PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

Synthesis of biofuels and fine chemicals over Supported Ionic Liquid Catalysts (SILCAs)

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- SUPPORTED IONIC LIQUID CATALYSTS
- SYNTHESIS OF BIOFUELS
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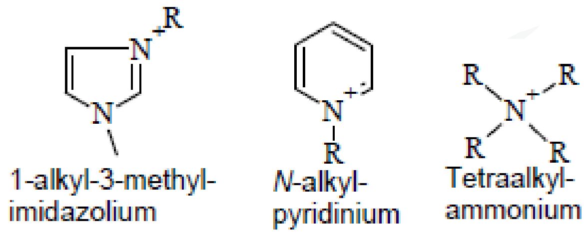
IONIC LIQUIDS

- Ionic compounds
- Melting point below 100˚C or room temperature
- Usually large organic cation and polyatomic inorganic or organic anion
- Negligible vapor pressure
- Wide liquidus range
- Unique solvation properties

Most commonly used cations



Some commonly used anions

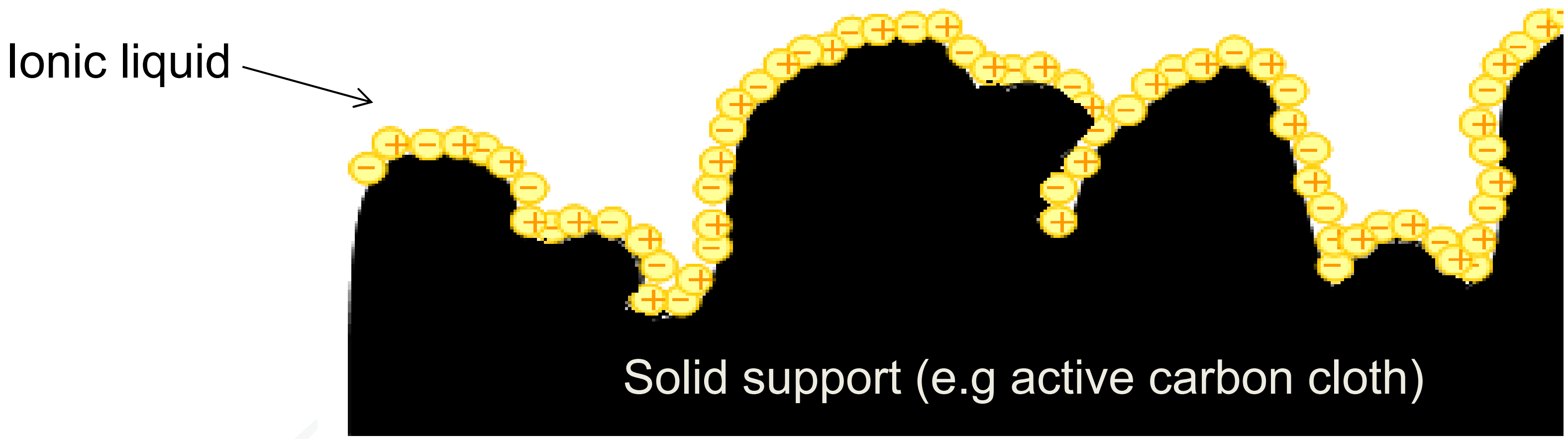
$CH_3CO_2^-$
$CF_3CO_2^-$
Br^-, Cl^-, I^-

WHY IONIC LIQUIDS ?

- More environmental benign processes
  - Less toxic and volatile solvents
- Reaction takes place at ionic atmosphere
  - Higher reaction rate
  - Better selectivity
- Different applications
  - Hydrogenation
  - Dehydration
  - Isomerisation

SUPPORTED IONIC LIQUID CATALYSTS

- A thin layer of ionic liquid immobilized on a solid support
- Metal compounds, metal nanoparticles or e.g. acid/alkaline modifiers residing in ionic liquid layer

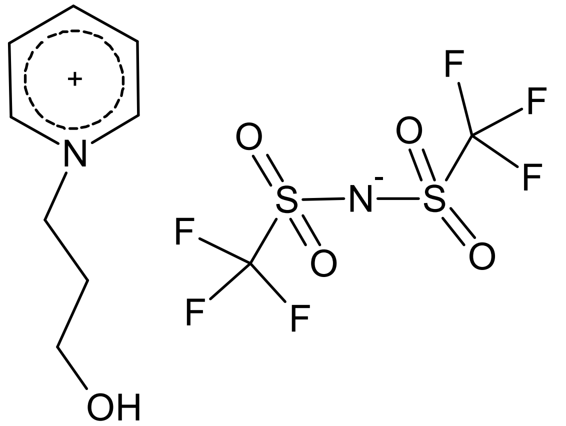


BENEFITS OF SILCA

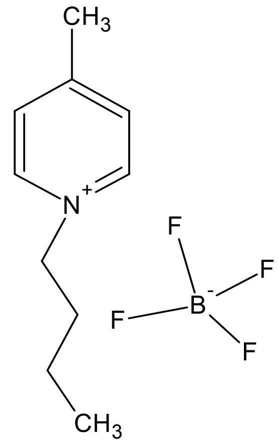
- Benefits of heterogeneous and homogeneous catalysis
- Easy separation of catalyst from the liquid phase
- Small amount of ionic liquid (IL) needed
- Two basic limitations
  - Decomposition temperature of the IL
  - IL should not be miscible with the reaction solvent

