Activity of $MgO\text{-}SiO_2$ catalysts in ethanol-to-butadiene reaction

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Historical review I.

1839: discovery of vulcanization

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, from acetaldehyde+ethanol mixture

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

Historical review II.

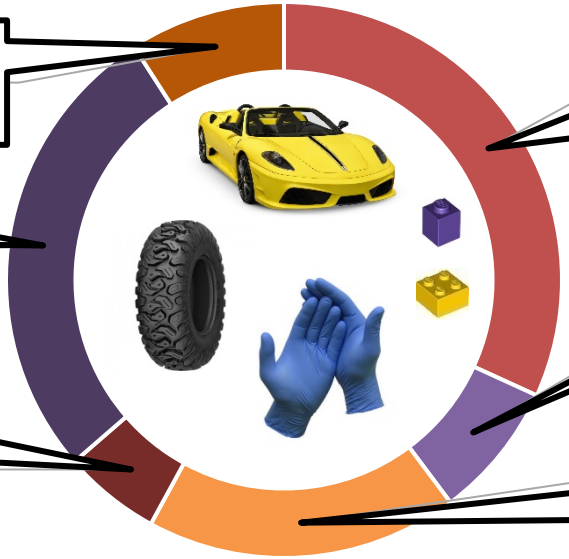
1950: butadiene from the ethylene procces, 99.9 %

