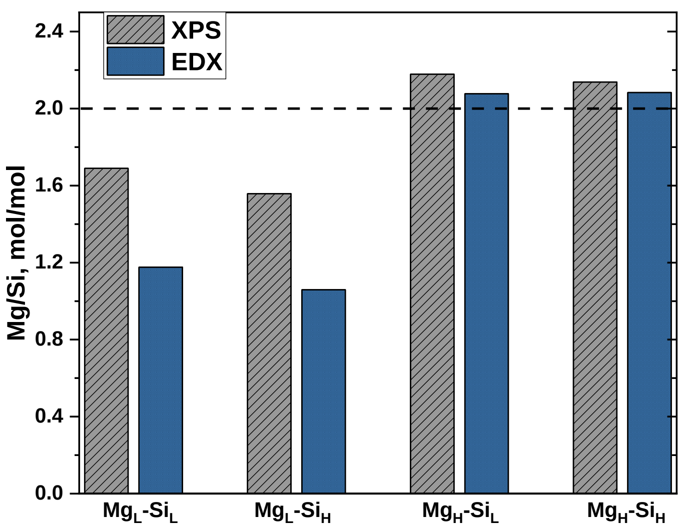
FT-IR



Catalytic test reactions

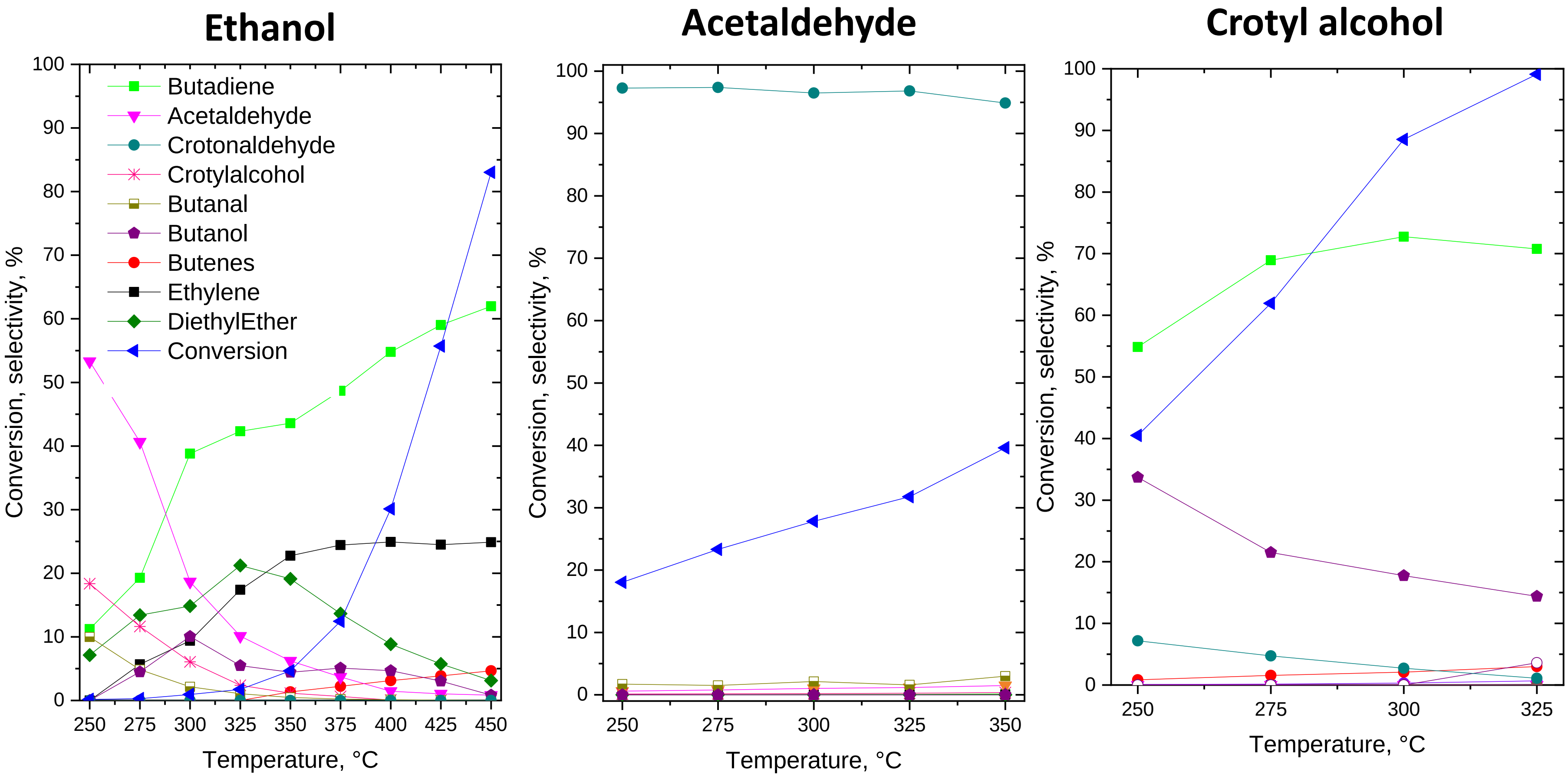


XPS and EDX



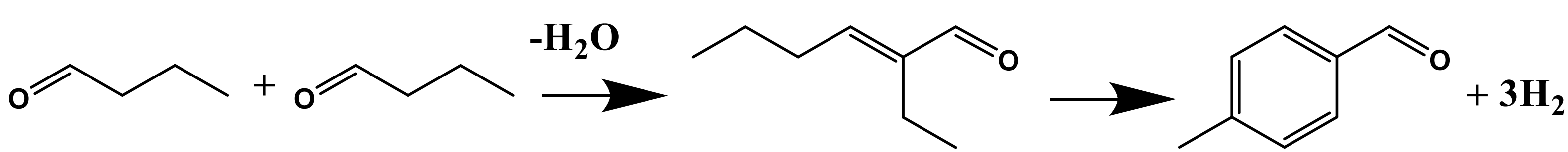
Mg_L, Mg_H – low and high SSA MgO, Si_L, Si_H low and high SSA SiO_2

Reaction of ethanol and intermediates over wet kneaded $MgO\text{-}SiO_2$ 2:1



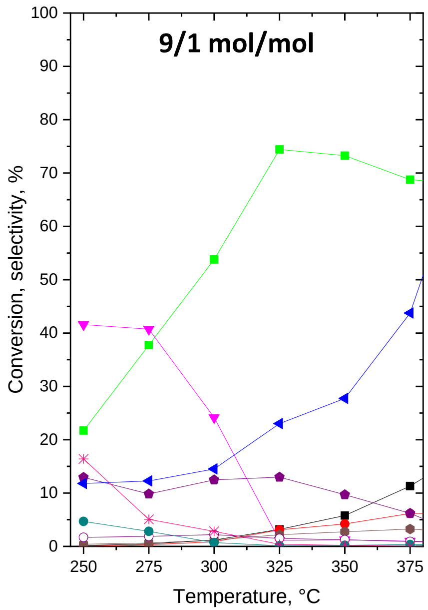
Crotonaldehyde: due to low hydrogen content very fast deactivation, however butanal, butanol and crotly alcohol also can be detected (hydrogen is evolved in the process of aromatization)