CATALYST PREPARATION

- Simple impregnation method is applied
- Ionic liquid and metal compound are dissolved into suitable solvent
- Solution is poured over support material (ACC or zeolite)
- Solvent evaporation
- Catalyst pretreatment/ reduction if needed



N-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)imide $[(C_3OH)Py][N(CF_3SO_2)_2]$

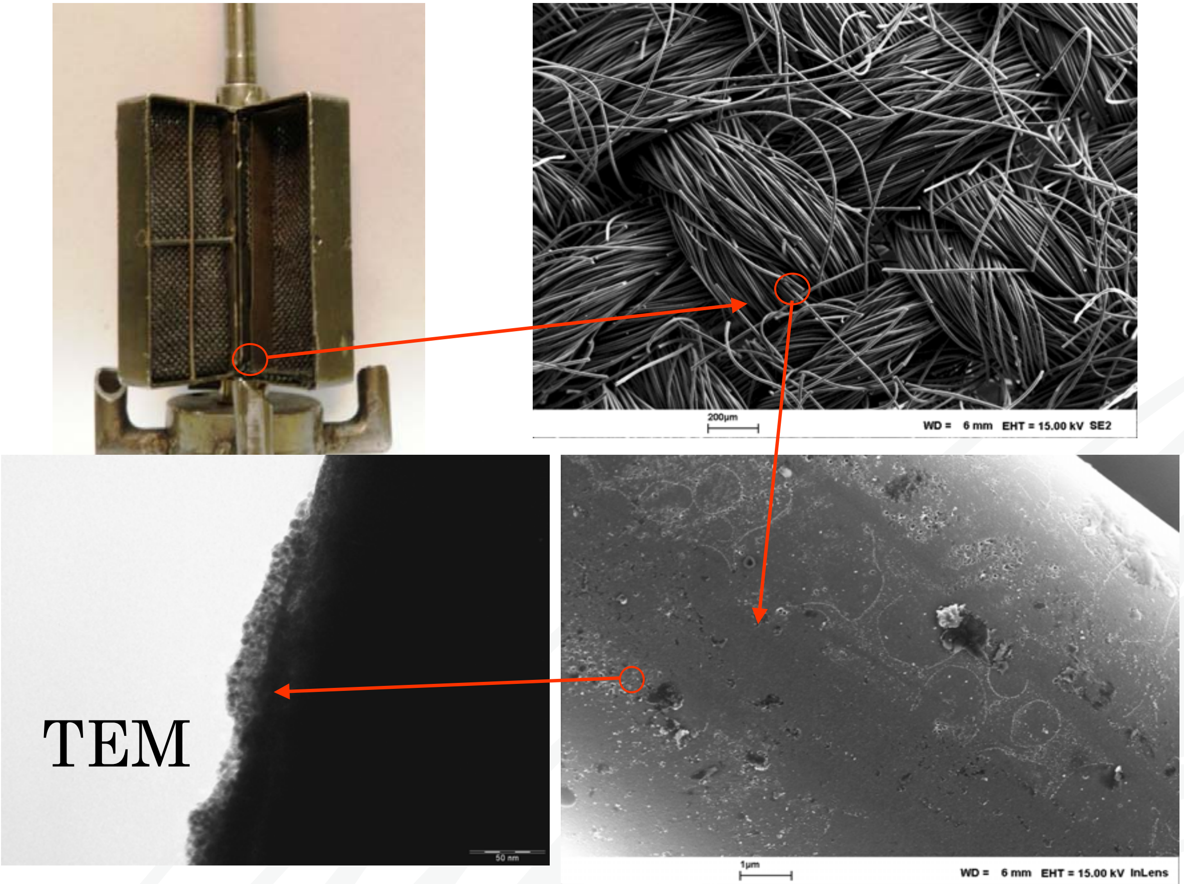


N-butyl-4-methylpyridinium tetrafluoroborate $[C_4C_1Py][BF_4]$

ACC (active carbon cloth)

CATALYST CHARACTERISATION (ACC)