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

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

BIOBUTTERFLY

1960 1970 1980 1990 2000 2010 2020



Nitrile and Polychloroprene 9%

Styrene Butadiene Rubber 32%

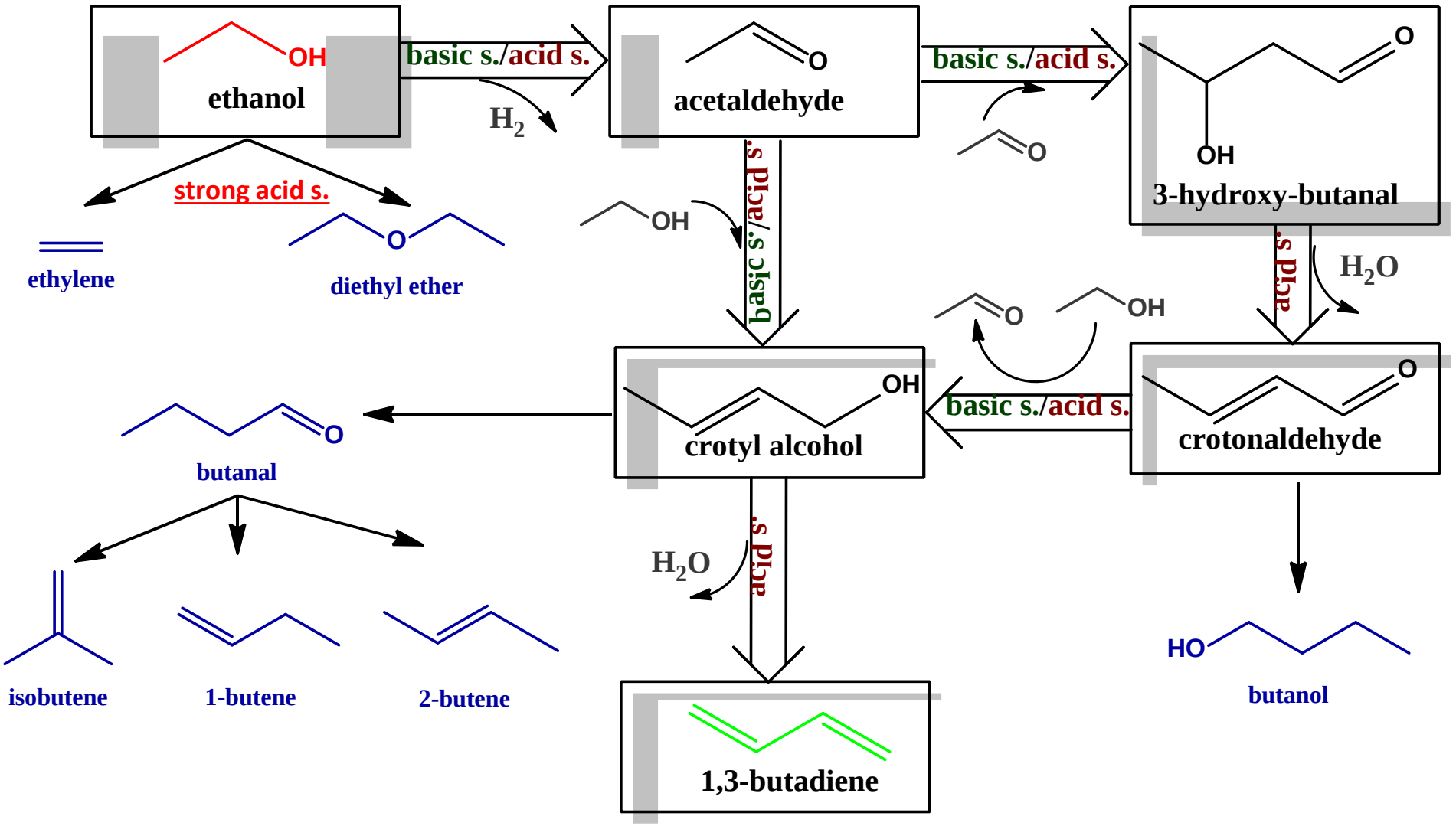
Polybutadiene 27%

Others 8%

Adiponitrile 6%

Arcylonitrile Butadiene Styrene 18%

Reaction mechanism of ethanol to butadiene transformation



Experimental methods

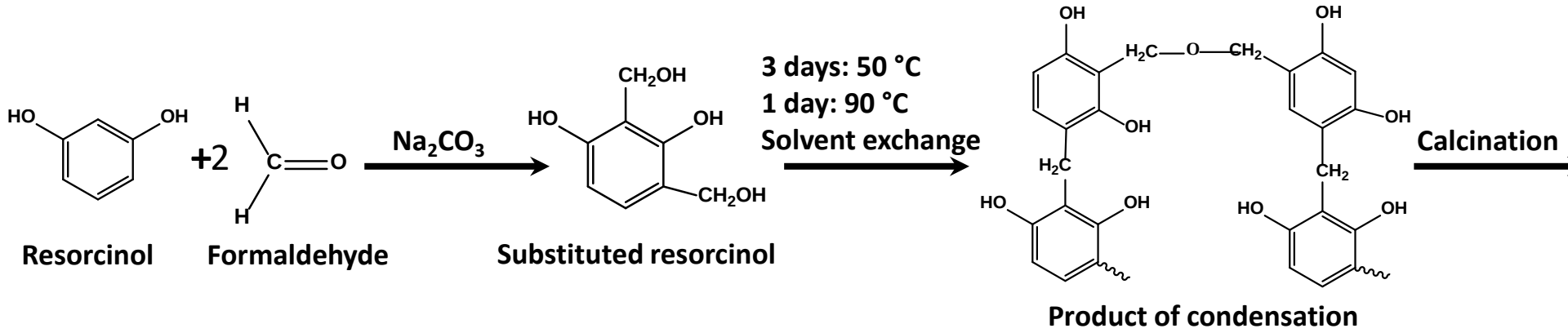
Characterization of catalysts

- Surface area measurements (BET method),
- X-ray diffraction (XRD),
- Basicity: $CDCl_3$ IR and CO_2 TPD,
- Acidity: pyridine IR and NH_3 TPD

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 with the sum of the carbon atoms in all product molecules

1st step: Resorcinol–formaldehyde polymerisation



Resorcinol Formaldehyde Substituted resorcinol

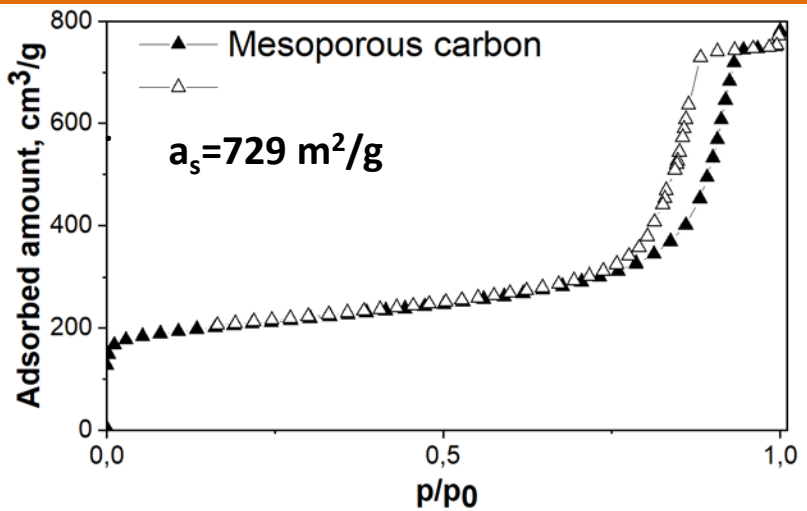
Product of condensation

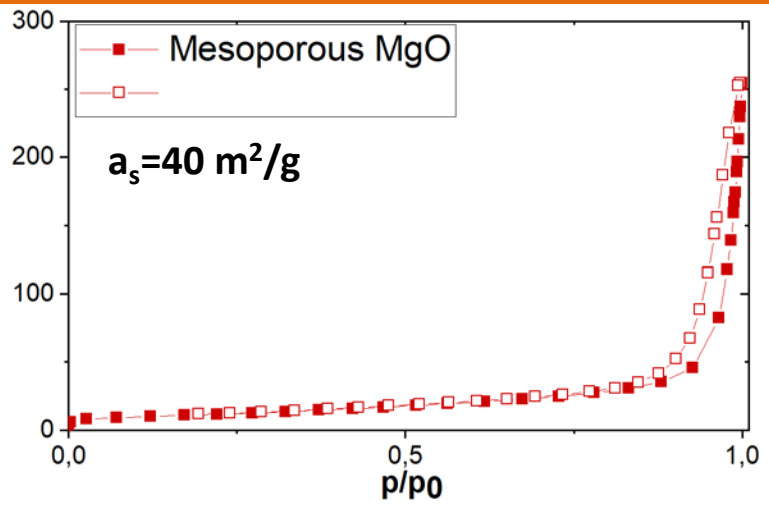
2nd step: Hard templating methods for synthesizing mesoporouse MgO

