Study of the ethanol-to-butadiene reaction using ethanol from renewable sources

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Project meeting
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Interreg, SKHU/1902/4.1/001/Bioeconomy

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Historical review I.

1839: discovery of vulcanization

2-methylbuta-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

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

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

Historical review II.

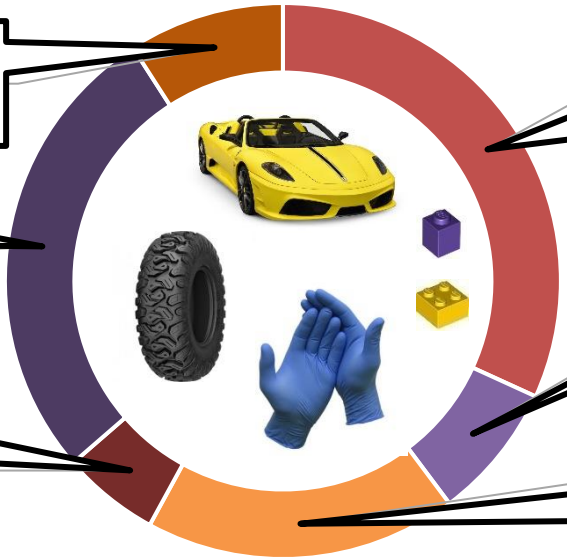
1950: butadiene from the ethylene process, 99.9 %

2011: Academic research for the ethanol-to-butadiene reaction, 0.1 % bioethanol

2015: The butadiene demand is 11 million tons in the World.