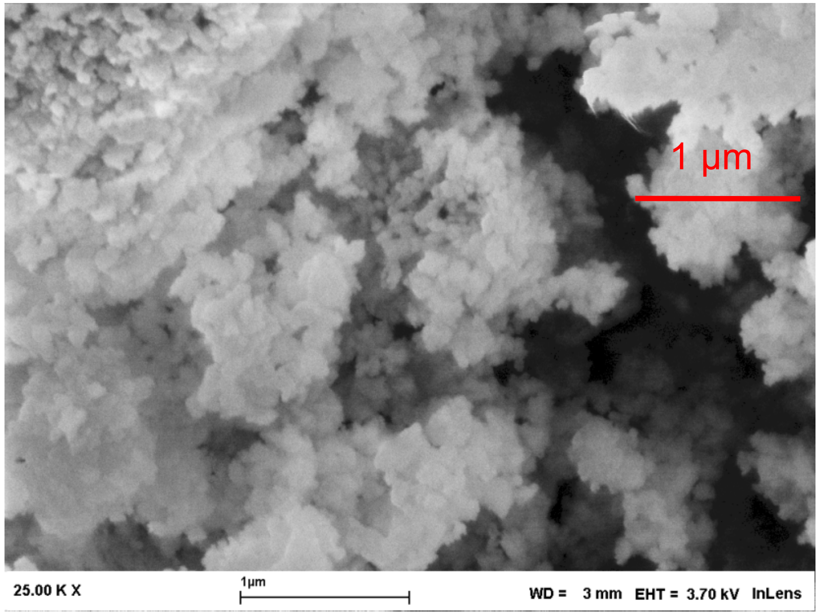
- SILCA catalyst Pd in $[(C_3OH)Py][N(CF_3SO_2)_2]/KOH(1:4)$ on ACC in macro-, micro- and nanoscale



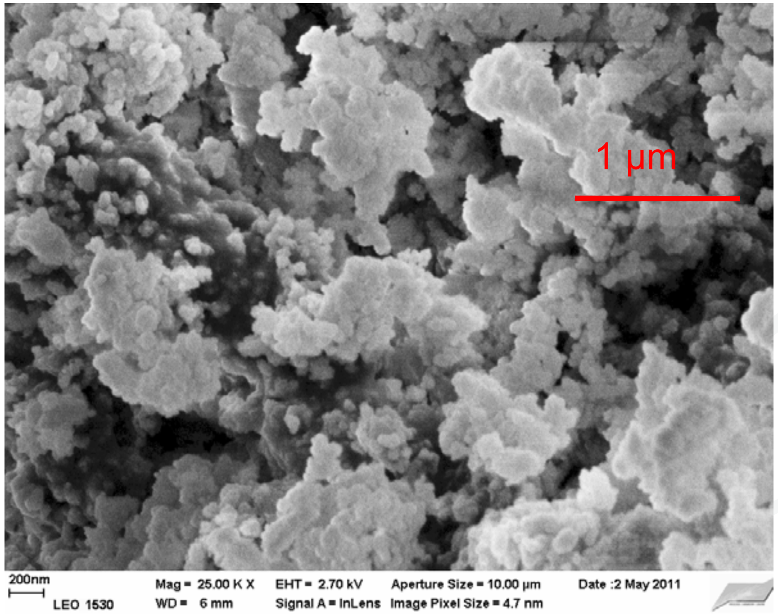
SEM

SEM

CATALYST CHARACTERISATION (ZEOLITES)



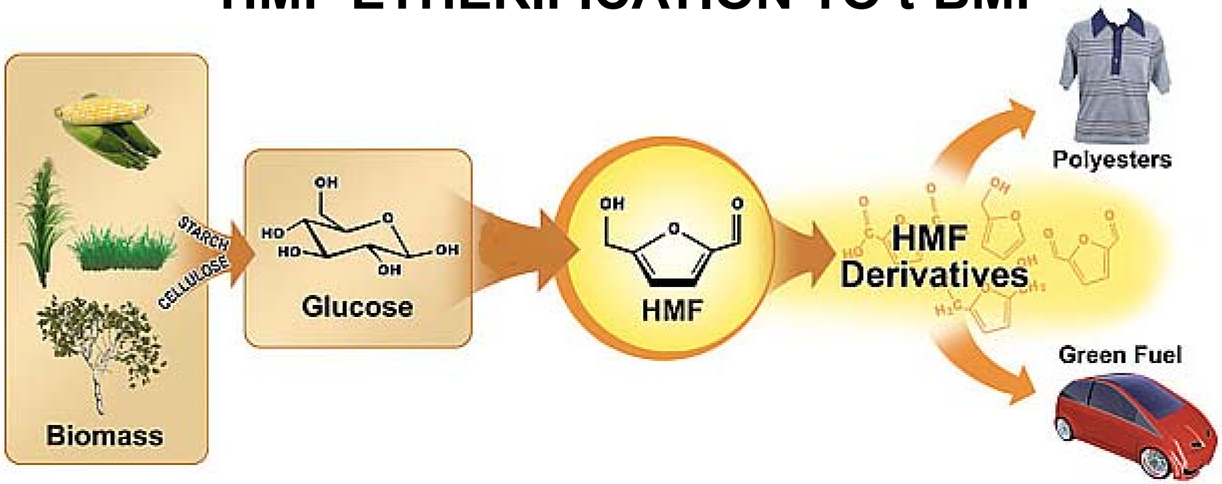
H-Beta-25 zeolite catalyst.