Mesoporous carbon

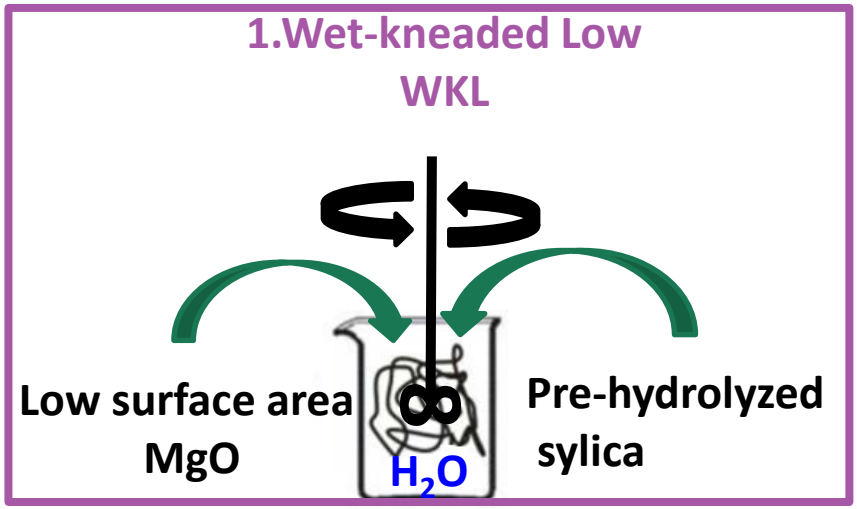
High surface area MgO

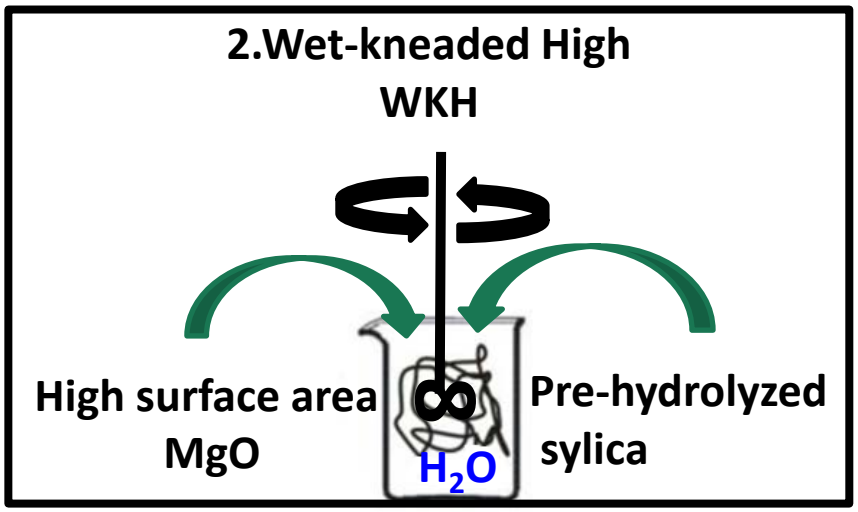
N_2 adsorption isotherms



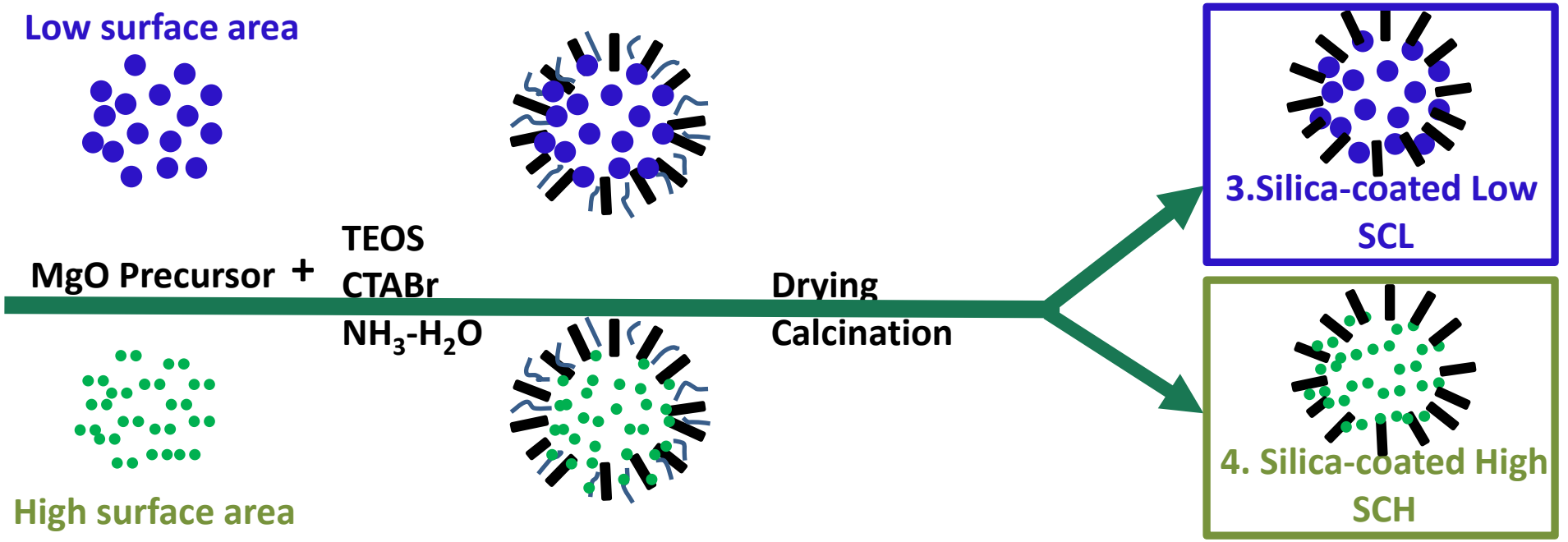


I. type: Wet kneading

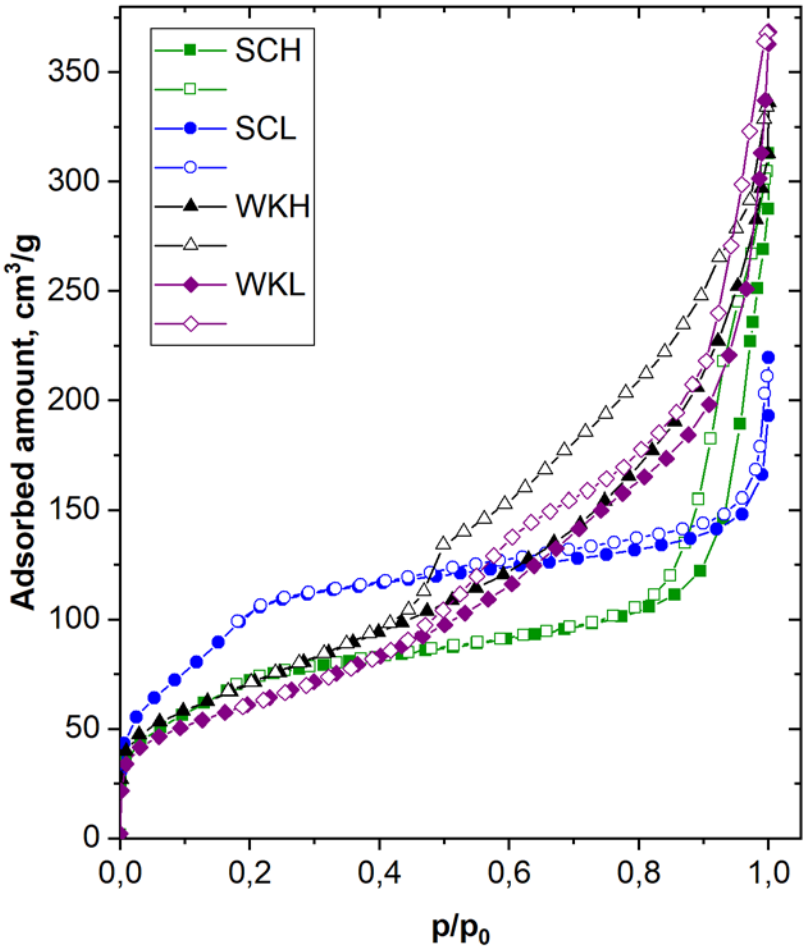


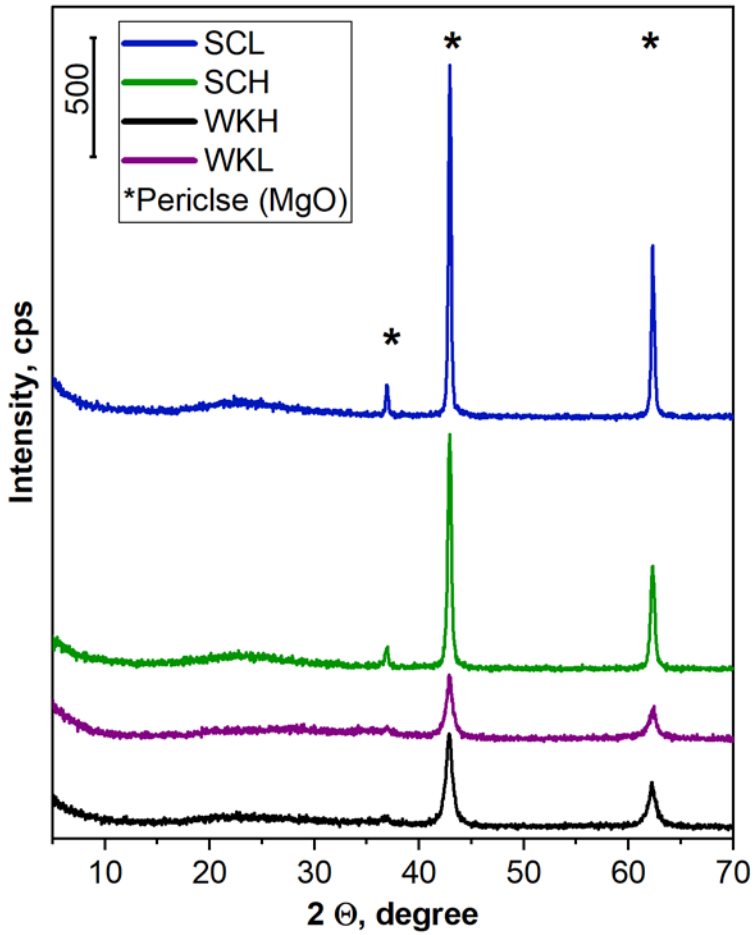