BIOBUTTERFLY

1960 1970 1980 1990 2000 2010 2020



Nitrile and Polychloroprene 9%

Styrene Butadiene Rubber 32%

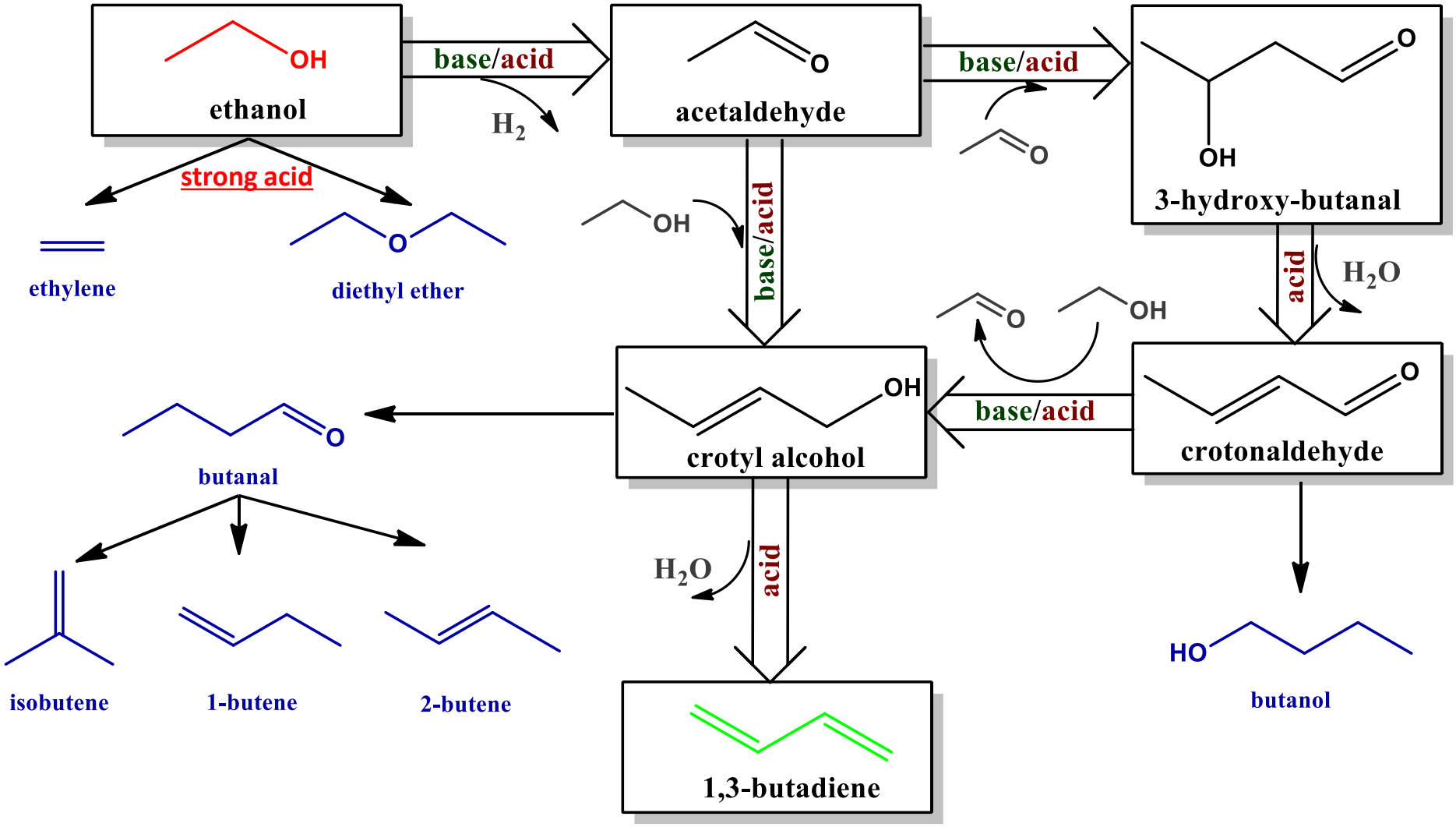
Polybutadiene 27%

Others 8%

Adiponitrile 6%

Arcylonitrile Butadiene Styrene 18%

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

Tested catalysts in the ethanol-butadiene reaction

I. Stage: talc like catalysts

***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

***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

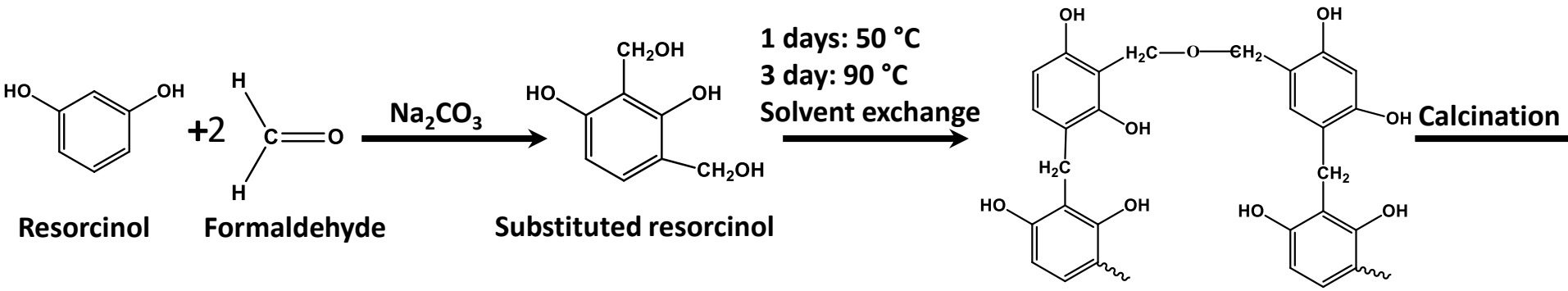
- Low-SSA MgO-SiO_2
- High-SSA MgO-SiO_2

3. Internal hydrolyzed family

- Low-SSA MgO-SiO_2
- High-SSA MgO-SiO_2

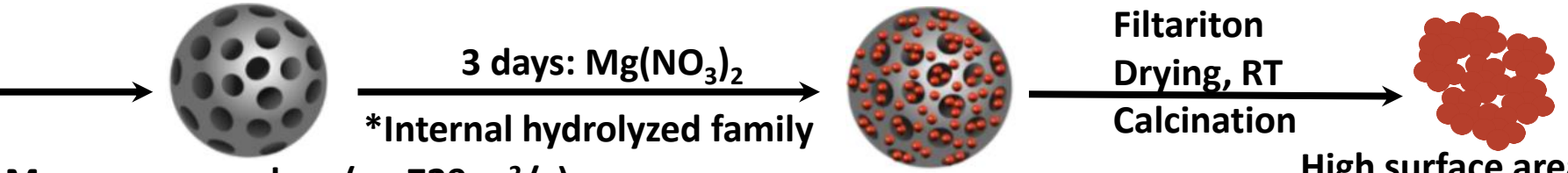
III. Stage: high SSA $MgO\text{-}SiO_2$ catalysts group

1st step: Resorcinol–formaldehyde polymerisation



Resorcinol | Formaldehyde | Substituted resorcinol | Product of condensation

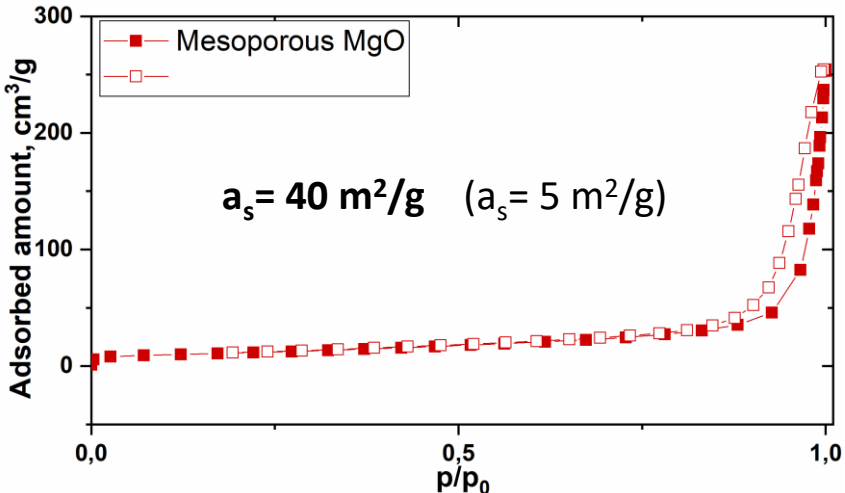
2nd step: Hard templating method for mesoporous MgO synthesis



Mesoporous carbon (a_s=729 m^2/g)