Butanal: aldol condensation and aromatization

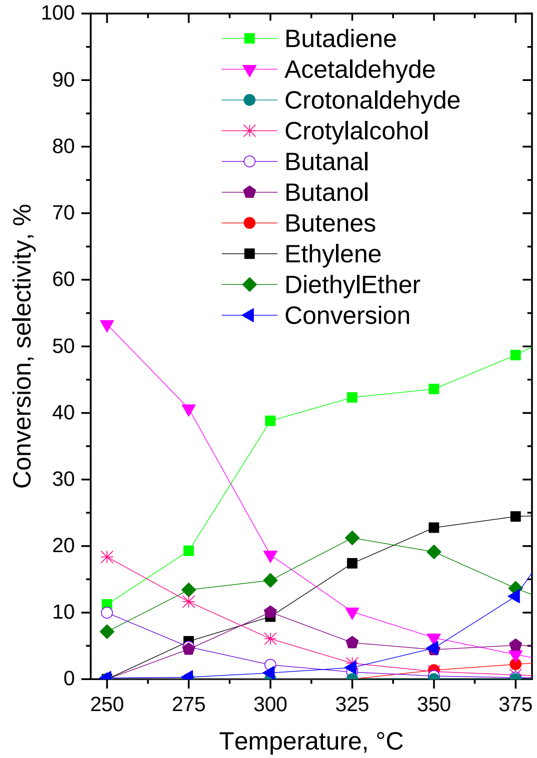


Reaction of ethanol/intermediate mixtures over MgO-SiO_2 2:1

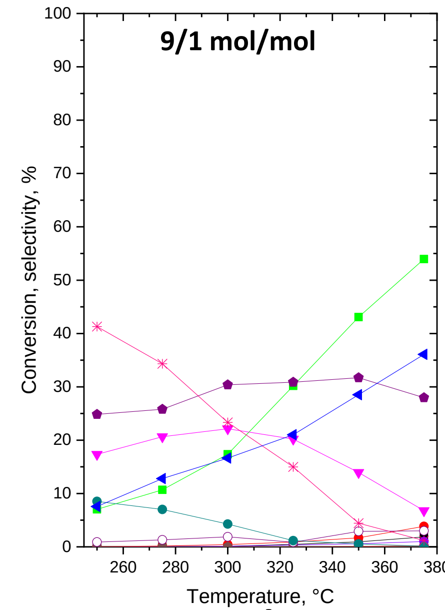
Ethanol/Acetaldehyde



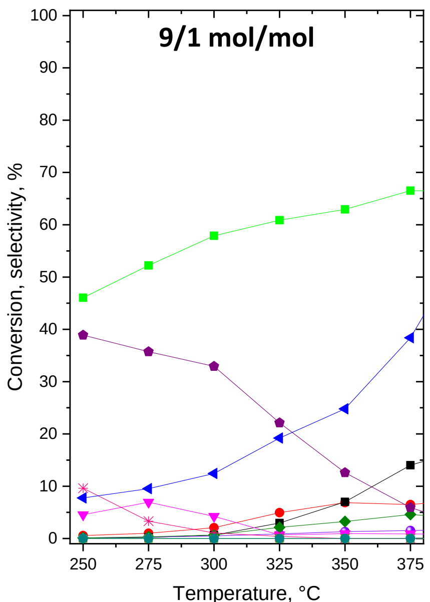
Ethanol



Ethanol/Crotonaldehyde

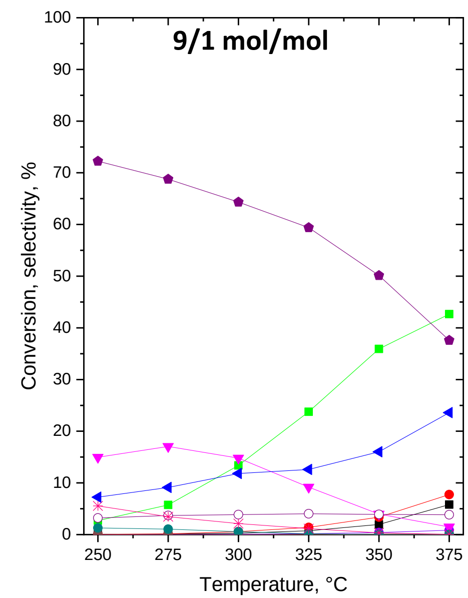


Ethanol/Crotylalcohol

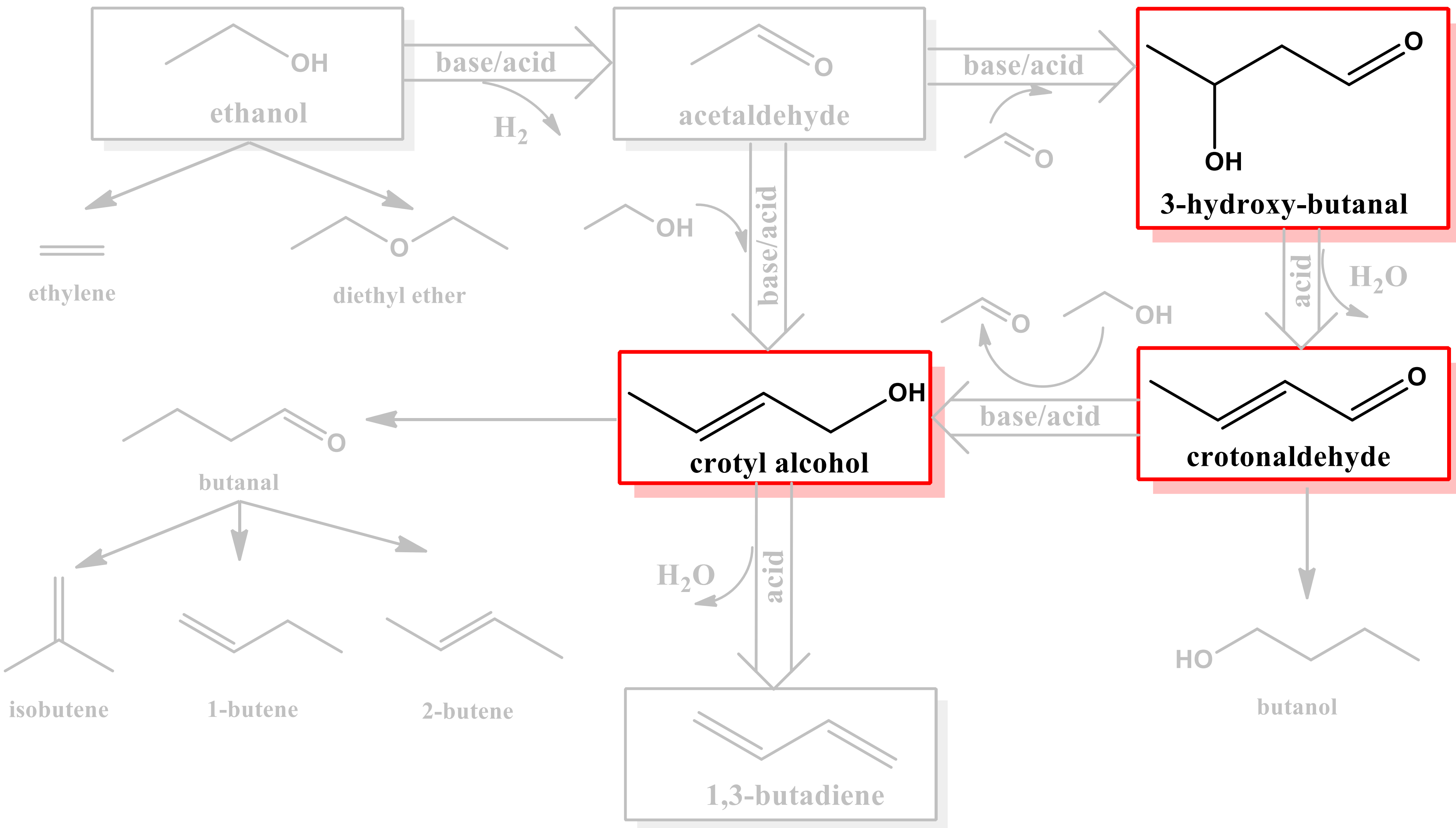


- Ethlyene and diethyl-ether selectivites are suppressed
- Acetaldehyde enhances butadiene selectivities.
- Higher butanol and crotylalcohol selectivities can be observed when crotonaldehyde is co-feeded.
- From crotylalcohol butanol is formed, especially at lower temperatures.
- From butanal butanol is the main product

Ethanol/Butanal

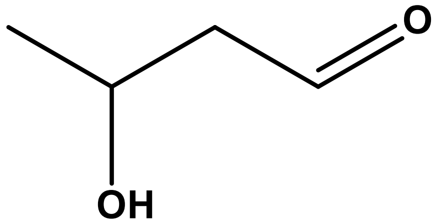


Reaction network



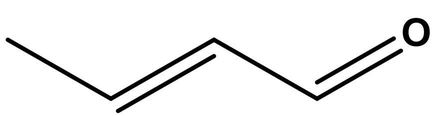
Conversion of the intermediates over MgO-SiO_2 catalysts

