Multifuntional Catalysis and Plant Chemistry

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Catalysis and Renewables/IC2MPoitiers-France

Journées Chevreul, Maisons-Alfort, June 5-6th 2012)

OUTLINE

General context

- Frontiers of catalysis in the 21st century
- SUSCHEM roadmap 2010
- PIPAME 2010 (60 pages over renewables chemistry)
- Heterogeneous catalysts

Catalysis and esters or/and glycerol

- Esters/Transesterification
- Glycerol/ethers, esters
- Glycerol as Solvent

Catalysis and lignocellulose

- Fractionation process
- Pre-treatment of cellulose-impact on the catalyst activity
- Synergistic effect between homogeneous,heterogeneous catalysts and physical pre-activation

Conclusion

Frontiers of catalysis in the 21st Century

Roadmap in catalysis

- 100% selectivity for all catalyst-based processes
- Replacement of fossil carbon by renewables
- C1 chemistry (methane, carbon dioxide) or water chemistry
- Renewable energies
- Photocatalysis

Breakthroughs will emerge from surface science and catalysis

- Inorganic-based nanocatalysts
- Carbon-based
- Hybrid (organic/inorganic), including enzymes, …

Gabor A. Somorjai, Heinz Frei, Jeong Y. Park, J. Am. Chem. Soc. ***2009,*** *131, 16589-16605.*

SUSCHEM roadmap 2010

Aim

Suschem is working to place chemistry at the heart of innovation and to propose solutions to the European commission to guide the structuring of the 8th framework programme (needs of chemical industry)

Main themes of roadmap

1/ Renewable raw materials and biosourced economy (catalysis)

2/ Chemistry and recycling

3/ Advanced materials (nanocatalysts)

4/ Chemistry for energy (catalysis)

5/ Eco-efficient processes (catalysis)

6/ Analysis, methods and performance

7/ Eco-design

8/ Innovation network

Green chemistry

P. Anastas

J. Warner

GREEN CHEMISTRY

(aim: design of products and processes that minimize the use and generation of hazardous substances)

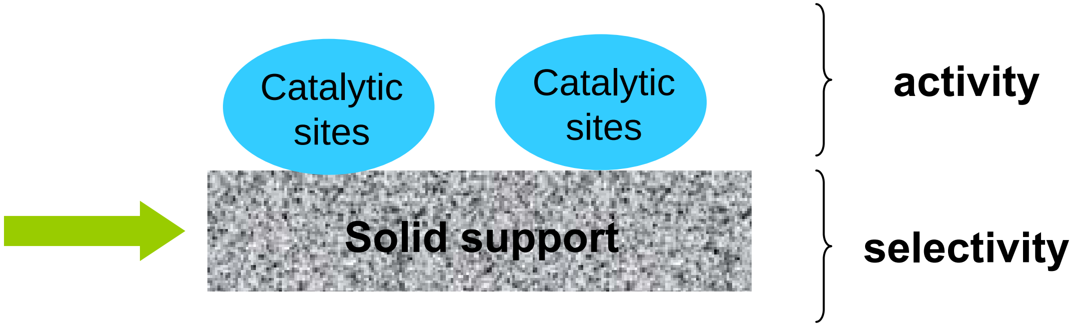
12 principles of Green Chemistry

1. **Prevention**
2. **Atom Economy**
3. **Less Hazardous Chemical Syntheses**
4. **Designing Safer Chemicals**
5. **Safer Solvents and Auxiliaries**
6. **Design for Energy Efficiency**
7. **Use of Renewable Feedstocks**
8. **Reduce Derivatives**
9. **Catalysis**
10. **Design for Degradation**
11. **Real-time analysis for Pollution Prevention**
12. **Inherently Safer Chemistry for Accident Prevention**

In 2020: Green chemical industry is expected to soar to 98.5 billions dollars

Catalysis : 13 billion dollars

Heterogeneous catalysts:
How to control the activity and the selectivity ?