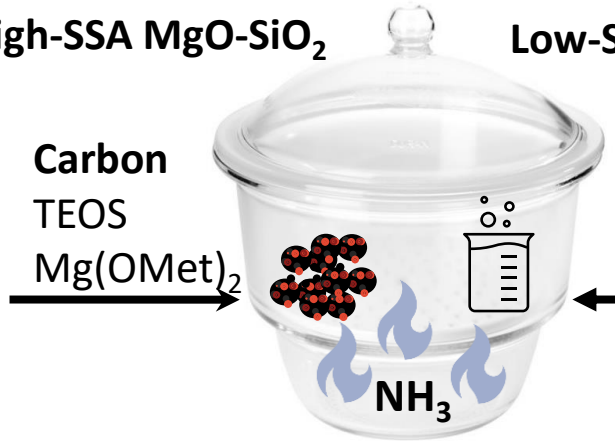
High surface area MgO

N_2 physisorption isotherm

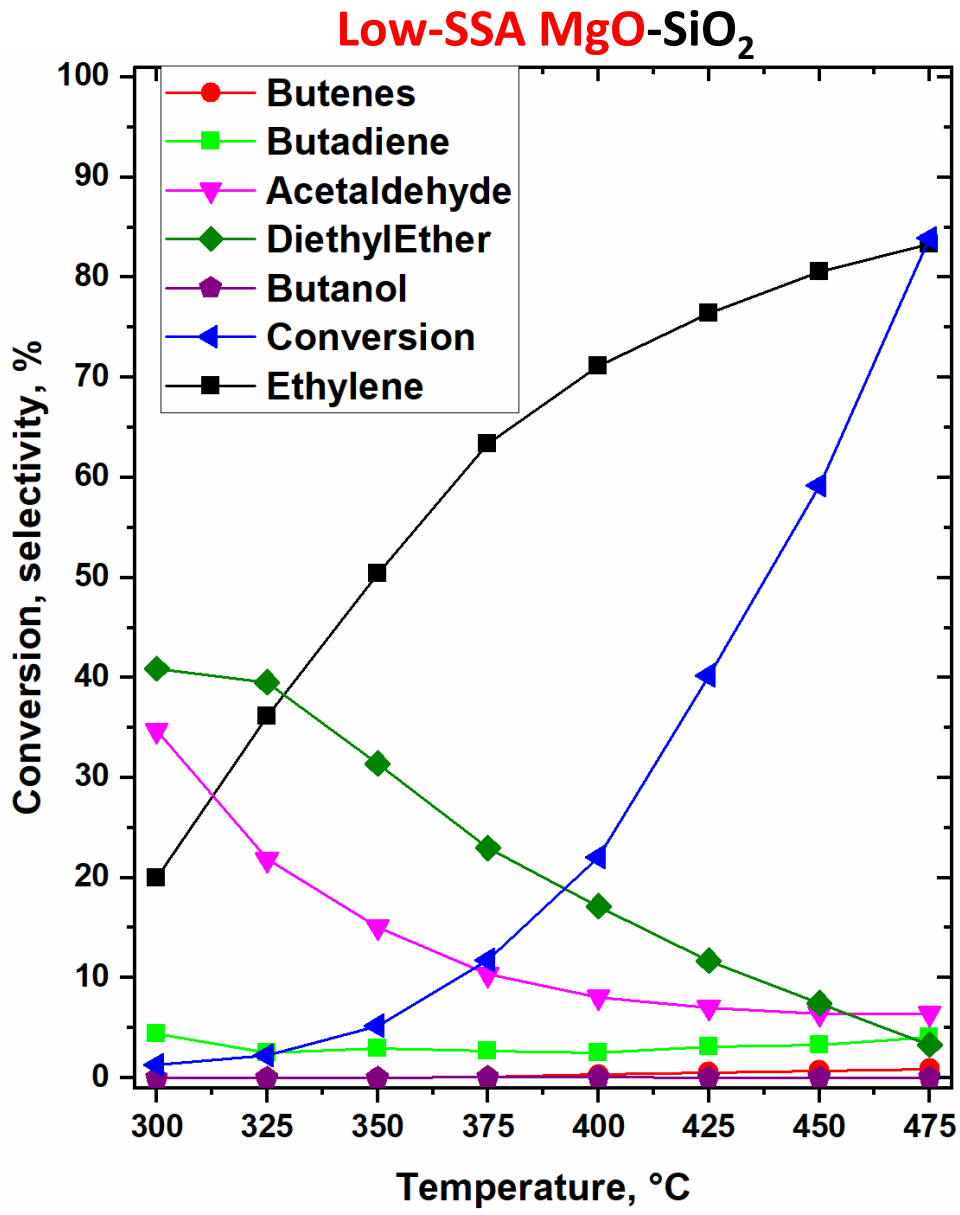


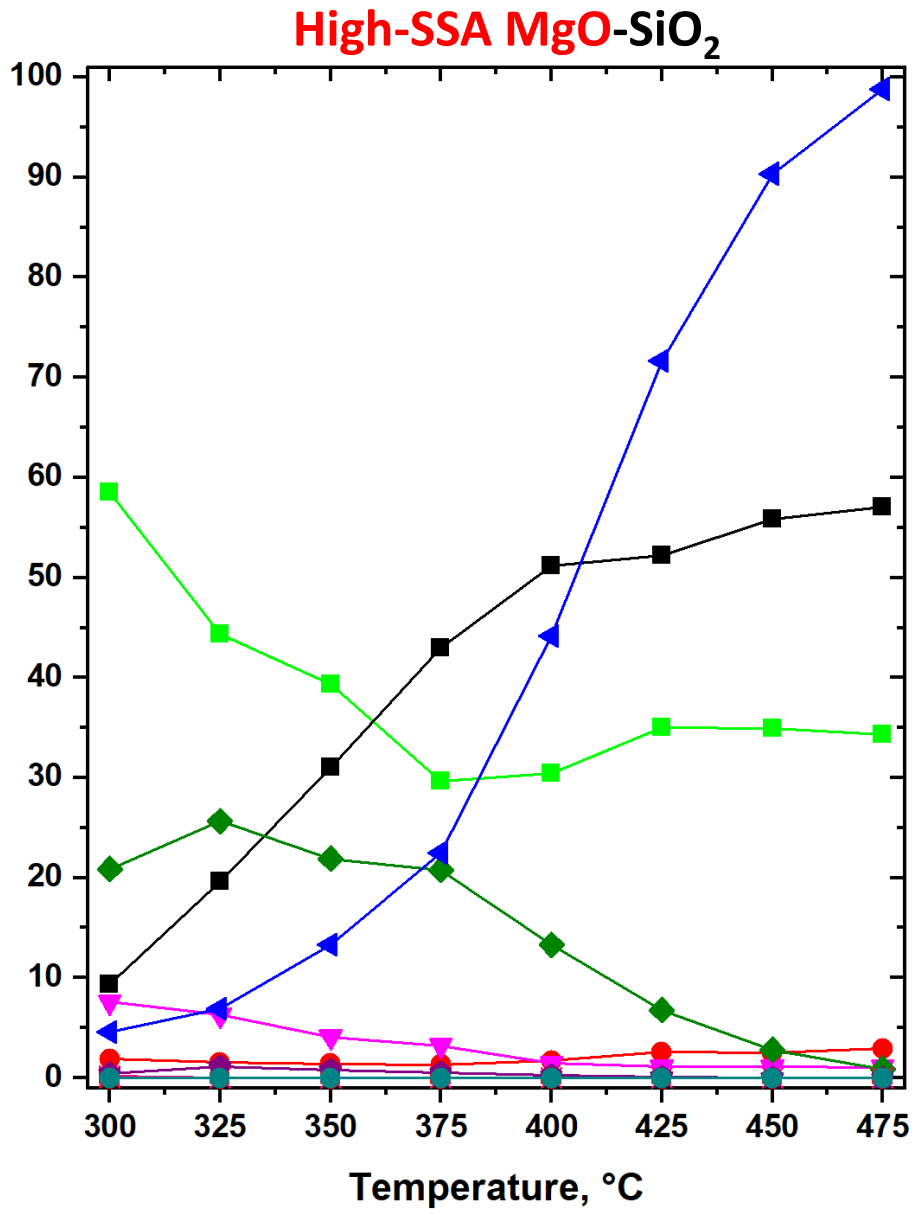