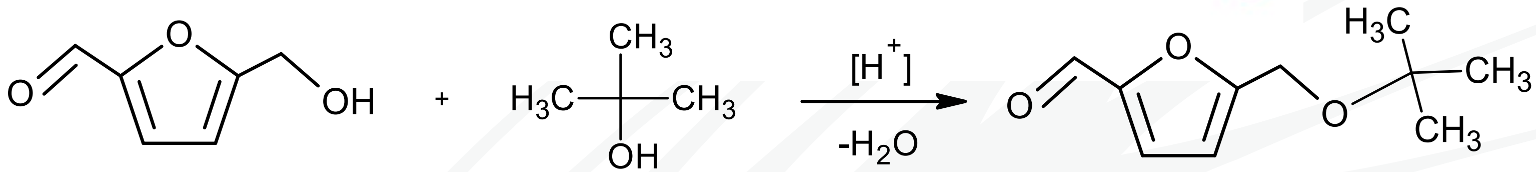


IL-H-Beta-25 zeolite catalyst.

SYNTHESIS OF BIOFUELS

HMF ETHERIFICATION TO t-BMF





5-hydroxymethylfurfural

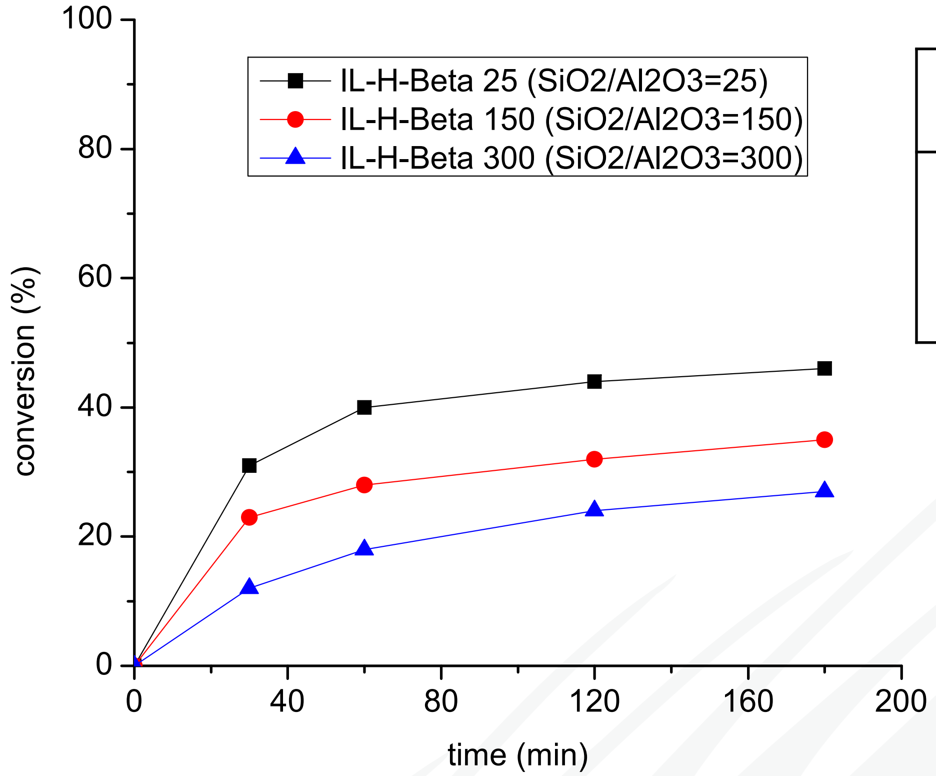
t-Butanol

5-tert-butoxymethylfurfural

HMF is a renewable building block for various (currently) petroleum derived chemicals.

E. Salminen, N. Kumar, P. Virtanen, M. Tenho, P. Mäki-Arvela, J.-P. Mikkola, Etherification of 5-Hydroxymethylfurfural to a Biodiesel Component Over Ionic Liquid Modified Zeolites, Topics in Catalysis, 56 (2013) 765.

CATALYST ACTIVITY AND SELECTIVITY



T = 120 °C, p(Ar) = 8 bar

Catalyst	tBMF selectivity [%]
IL-H-Beta 25	83
IL-H-Beta 150	76
IL-H-Beta 300	72

Catalyst	Conversion (%)
H-Beta 25	36
H-Beta 150	30
H-Beta 300	25
IL-H-Beta 25	46
IL-H-Beta 150	35
IL-H-Beta 300	27