Heterogeneous catalysts

SELECTIVITY

Surface porosity

Catalysis in constrained geometry

⬇

Diffusional limitations

⬇

Ex. : controlled polymerization

Surface polarity

Preferential adsorption of some reactants

⬇

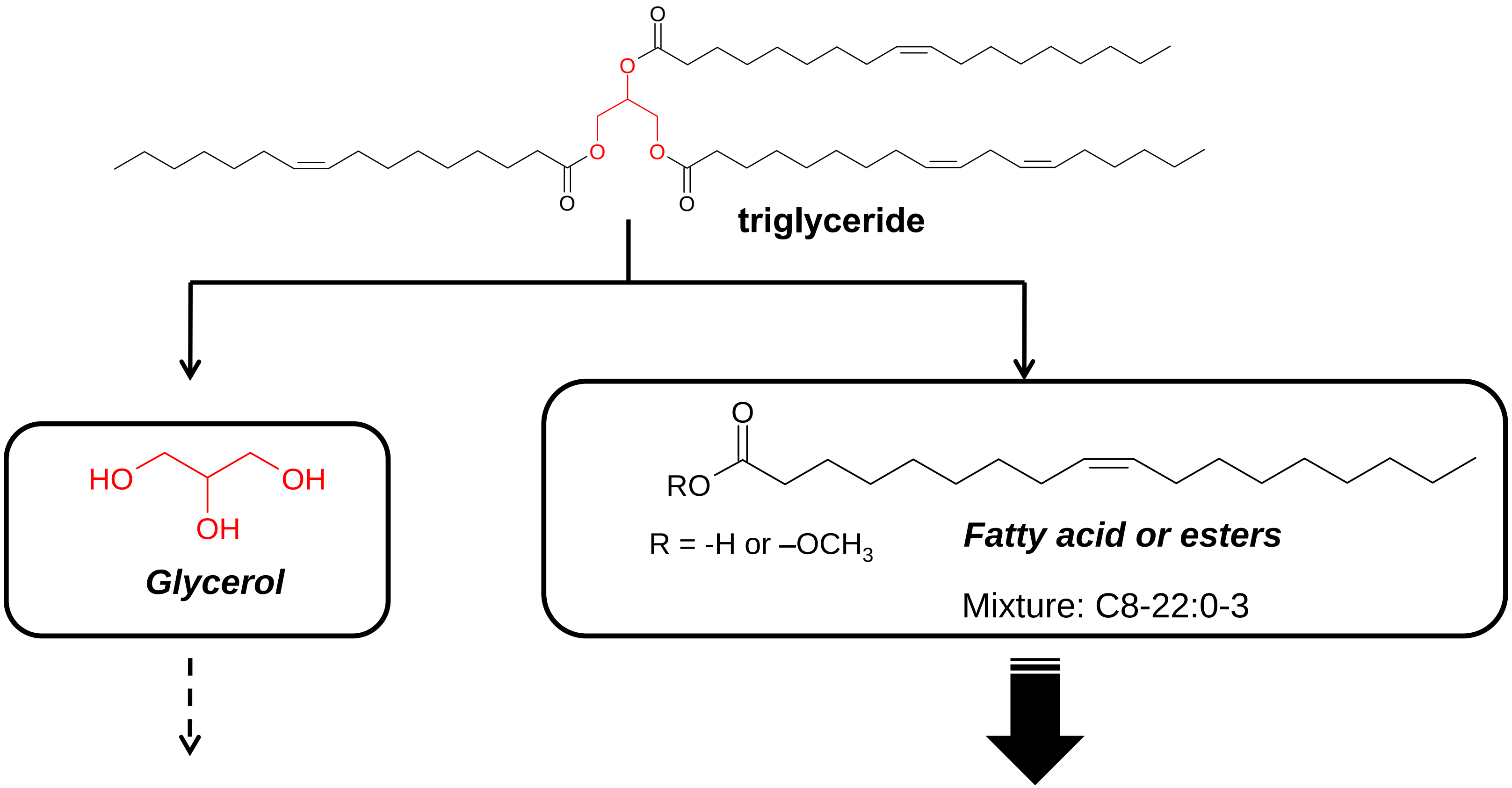
Rapid desorption of reaction products from the catalytic surface

⬇

Ex. : selective esterification of polyols

HOMOGENEOUS and HETEROGENEOUS CATALYSIS AND VEGETABLE OILS

Homogeneous and Heterogeneous catalysis and vegetable oils



triglyceride

Glycerol

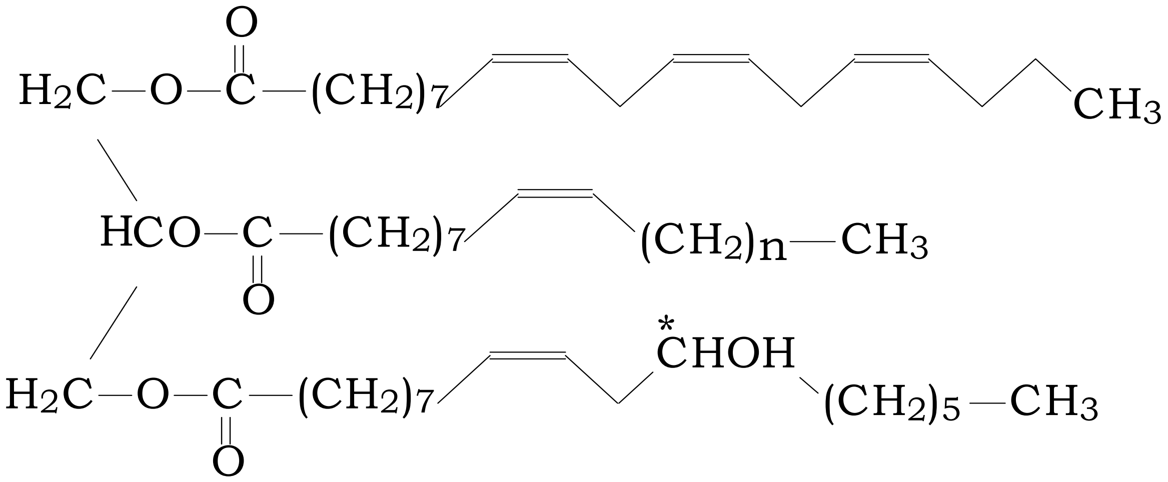
R = -H or –OCH_3

Fatty acid or esters

Mixture: C8-22:0-3

surfactant

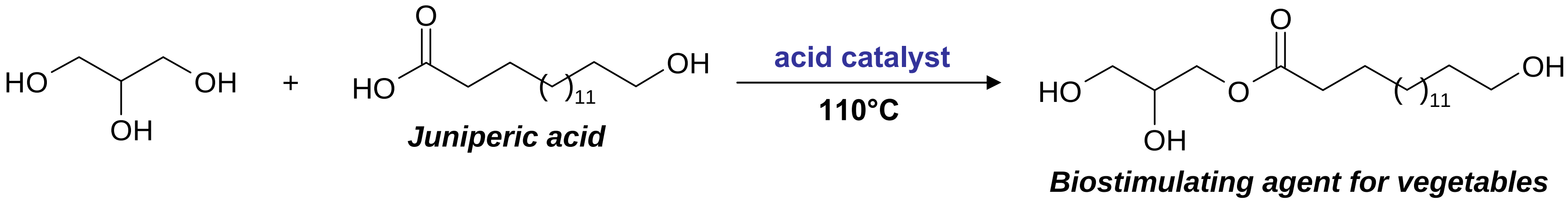
Triesters, Esters, Acids and Glycerol

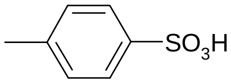
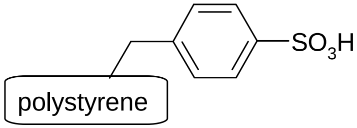
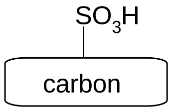