II. type: Sylica coating



N_2 physisorption isotherms and XRD patterns of the samples

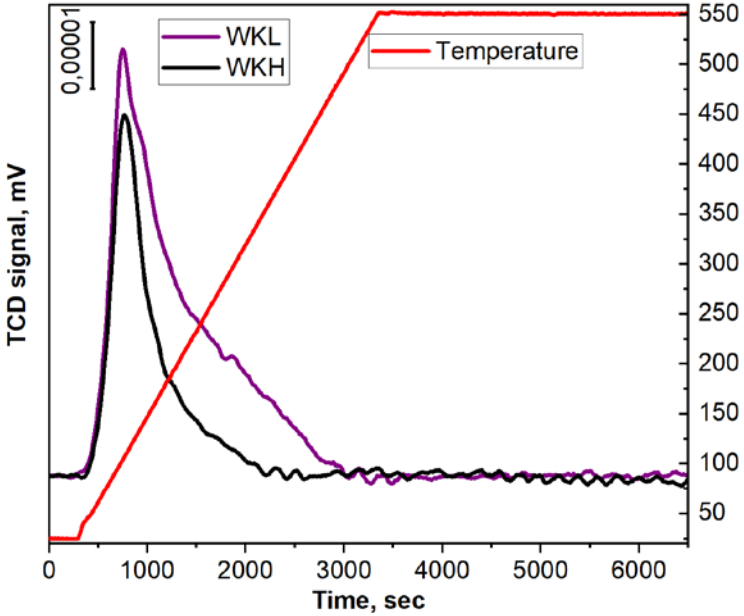




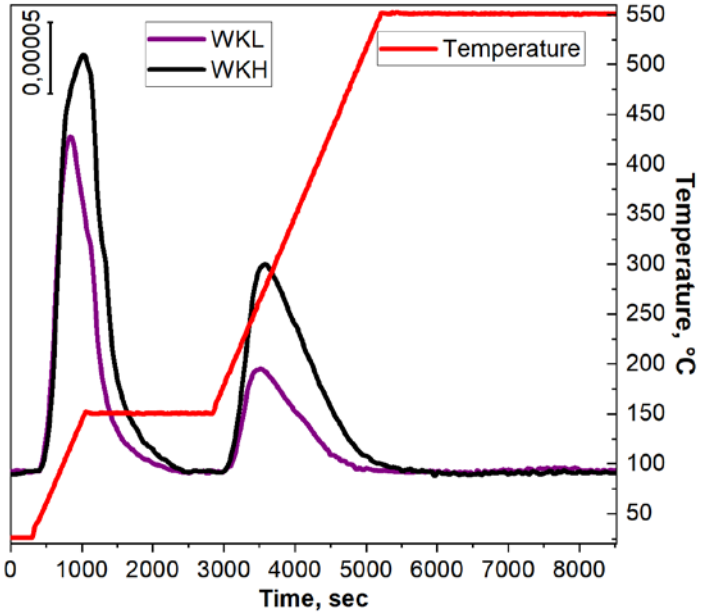
	Pore volume, cm^3g^{-1} [a]	Specific surface area, m^2g^{-1}	Crystalite size, nm [b]
SCH	0.41	279	55
SCL	0.26	374	123
WKL	0.49	226	21
WKH	0.46	259	25