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



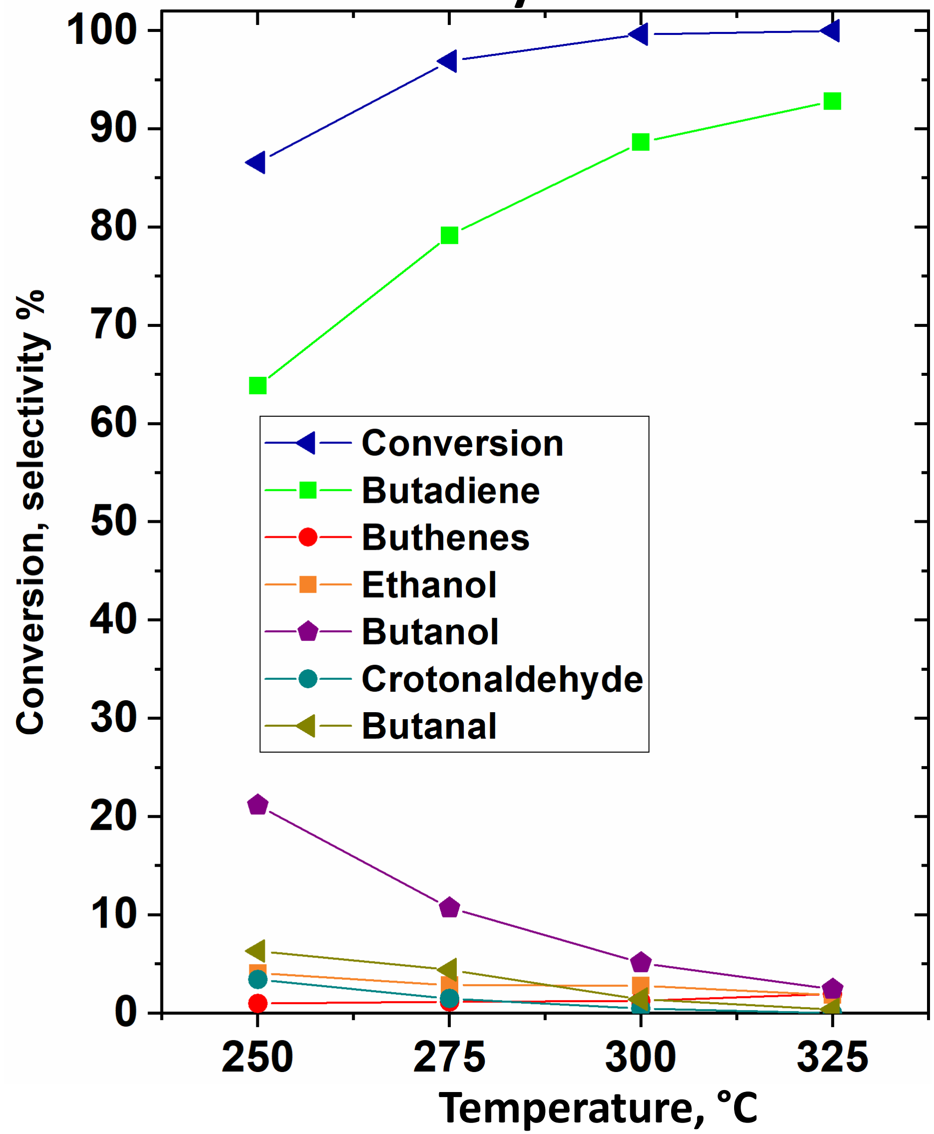
3-hydroxy-butanal

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)

Questions about the mechanism

- The probability of a bimolecular reaction is low at low conversion levels and low acetaldehyde concentrations.