a_s= 40 m^2/g (a_s= 5 m^2/g)

Internal hydrolyzed family



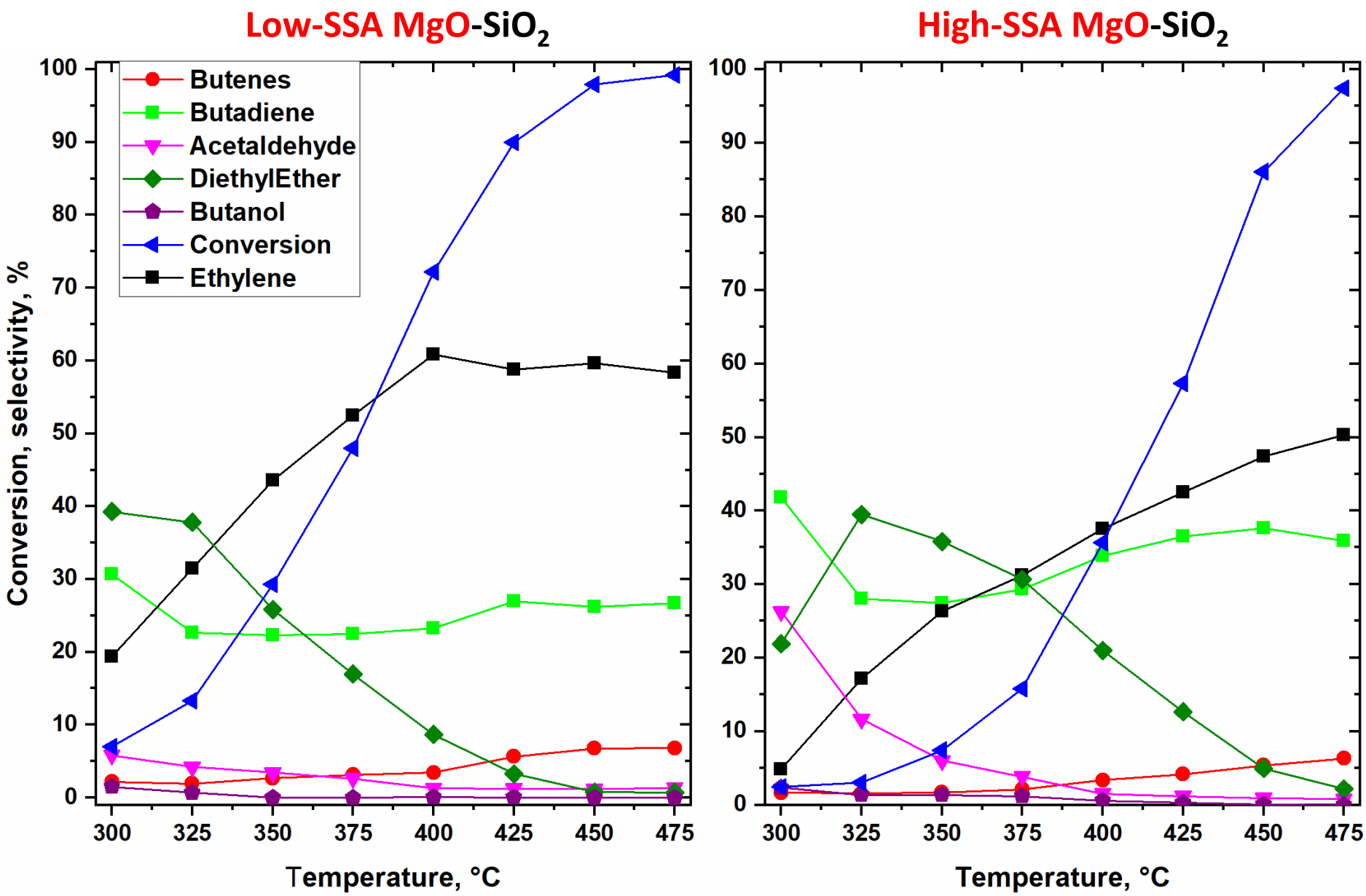
Ethanol conversion over silica-coated family