a: Gurvich methode, b: XRD

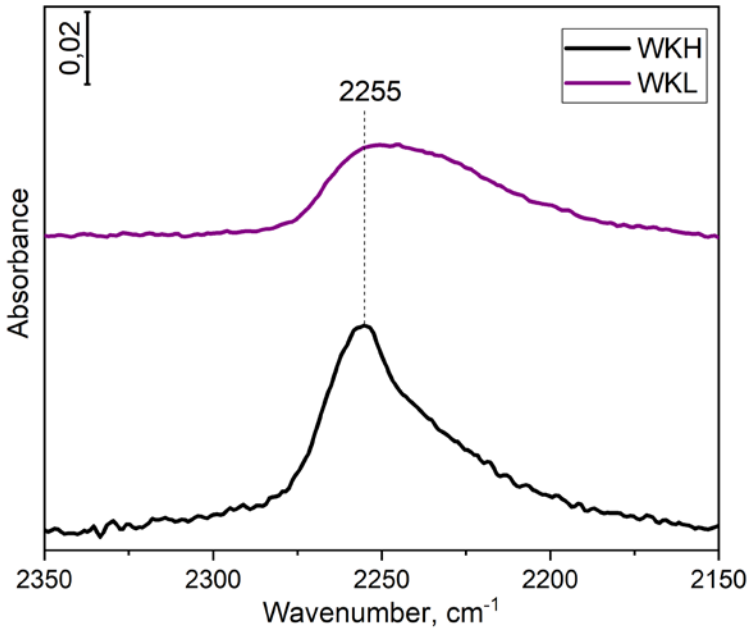
CO_2 TPD



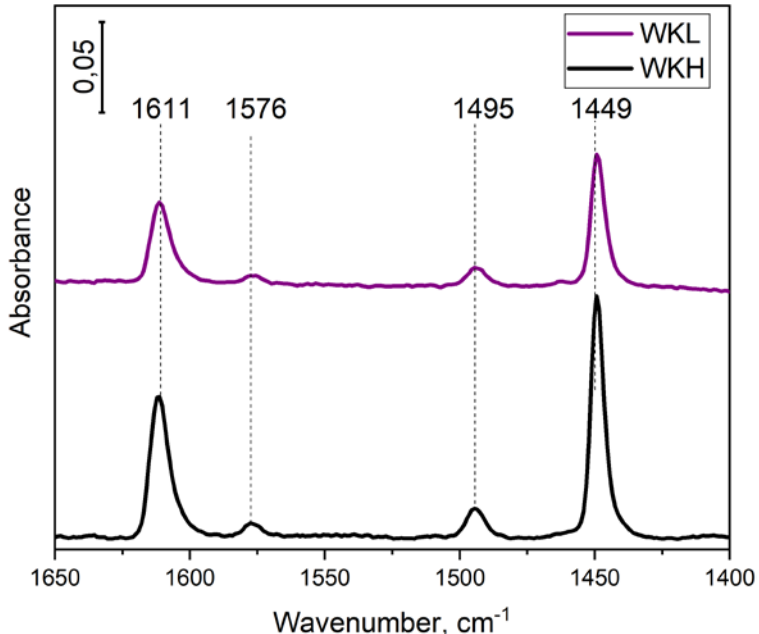
NH_3 TPD



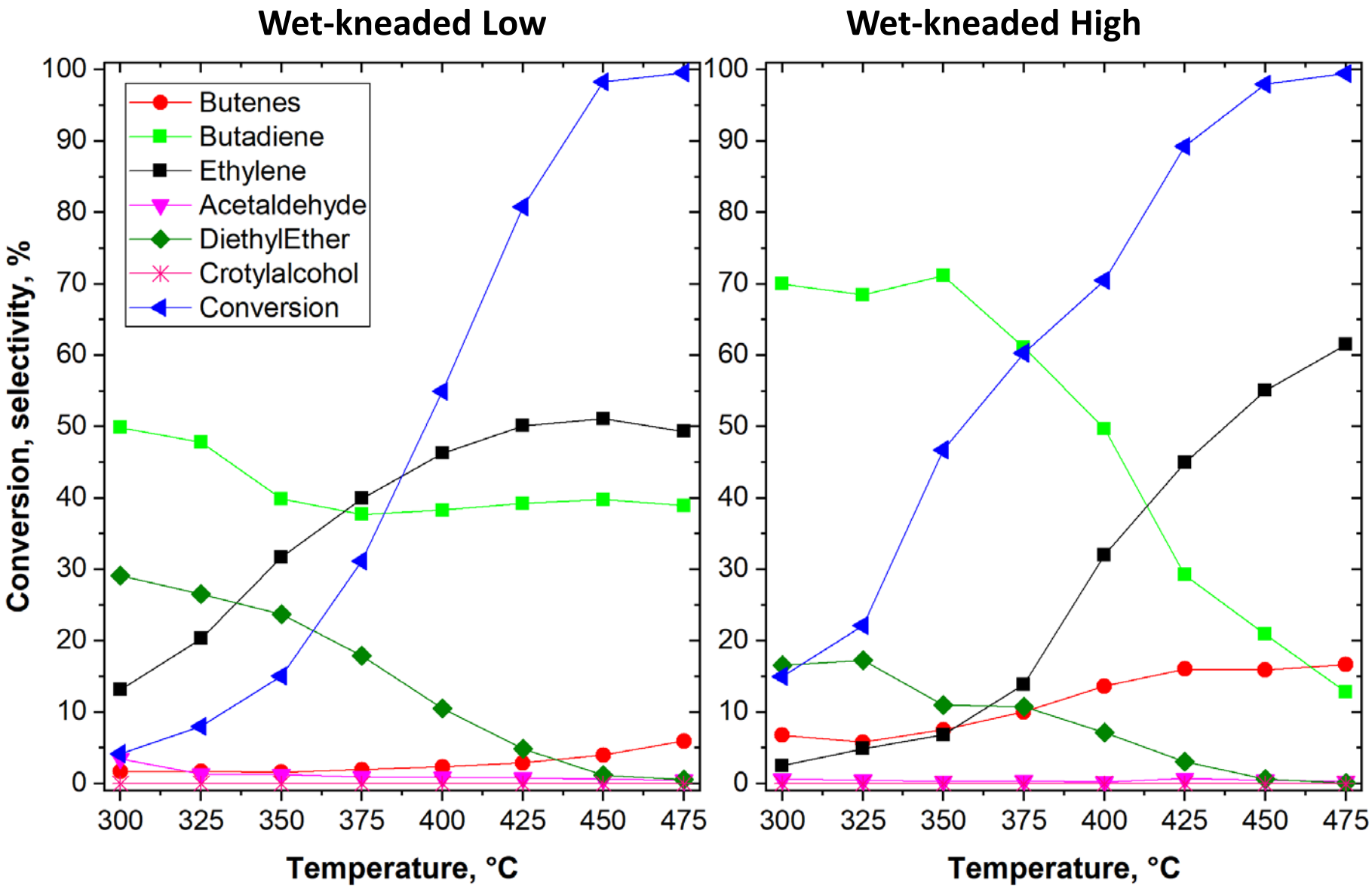
$CDCl_3$ IR, measured at RT



Pyridine IR, degassed at 200 °C