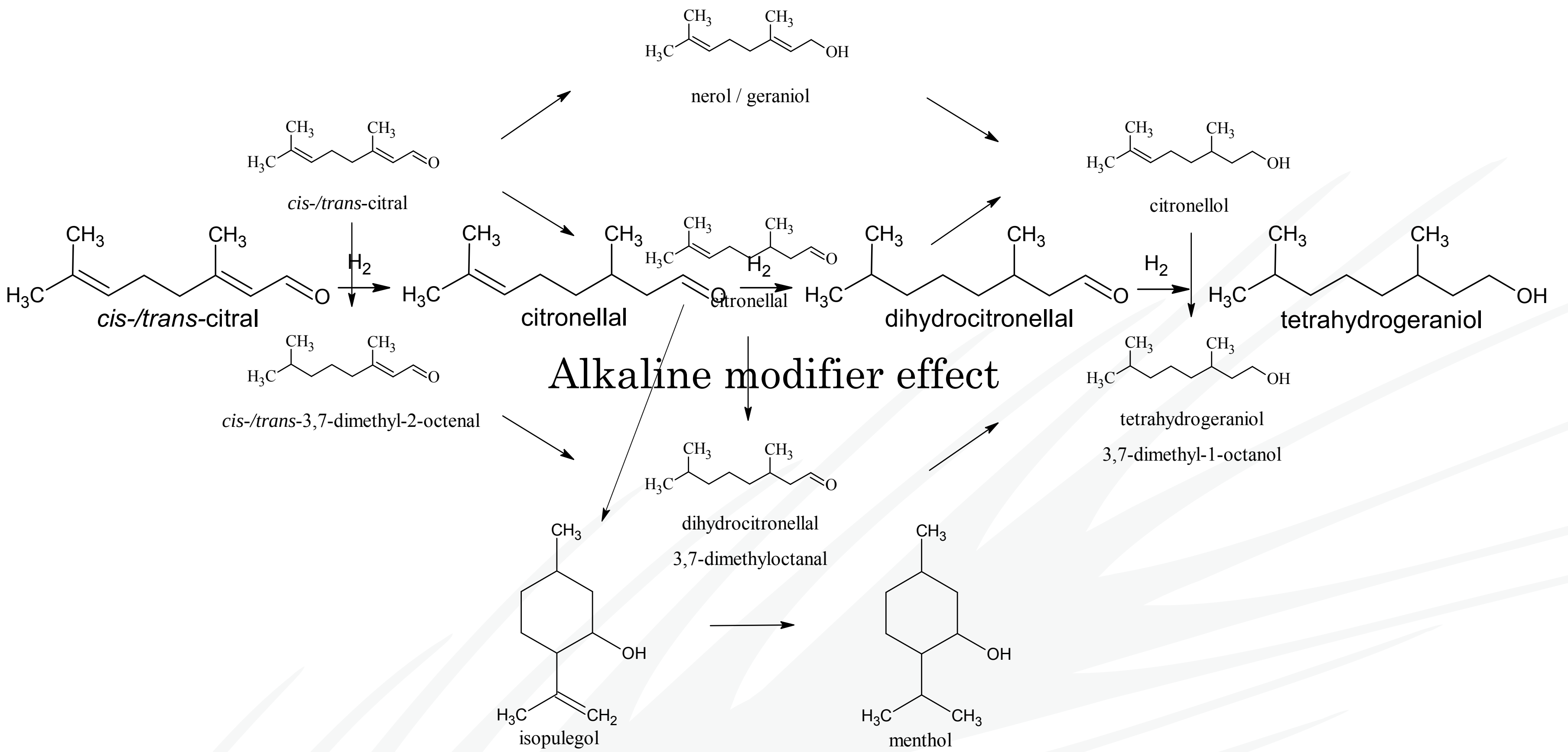
Reaction time: 3h
T = 120 °C, p(Ar) = 8 bar

CONCLUSIONS

- High selectivities of tBMF were obtained with zeolites modified with Lewis acidic ionic liquids.
- Formation of HMF ethers is associated with the presence of Lewis acid sites.
- Modification of zeolites with ionic liquid did not influence the morphology of the zeolites (XRD/SEM).