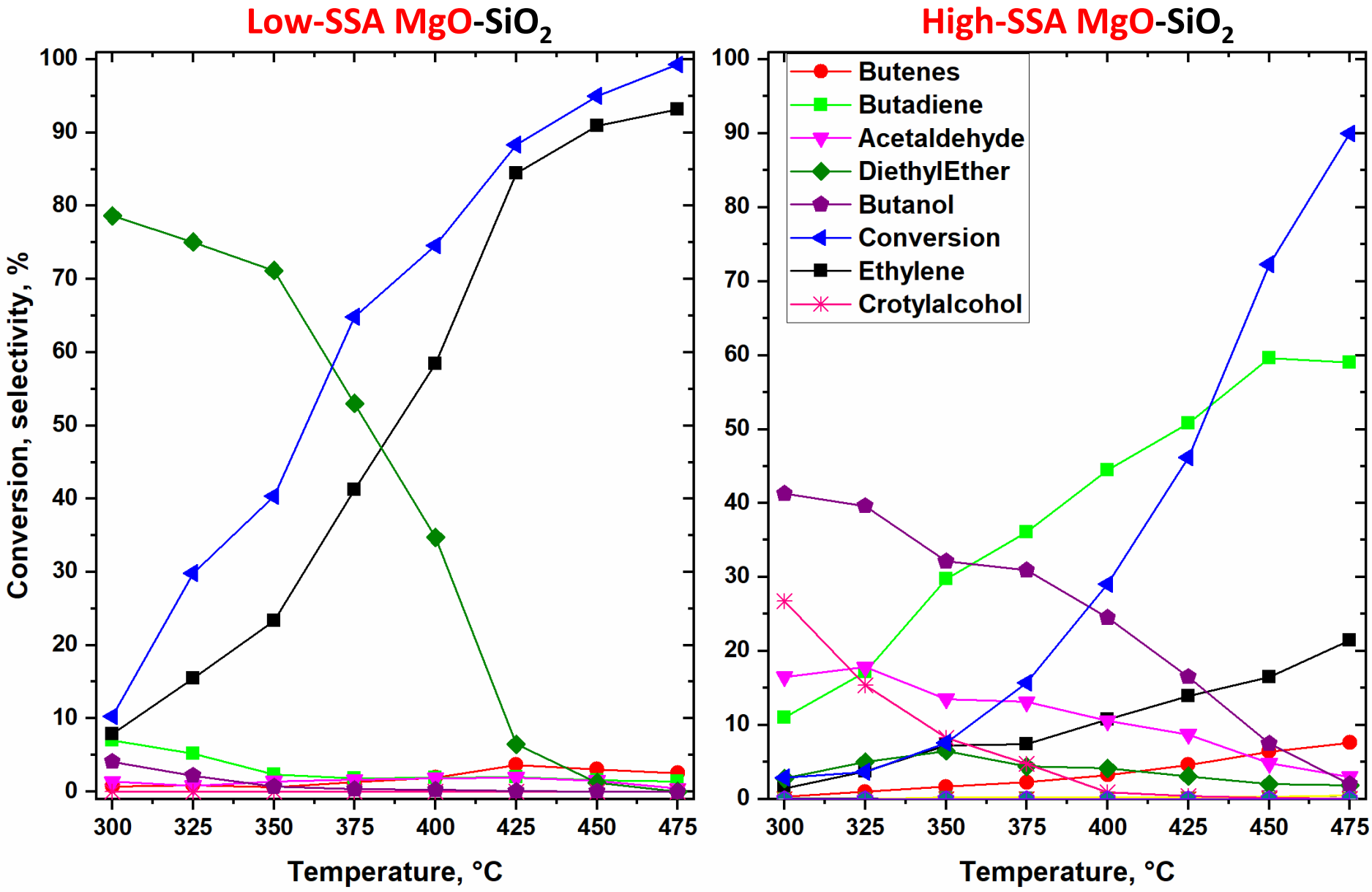
1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