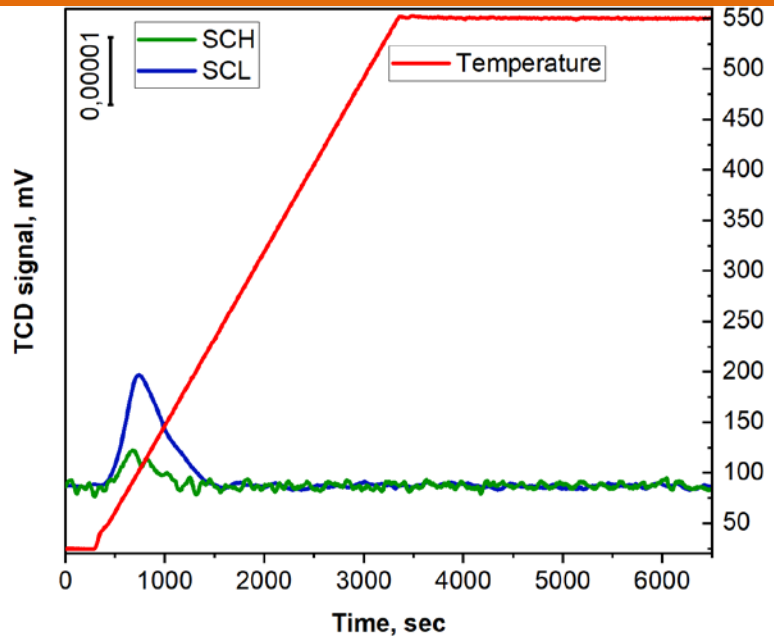


Conversion of ethanol over pure WK-type catalysts

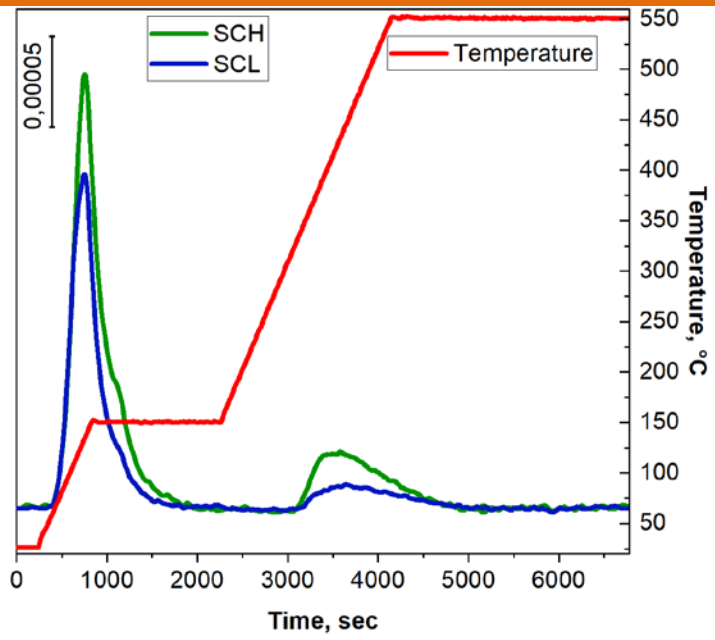


1 g catalyst, 0.5 g ethanol/(g_{cat}*h), 30 ml/min (4.4 ml/min ethanol + 25.6 ml/min He)