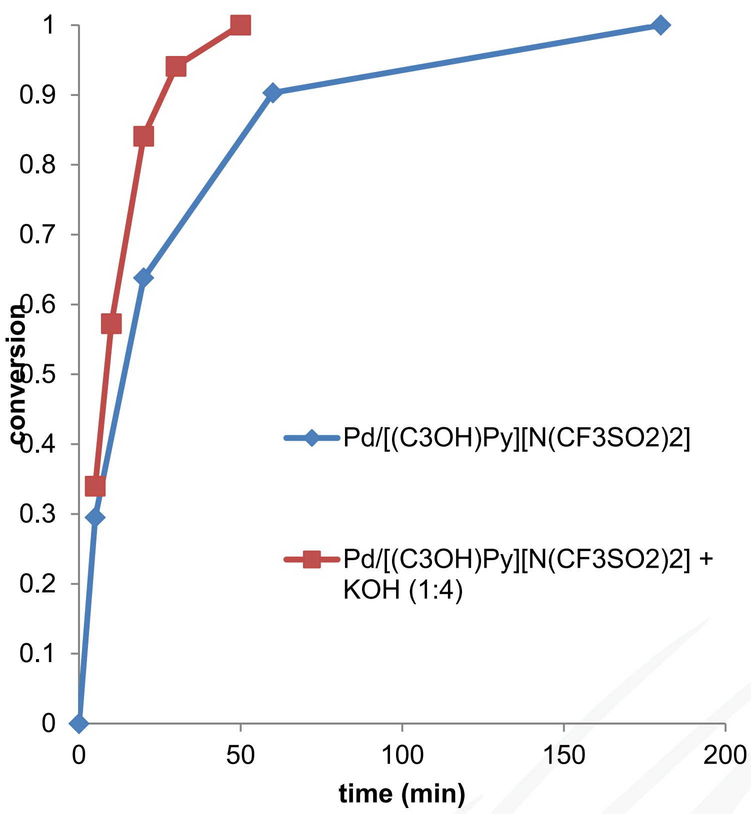
SYNTHESIS OF FINE CHEMICALS

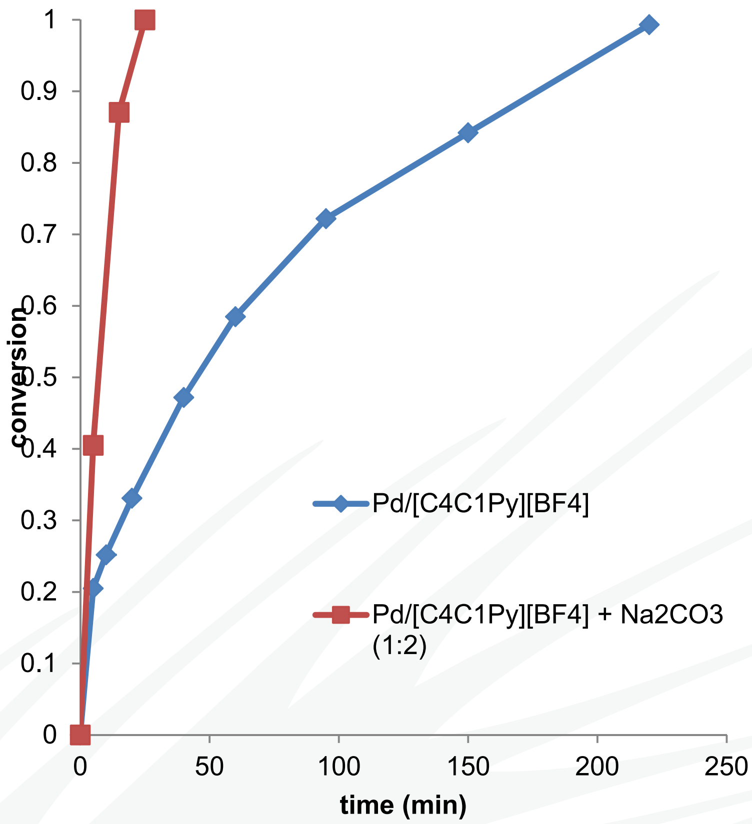
CITRAL HYDROGENATION TO CITRONELLAL



E. Salminen, P. Virtanen, K. Kordas, J.-P. Mikkola, Alkaline modifiers as performance boosters in citral hydrogenation over Supported Ionic Liquid Catalysts (SILCAs), Catalysis Today, 196 (2012) 126.