From unsaturated esters or fatty acids over heterogeneous catalysts

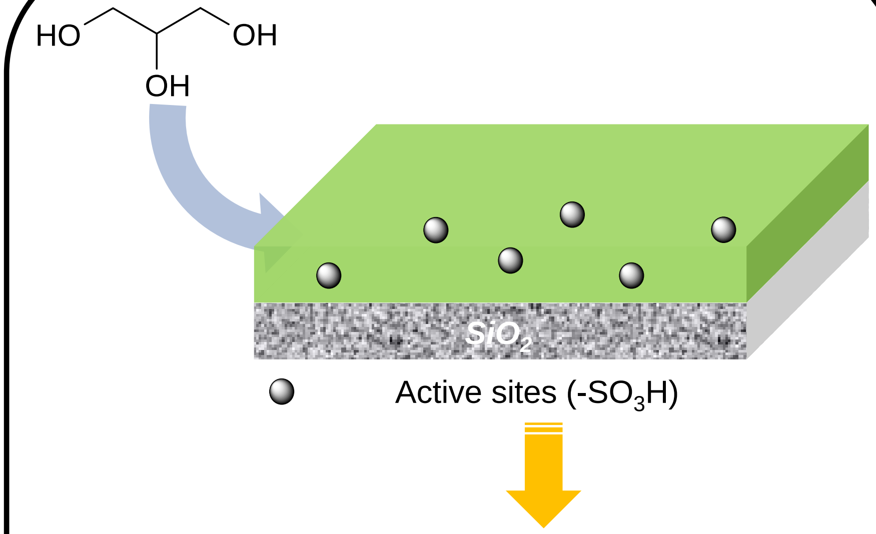
Selective transesterification or esterification
Epoxidation (and opening)
Ozonolysis
Dimerisation
Metathesis, co-metathesis
Diels-alder
Reductive amination
Selective hydrogenation
Hydrogenolysis
Isomerisation
Amidation
Carboxylation
Sulfonation
….

Esterification with hydroxylated fatty acids



Catalyst	Conv. (%)	Yield (%)
	99	35
	97	25
	90	12
Zeolite CBV-720	95	17

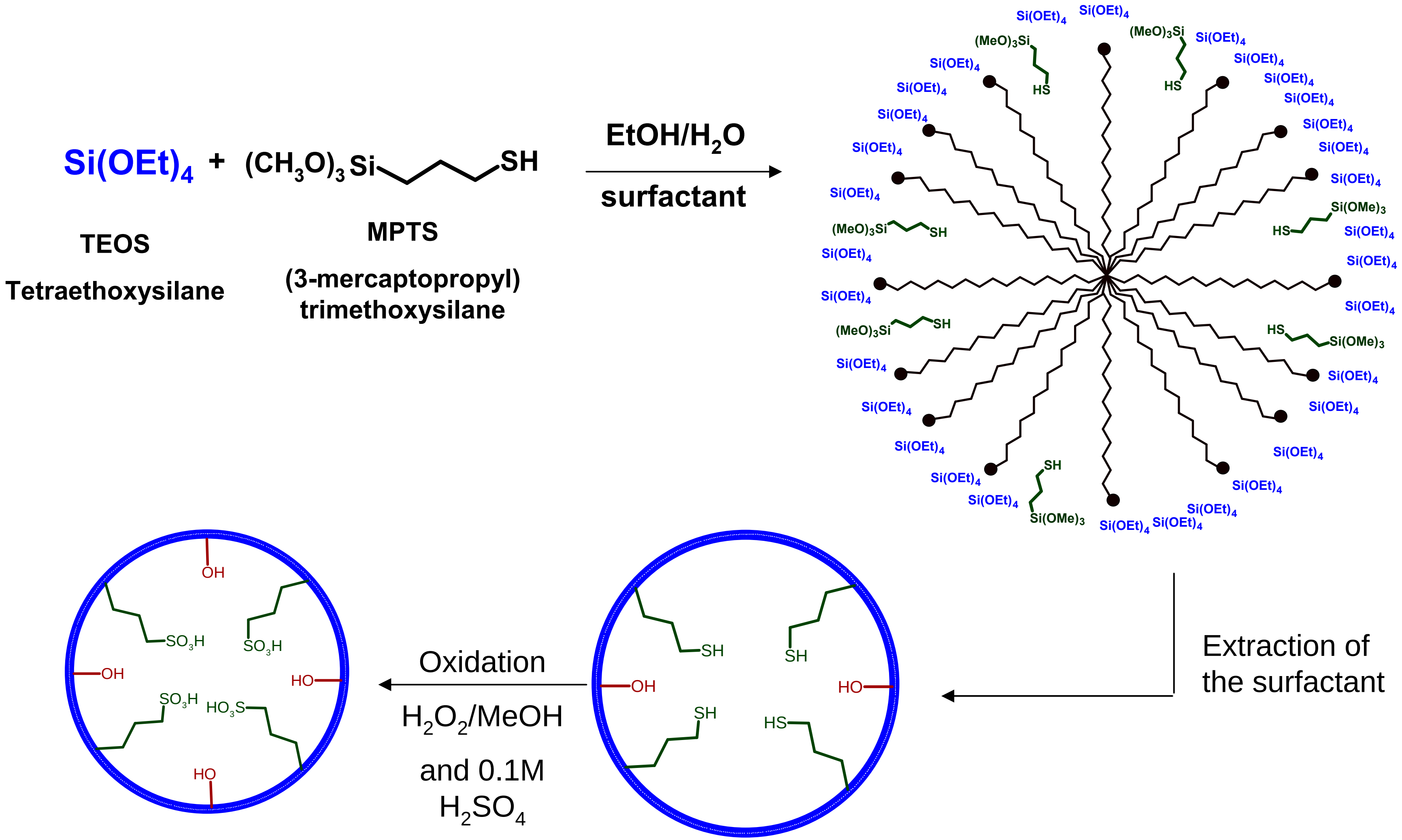
Main polymerization of the hydroxylated fatty acid