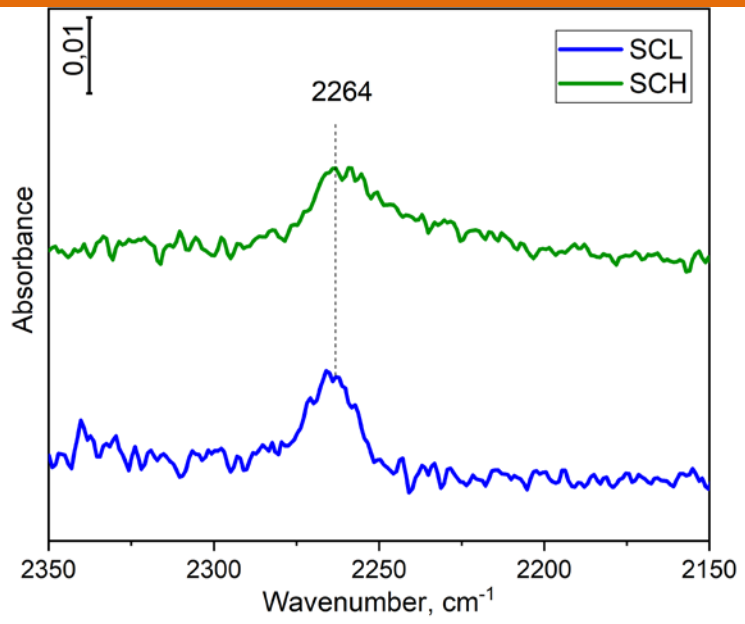
CO_2 TPD



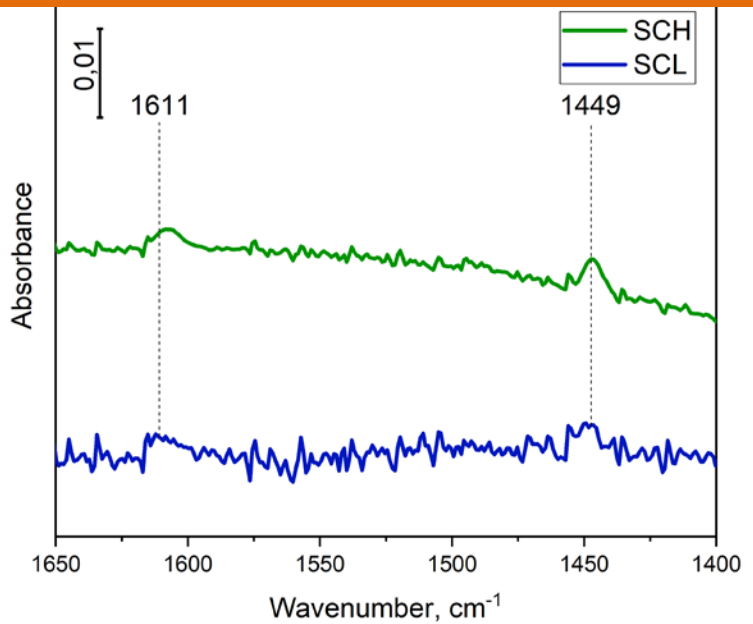
NH_3 TPD



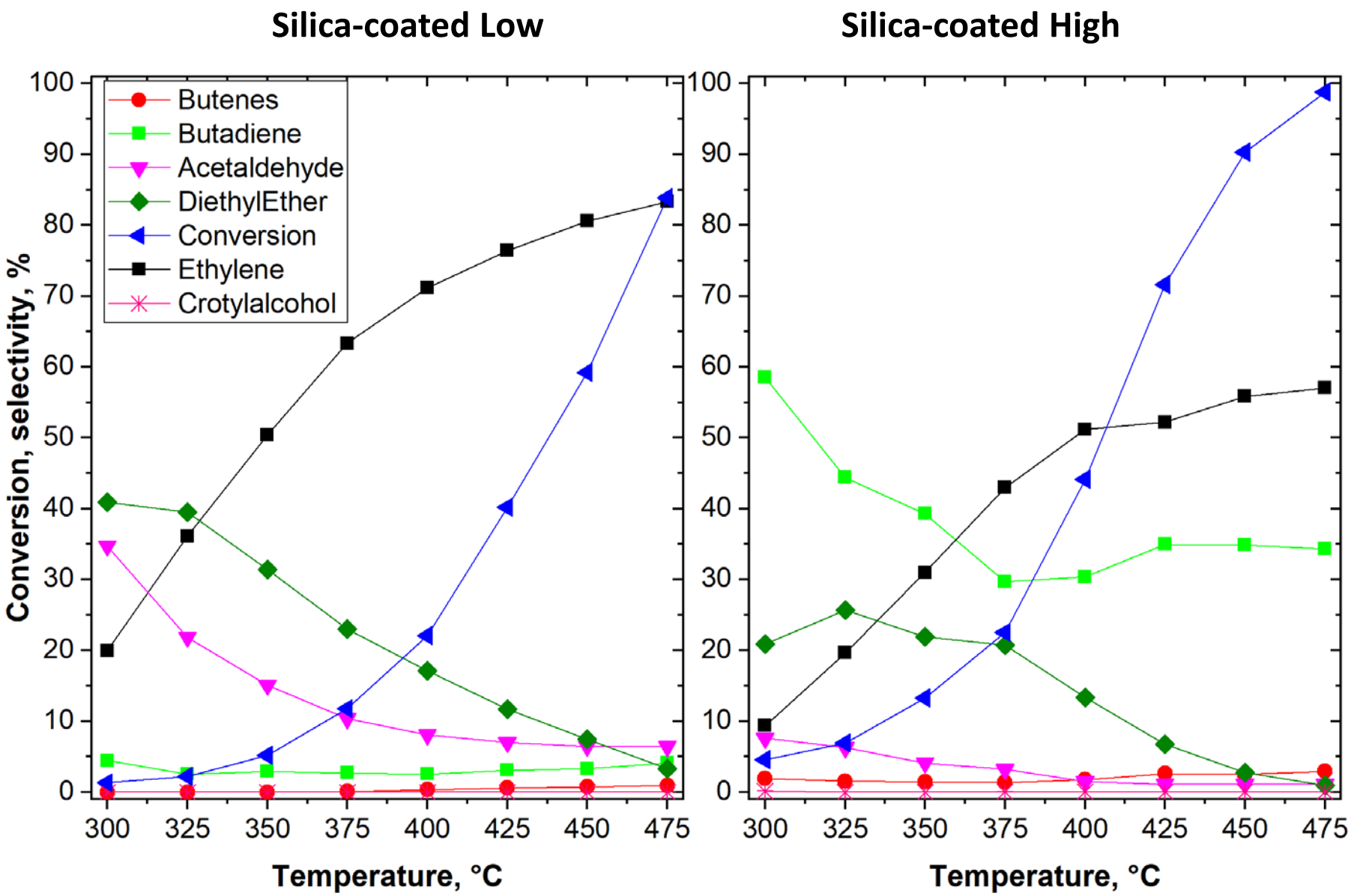
$CDCl_3$ IR, measured at RT



Pyridine IR, degassed at 450 °C



Conversion of ethanol over pure SC-type catalysts



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

SUMMARY

- Two catalysts group were sintetized by wet kneading and silica coating methods. The SC samples appeared as a combination of the structure of parent MgO and MCM-41, while the WK samples appeared as a combination of the two oxides.

- The results of the catalytic test reactions showed that in the case of the catalysts made of high surface area MgO achieved significantly higher BD yields than over the sample made of low surface area MgO. In the case of WK samples, the WKH was favorable only in the low temperature range, because at higher temperatures the dehydration of ethanol suppresses the BD yields.

- The higher BD yields 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.