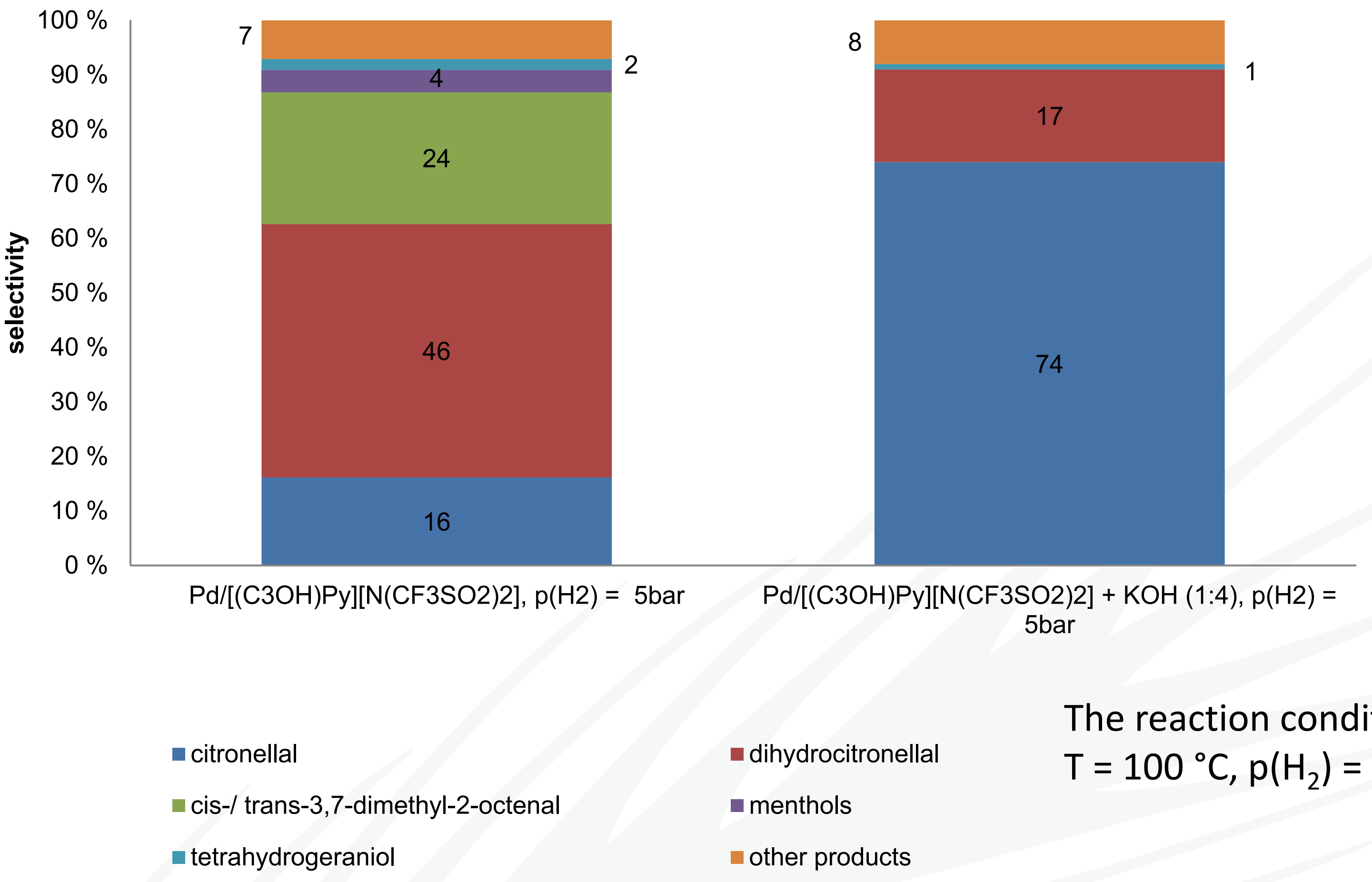
CATALYST ACTIVITY





The reaction conditions were T = 100 °C, $p(H_2)$ = 10 bar

CATALYST SELECTIVITY



The reaction conditions were
T = 100 °C, $p(H_2)$ = 5 bar

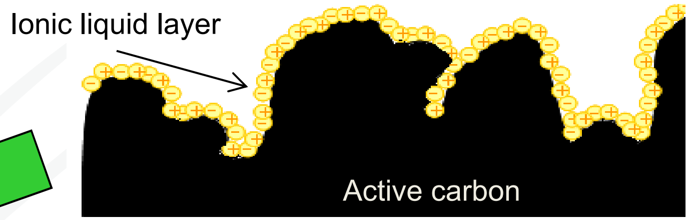
CONCLUSIONS

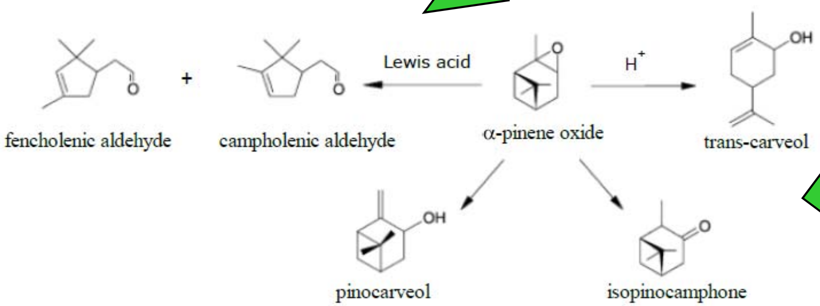
- Reaction rate can be influenced by different modifiers and also by different ionic liquids
- Alkaline modifiers enhance the activity and increase the selectivity of citronellal
- Highly selective reaction route was accomplished.
  - Only conjugated double bond is hydrogenated in the first phase

SYNTHESIS OF FINE CHEMICALS

α-PINENE OXIDE ISOMERISATION TO CAMPHOLENIC ALDEHYDE

-Monoterpenes (*e.g. α*-pinene) are the major components of resin
-Epoxidation of monoterpenes to oxides (*e.g.* **α-pinene oxide**)
-Isomerization of terpene oxides to value-added compounds (e.g. campholenic aldehyde)