Selective adsorption of glycerol on the catalyst surface

Chem. Commun., **2007,** 22, 2222

Catalyst synthesis



$Si(OEt)_4$ + $(CH_3O)_3Si$–SH

TEOS

Tetraethoxysilane

MPTS

(3-mercaptopropyl) trimethoxysilane

$EtOH/H_2O$

surfactant

Extraction of the surfactant

Oxidation

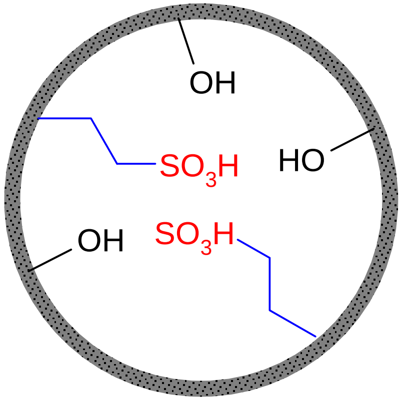
H_2O_2/MeOH

and 0.1M H_2SO_4

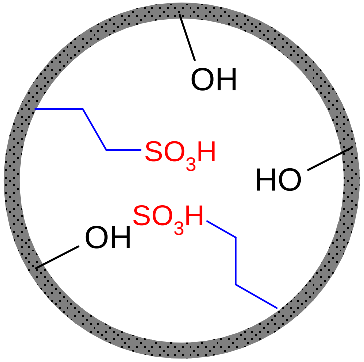
SBA-15-SO_3H: acid medium (pH<1), Pluronic® P123

HMS-SO_3H: basic medium(pH=11), hexadecylamine

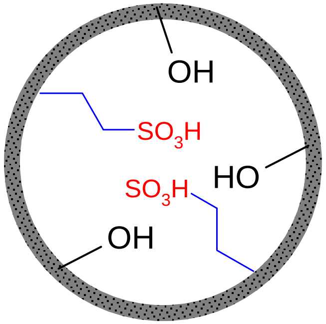
Esterification over silica-suported –SO_3H



SBA-15-SO_3H
Pore diameter = 3,5 nm
Specific area = 742 m^2/g
$[H^+]$ = 0,44 mmol/g



HMS_1-SO_3H
Pore diameter = 2,8 nm
Specific area = 1093 m^2/g
$[H^+]$ = 0,21 mmol/g



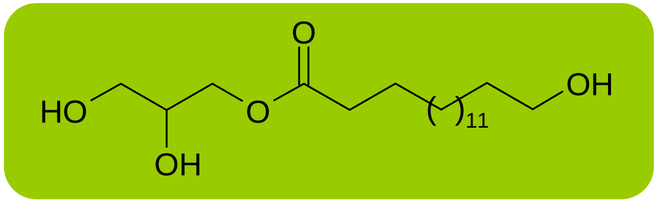
HMS_2-SO_3H
Pore diameter = 2,3 nm
Specific area = 1290 m^2/g
$[H^+]$ = 0,24 mmol/g

80%
TOF = 11h^{-1}

PTSA
35%
TOF = 45h^{-1}

80%
TOF = 10.5h^{-1}

Synergistic effect hydrophilicity-porosity

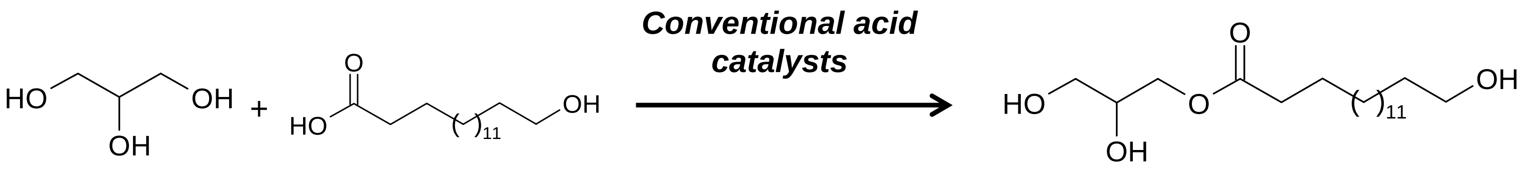


91%

TOF = 4.5h^{-1}

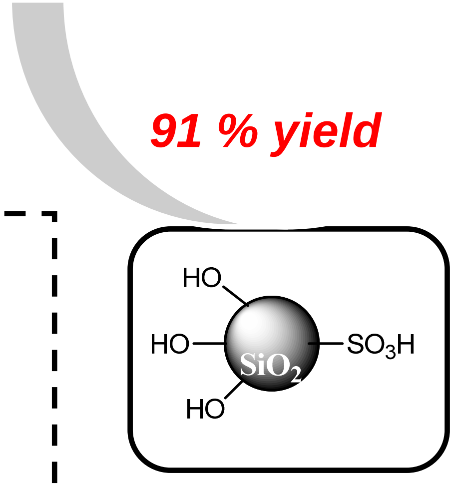
A. Karam, Y. Gu, F. Jérôme, J.-P. Douliez, J. Barrault, *Chem. Commun.*, **2007**, *22*, 2222