- The results of acidity/basicity characterizations showed that the samples made of high surface area MgO contain more and stronger acidic sites and in parallel, fewer and weaker basic sites. The increased acidity is explained by the higher number of Mg-O-Si bonds formed. In our opinion, the bonds formed in this way reduce the basicity of MgO.

- In order to support our above findings, we plan to further investigate the surface Mg/Si distribution of the catalysts by XPS and SEM-EDX methods

Thank you for your attention

Acknowledgments

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Influence of acid–base properties on the Lebedev ethanol-to-butadiene process catalyzed by SiO_2–MgO materials†

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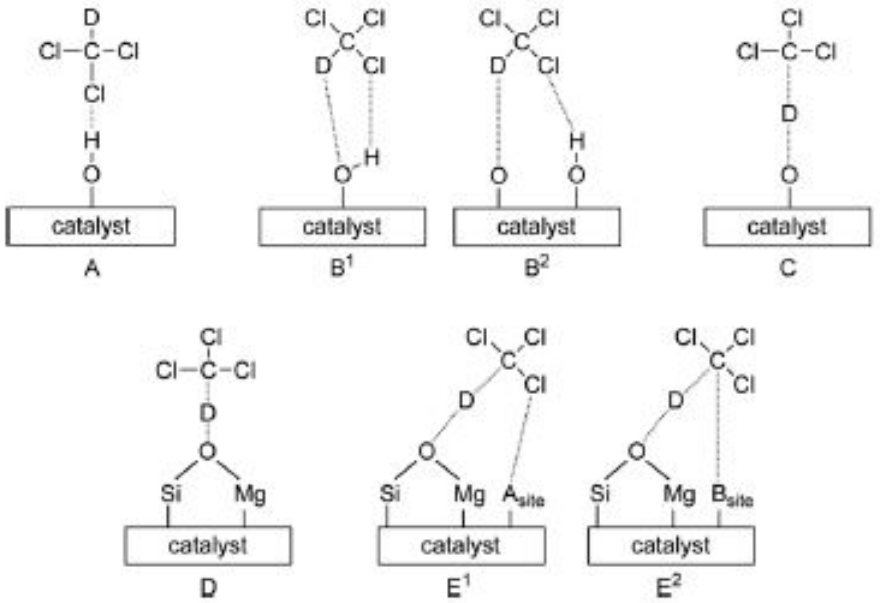

Scheme 3 Schematic representation of the interactions for $CDCl_3$ with basic sites of a solid catalyst. Structures A–C are reported by Ono *et al.*[20] Structures D, E^1 and E^2 are postulated in the present study. A_{site} and B_{site} represent acidic and basic sites, respectively.

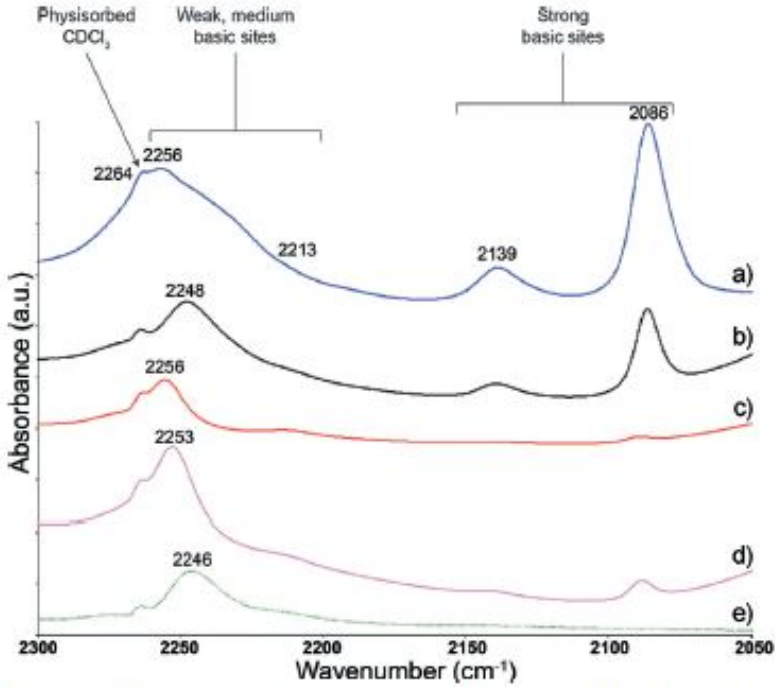

Fig. 7 FT-IR spectra of a) SiO_2–MgO (VI), b) SiO_2–MgO (II), c) SiO_2–MgO (III), d) SiO_2–MgO (IV) and e) MgO after adsorption of $CDCl_3$. The spectra, taken at 323 K in the region 2300–2050 cm^{-1}, are offset for clarity.