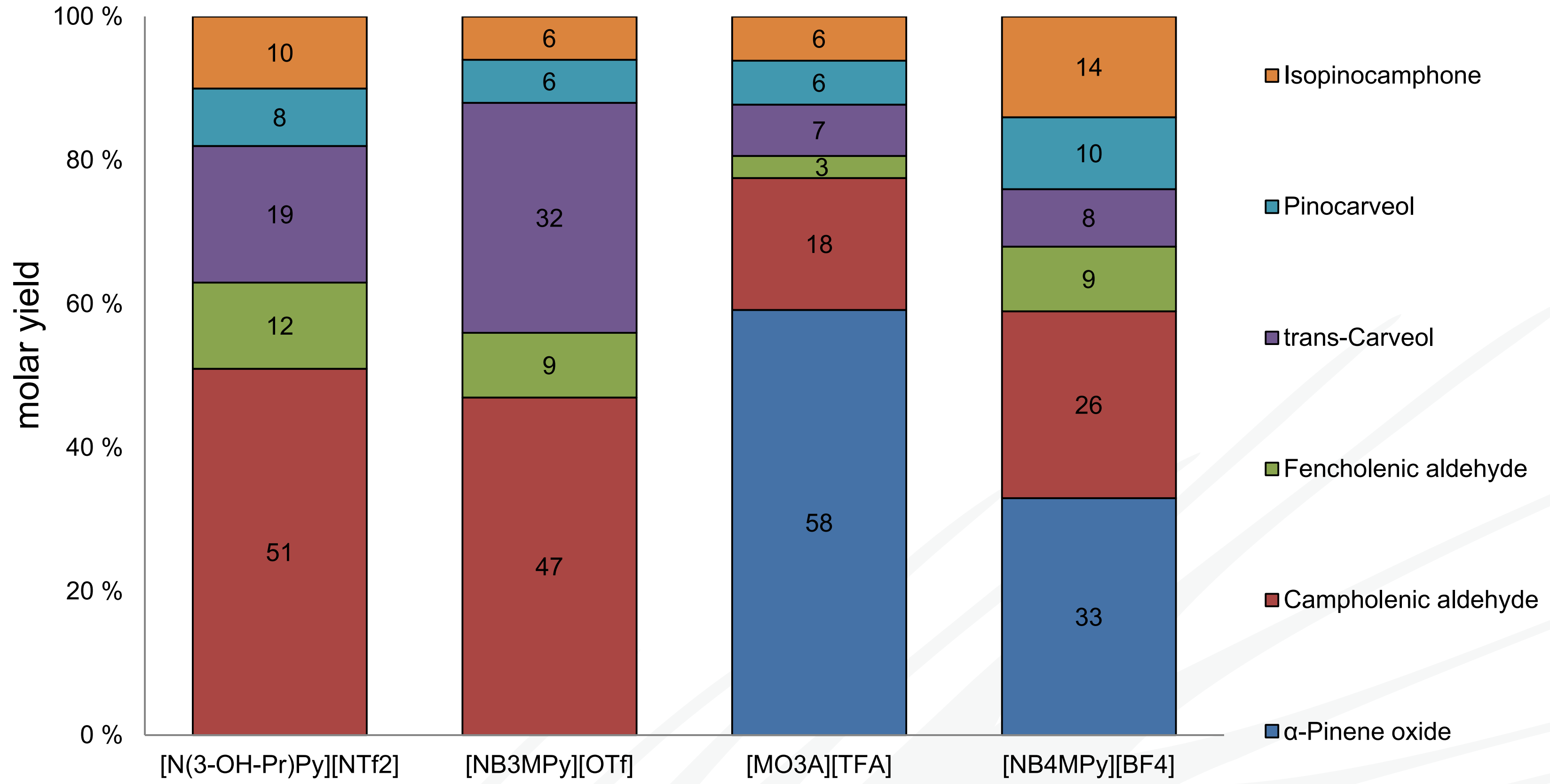




Activity and selectivity of the catalysts are dependent upon the nature of ionic liquid and Lewic acid modifier

Campholenic aldehyde molar yield ≈ 62 %

RESULTS



$m(SnCl_2)$ = 68 mg
m(IL)= 150 mg

Reaction conditions were T=70 °C, p(Ar) = 5, $C_{o,\ \alpha\text{-Pinene}}$=0.012 M and V_{hexane} = 250 ml.
Reaction time = 4 h

RESULTS

Molar yields of products from α-pinene oxide isomerisation reactions (after 4 hours). $n(IL):n(M_xCl_y) = 1:1$.

Entry	Catalyst	Conversion [%]	Campholenic aldehyde yield [%]	Fencholenic aldehyde yield [%]	trans-Carveol yield [%]
1	$FeCl_3$/IL/ACC	81	44 (49)	7	17
2	$CrCl_3$/IL/ACC	83	40 (46)	8	26
3	$SnCl_2$/IL/ACC	100	51	12	19
4[a]	$SnCl_2$/IL/ACC	100	57	12	20
5[a,b]	$SnCl_2$/IL/ACC	100	62	10	23

[a] $m(SnCl_2)$=135 mg. ($n(IL):n(M_xCl_y)$=1:2)

[b] Toluene as a solvent

IL= $[N(3\text{-}OH\text{-}Pr)Py][NTf_2]$

CONCLUSIONS

- Reusable catalysts with high selectivity towards campholenic aldehyde were accomplished
- The nature of the ionic liquid in SILCA influences the activity and selectivity of the catalyst

ACKNOWLEDGEMENTS

- Financial support from the Academy of Finland collaborative project with the DST India is gratefully acknowledged. Also, the Swedish BIO4ENERGY programme and COST action CM0903 (UbioChem) are acknowledged.

COST ACTION CM0903