Esterification over silica-suported –SO_3H

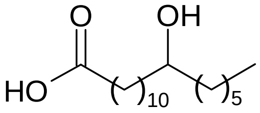


Juniperic acid

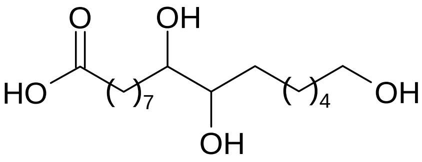
12-35% yield



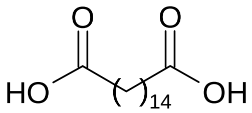
91 % yield



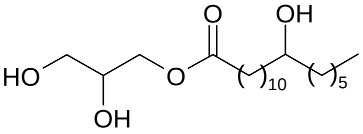
12-hydroxystearic acid



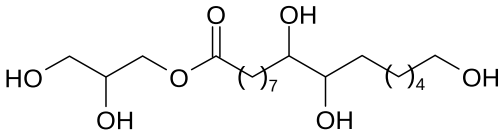
Aleuritic acid



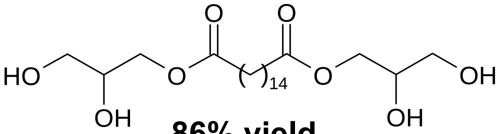
Thapsic acid



77% yield



92% yield



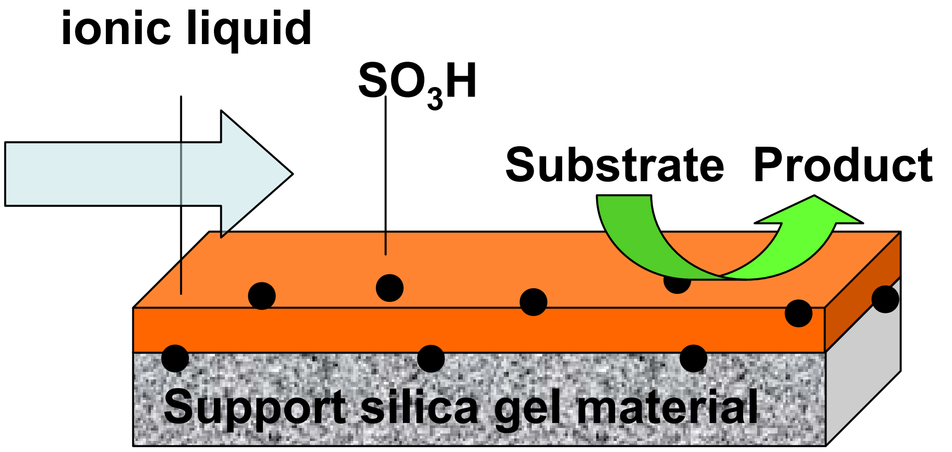
86% yield

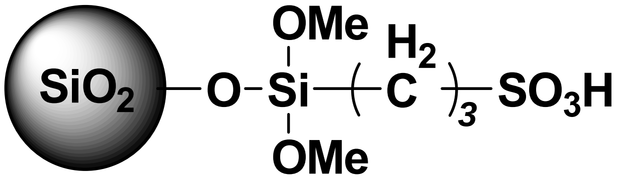
Chem. Commun., **2007,** 22, 2222

Ionic liquid-assisted catalysis by silica based hybrid materials

Proposal:

Acid catalysis based ionic liquid-assisted silica-supported sulfonic acid catalysts in aqueous solution.



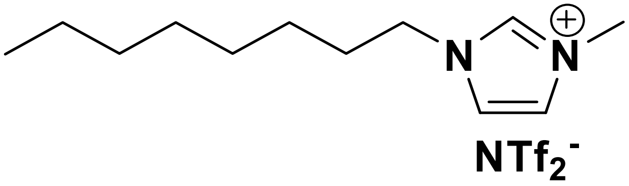


$$SiO_2-O-Si(OMe)_2-(CH_2)_3-SO_3H$$

Silica-SO_3H **1**: IEC = 0.57 mmol/g
Silica-SO_3H **2**: IEC = 0.45 mmol/g
Silica-SO_3H **3**: IEC = 0.32 mmol/g

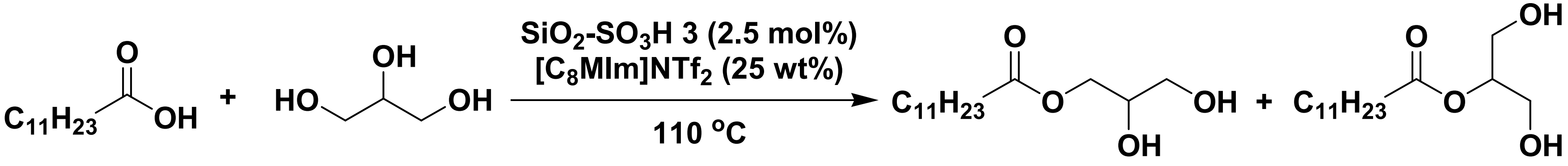
Ionic Liquid:

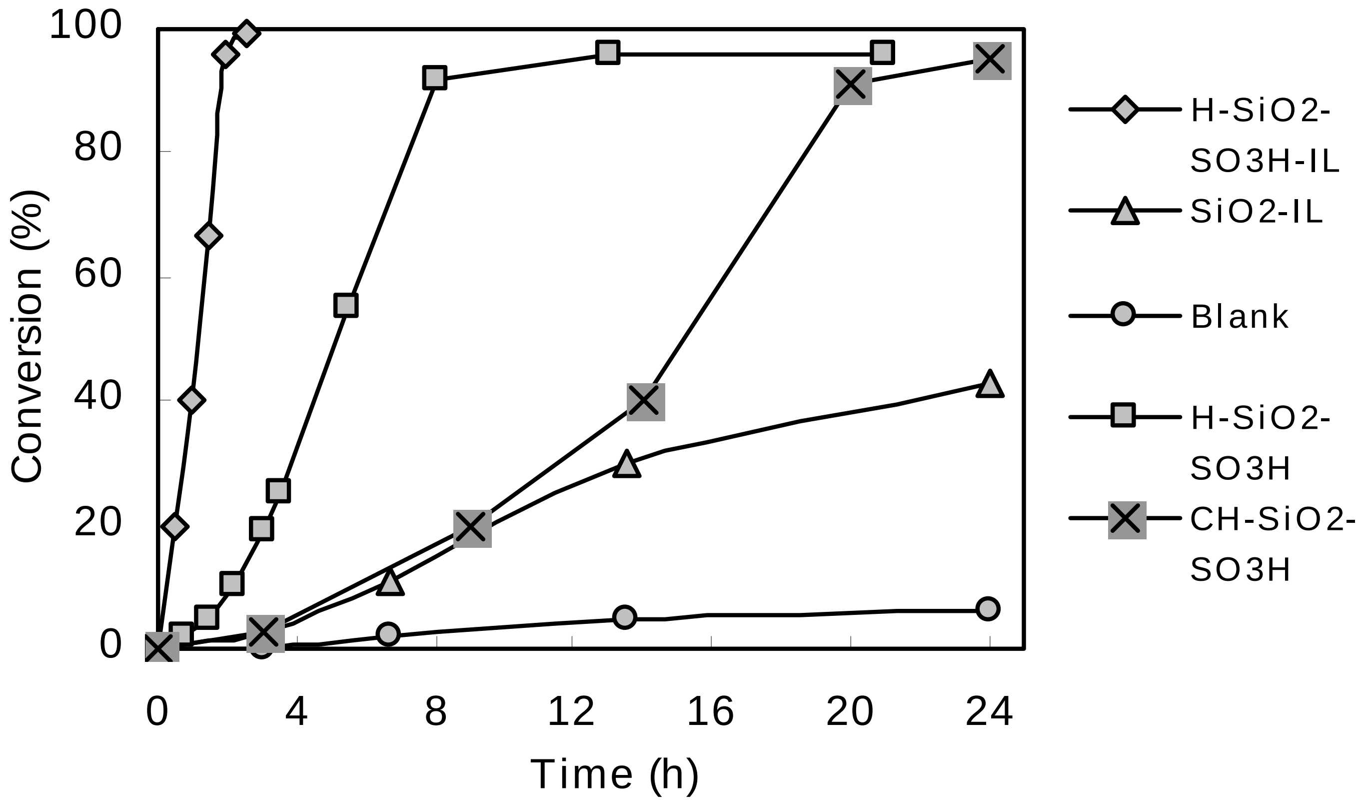
$[C_8MIm]NTf_2$



Yanlong Gu, François Jerome and joel Barrault, Org. Lett., 2007, 9,16, 3145-3148

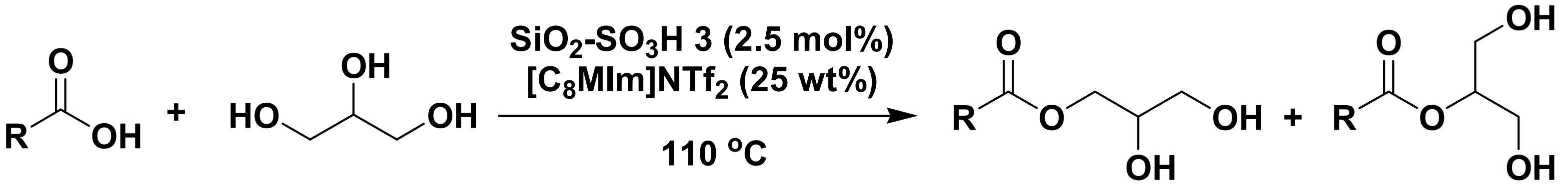
Glycerol esterification using SiO_2-SO_3H-IL as catalyst





Yanlong Gu, François Jerome and joel Barrault, Org. Lett., 2007, 9,16, 3145-3148

Substrate scope for esterification in glycerol using SiO_2-SO_3H-IL as catalyst



Entry	Fatty acid	Time (h)	Conv. (%)	Sel. (%)
1	Decanoic acid	2	99	83
2	Undecanoic acid	2	98	82
3	10-Decenoic acid	2	99	83
4	11-Bromoundecenoic acid	4	98	80
5	Myristic acid	6	95	80
6	Palmitic acid	8	94	75
7	Stearic acid	12	91	74
8[a]	Lauric acid	2	97	82

[a]: reused in the third run.

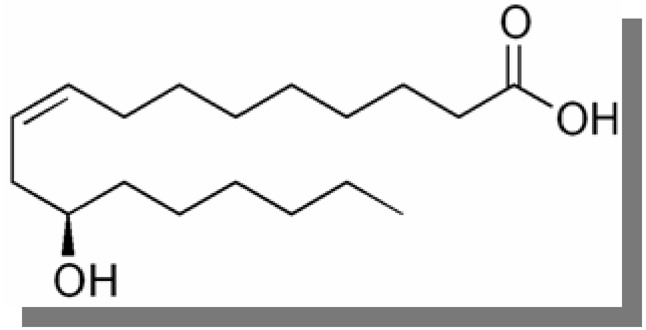
Yanlong Gu, François Jerome and joel Barrault, Org. Lett., 2007, 9,16, 3145-3148