Ethanol conversion over wet-kneaded family



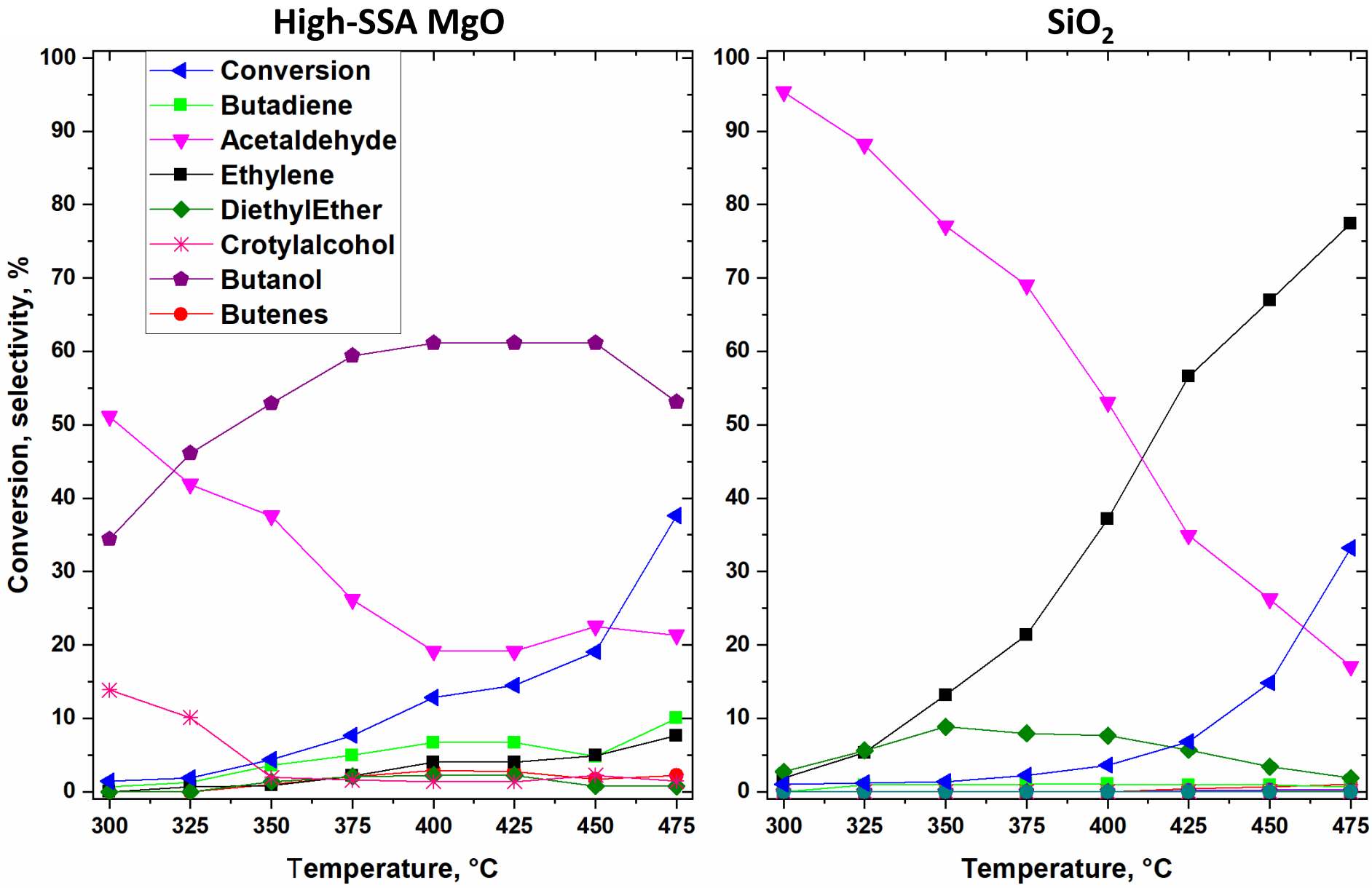
1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

Ethanol conversion over internal hydrolyzed family



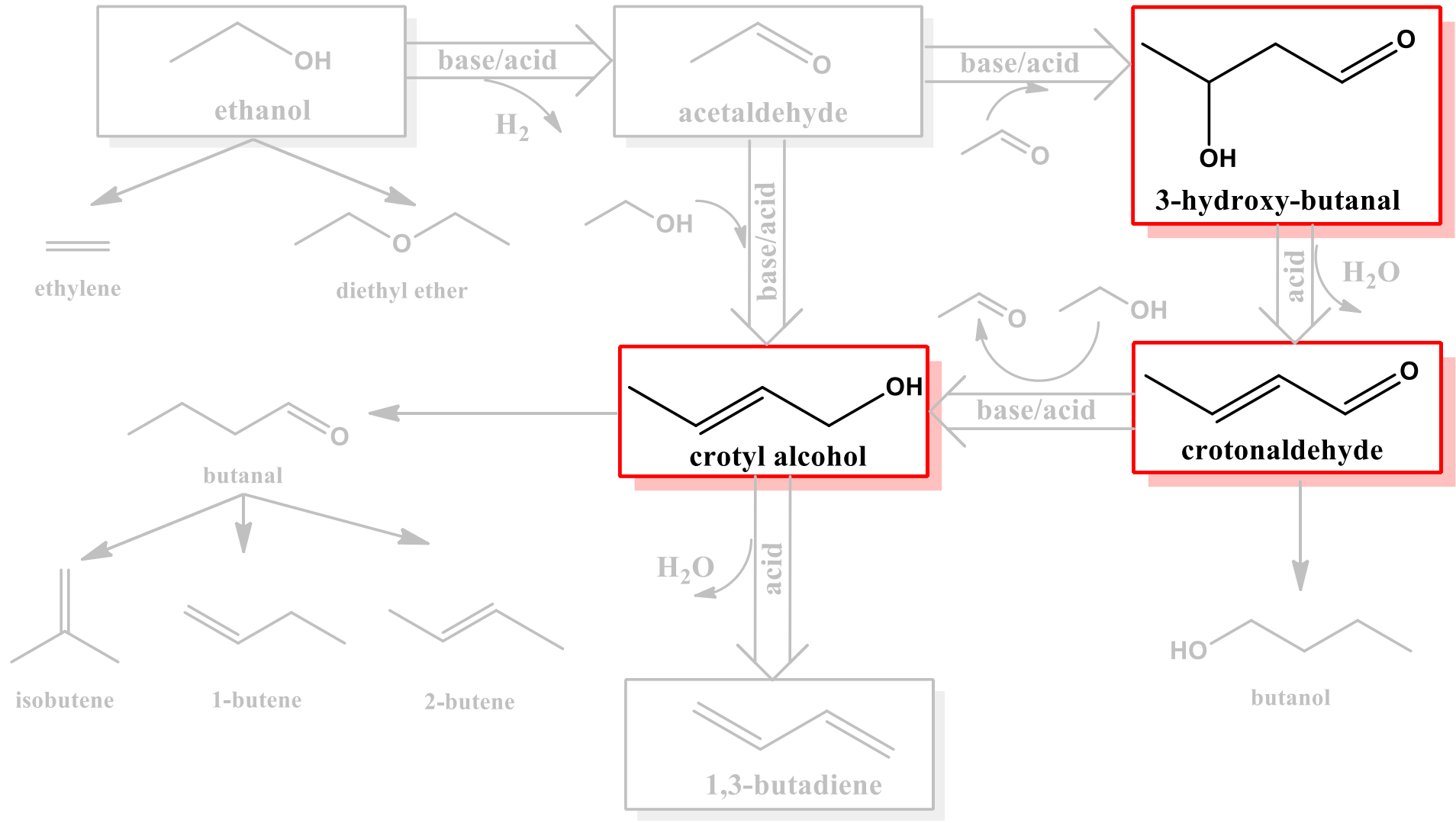
1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