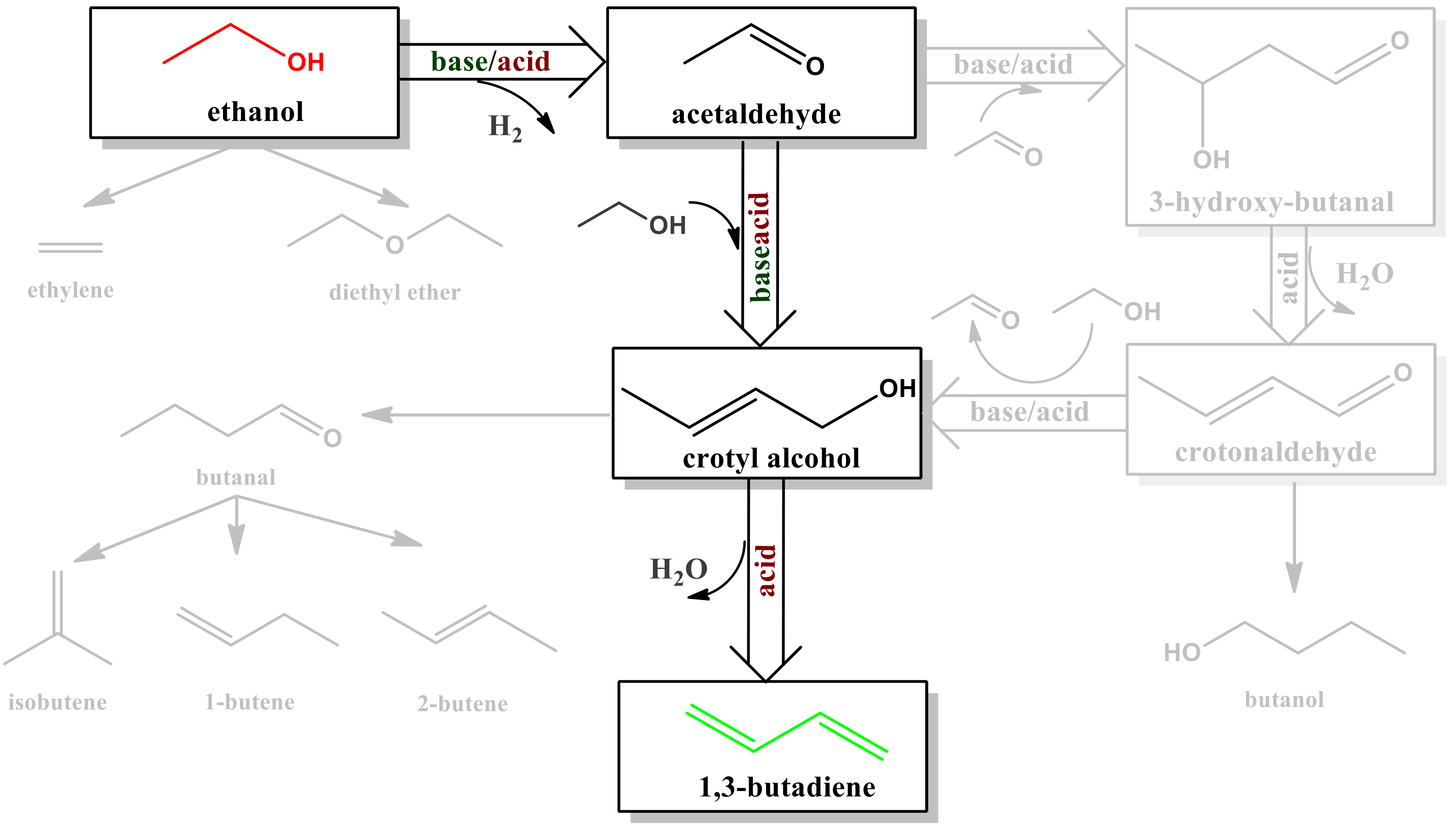
- The facile conversion of ethanol/crotonaldehyde mixture to butadiene does not evidence that the reaction of pure ethanol proceeds via crotonaldehyde intermediate.

- If crotonaldehyde is an intermediate, it should appear in the product mixture, especially at low space times.

- The 3-hydroxybutanal, which is very unstable at room temperature must be converted to crotonaldehyde with high selectivity.

- Under certain conditions, in addition to butanol, hexanol and 2-ethyl-1-butanol (and higher homologues) are also formed in the reaction, and the appearance of these products is difficult to interpret through the aldol condensation mechanism.

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 sample impregnated by metal oxide retaines the original properties of the support (In_2O_3/OPMET)
- 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 you kind attention!

Ministry of Innovation and Technology 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)

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NATIONAL RESEARCH, DEVELOPMENT AND INNOVATION OFFICE HUNGARY

PROGRAM FINANCED FROM THE NRDI FUND

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences

Budapest, Hungary