MICROWAVE-ASSISTED TRANSESTERIFICATION OF CASTOR OIL

Castor seed oil

Fatty acids present in castor seed oil

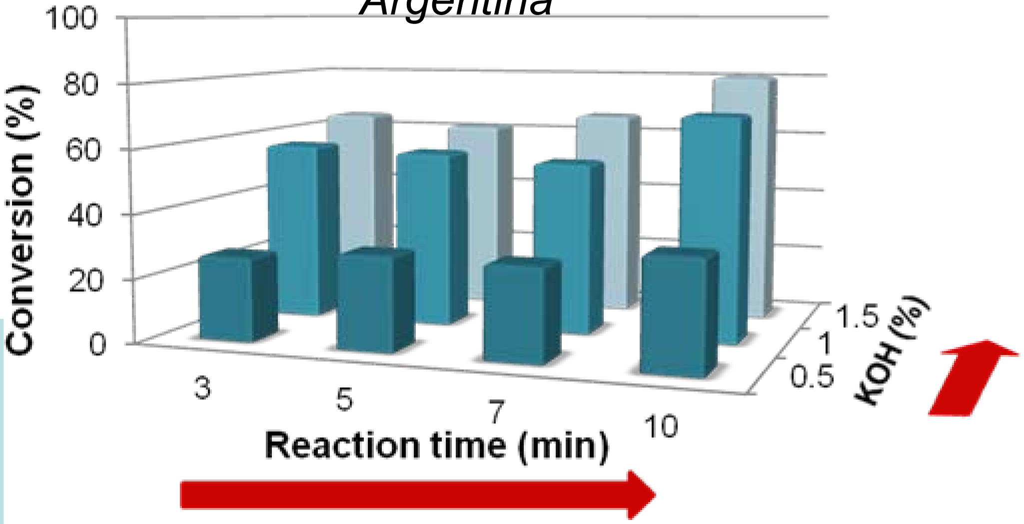
Fatty acid	Percentage (%)
12-OH-9-C18:1 Ricinoleic	88.1
C18:1 Oleic	4.3
C18:2 Linoleic	4.2
C18:0 Stearic	1.6
C16:0 Palmitic	1.0
C18:3 Linolenic	0.7
C20:0 Araquidic	<0.1
C22:0 Behenic	<0.1



Ogunniyi. 2006.Bioresour. Technol. 97: 1086-1091
Meneghetti et al., 2006. JAOCS. 83: 819-822

Effect of reaction time and catalyst concentration on biodiesel conversion
Molar ratio EtOH:oil 10:1, T = 60°C

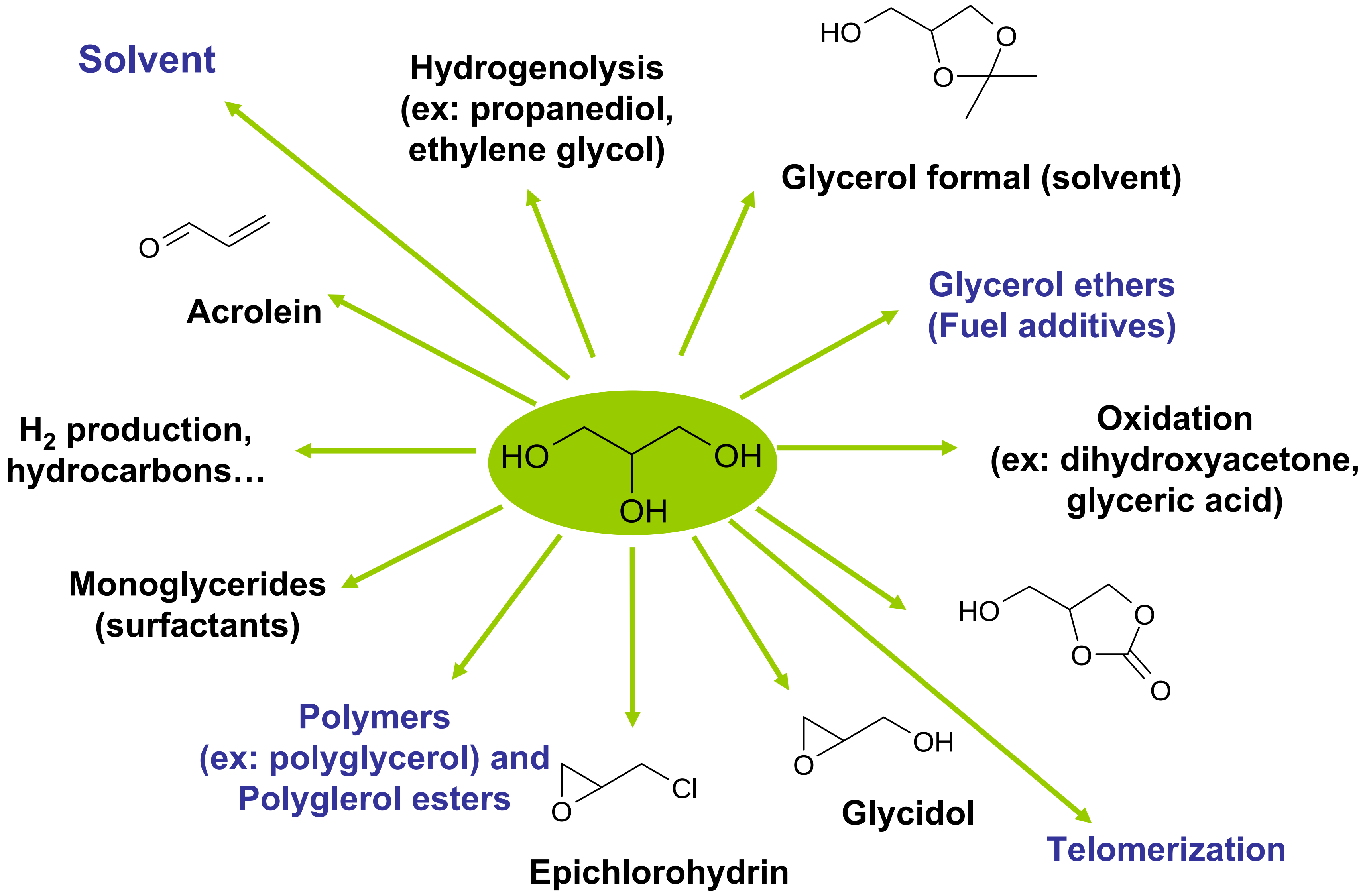
Publication accepted next ‘Simposio IBA de catalisis’, 09-2012, Santa Fe - Argentina