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



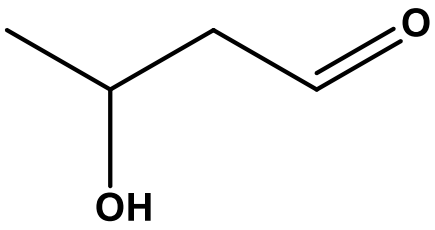
1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)

Reaction network



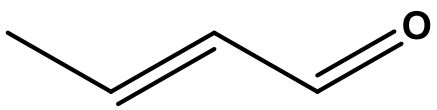
Conversion of the 3 intermediates over $MgO\text{-}SiO_2$ catalysts

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

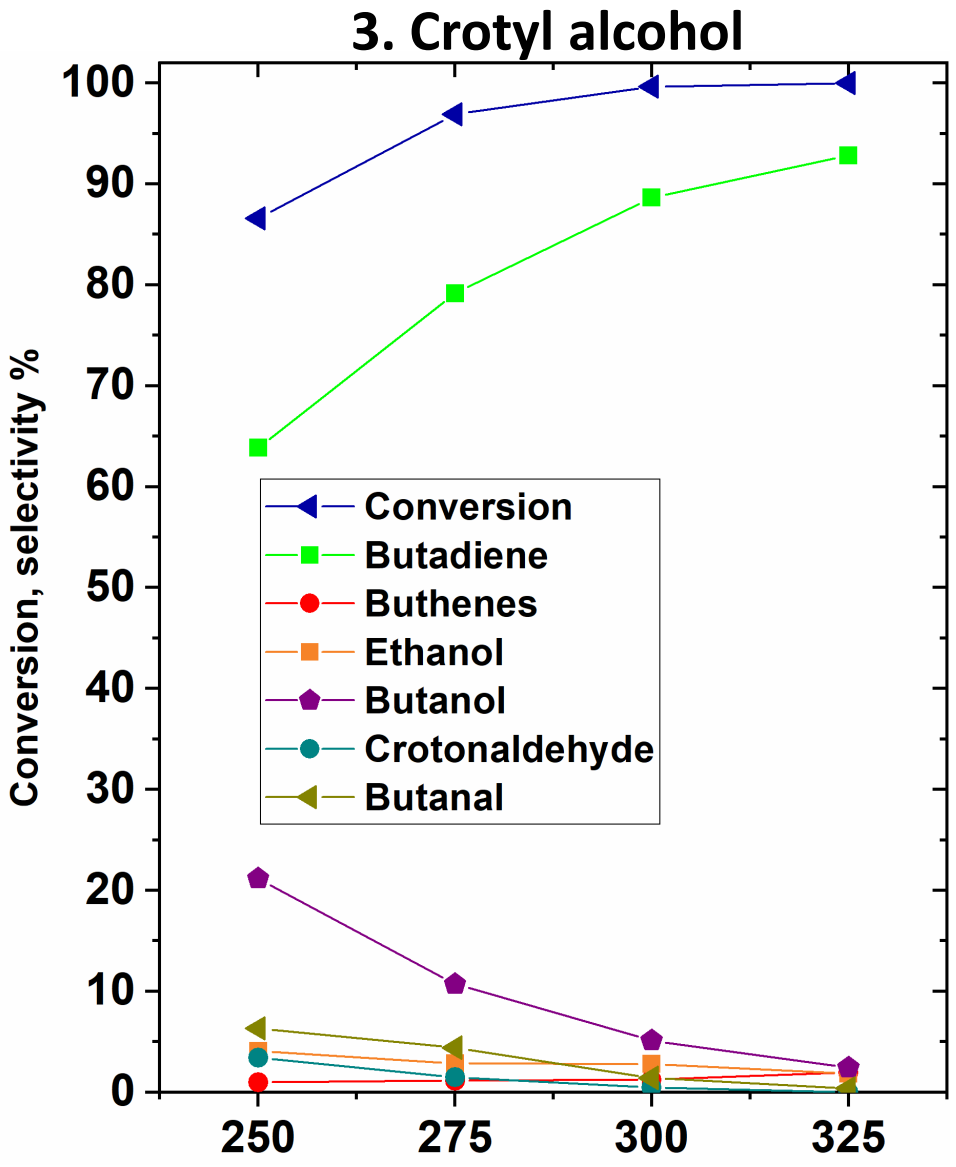


3-hydroxy-butanal

2. **Crotonaldehyde**
   - Polymerized products
   - Molecular H_2

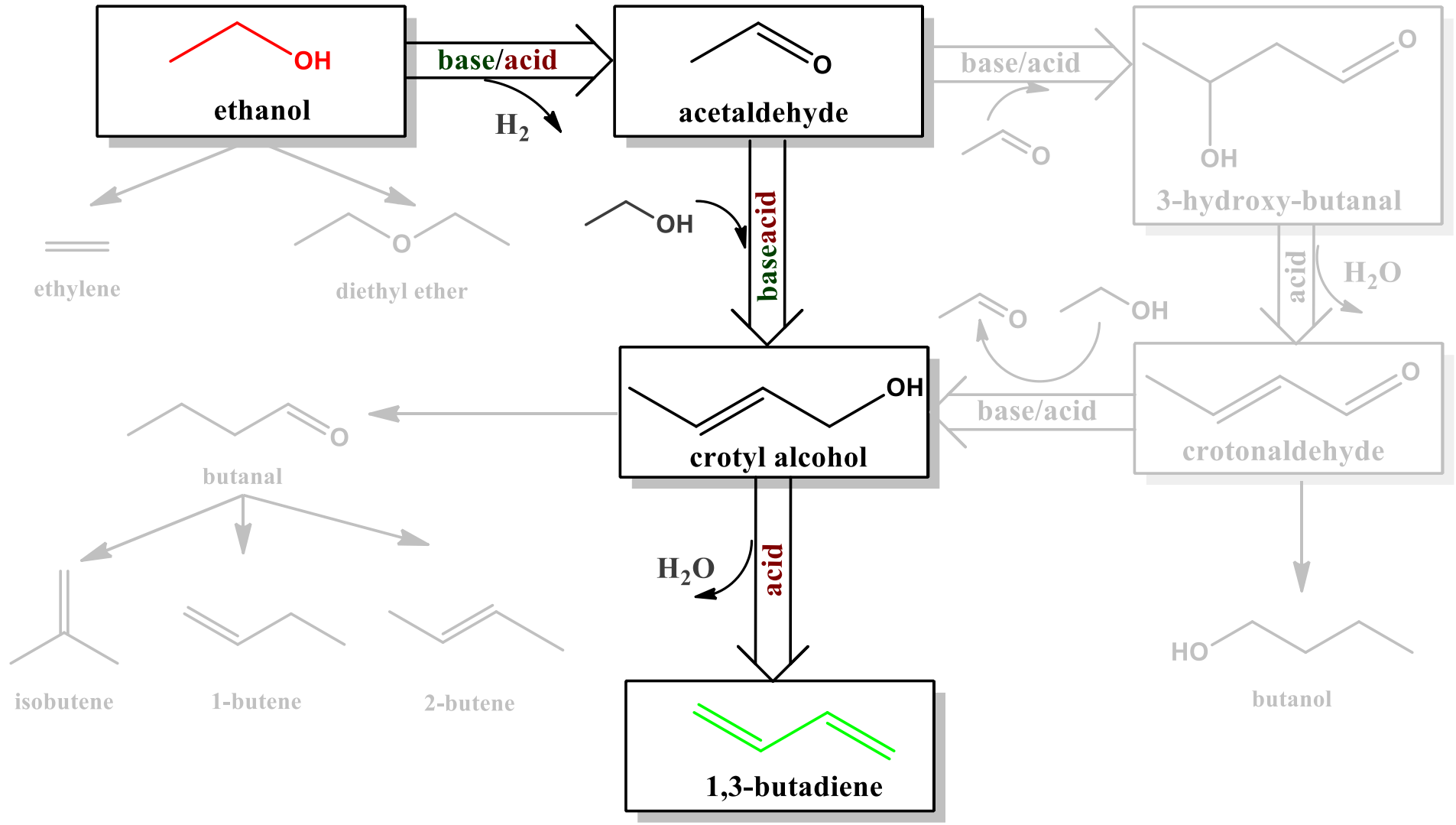


crotonaldehyde



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

- The optimal catalyst in the ethanol-butadiene reaction:

  - ✓ High surface area, porous structure,
  - ✓ active in dehydrogenation,
  - ✓ moderate dehydration activity.

- At comparable ethanol conversions the BD yields over the high SSA MgO-SiO_2 catalysts, made using carbon template, were of significantly higher than that over the low SSA MgO-SiO_2 catalysts.

- The favorable activity of the high SSA MgO-SiO_2 catalysts was explained by the more intimate interaction of the MgO and SiO_2 catalyst components: basic MgO sites facilitate ethanol coupling, whereas acidic mixed oxide phase provides adequate dehydration activity.

- Based on our experiments, we described the probable ethanol-butadiene pathway.

Thank you for your attention!

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www.skhu.eu

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www.ttk.hu/palyazatok/bioeconomy