Conversion:
conventional heating
78,6%
60°C, 1.5% KOH, molar ratio 10:1, 1 h)

	Reaction time (min)			
	3	**5**	**7**	**10**
Catalyst concentration (% w/w)				
0.5	26.5	29.5	29.0	34.3
1.0	57.2	56.0	54.2	70.3
1.5	64.6	61.6	66.3	**80.1**

Glycerol: selective and catalytic activation and uses



Solvent

Hydrogenolysis
(ex: propanediol,
ethylene glycol)

Glycerol formal (solvent)

Acrolein

Glycerol ethers
(Fuel additives)

H_2 production,
hydrocarbons…

Oxidation
(ex: dihydroxyacetone,
glyceric acid)

Monoglycerides
(surfactants)

Polymers
(ex: polyglycerol) and
Polyglerol esters

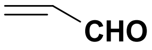
Epichlorohydrin

Glycidol

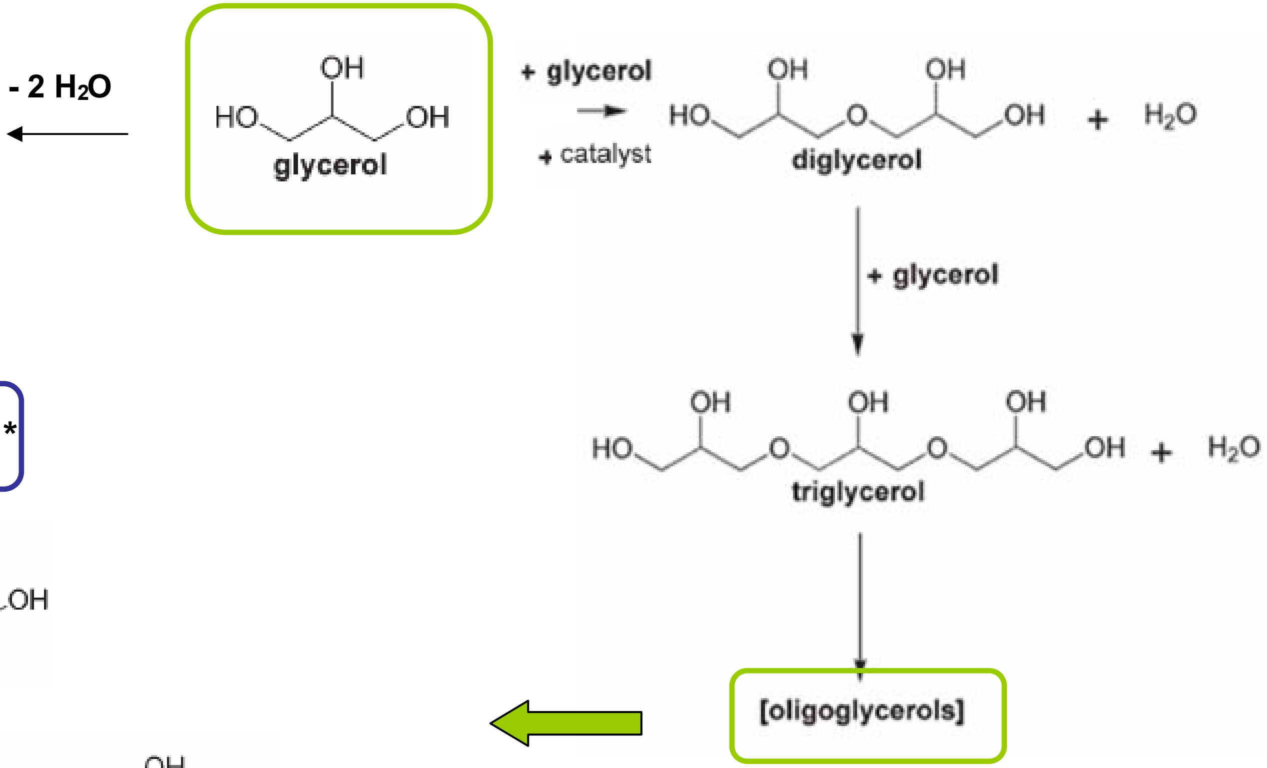
Telomerization

Catalytic oligomerization of glycerol

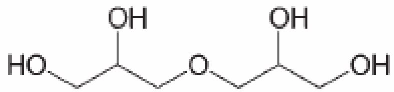
Undesired product



acrolein

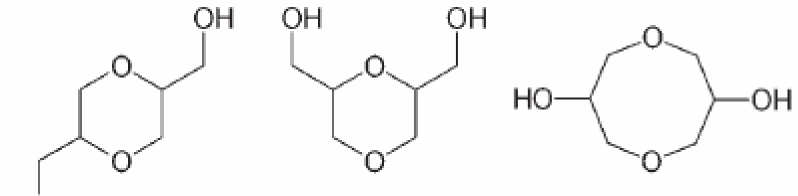


Regioisomers *

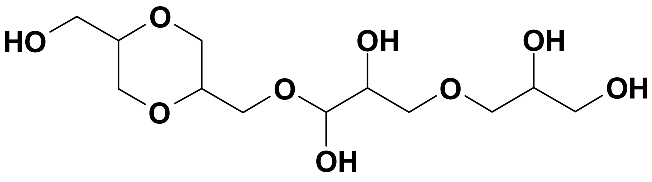


linear diglycerol

branched diglycerols



cyclic diglycerols



Selective synthesis of polyglycerols: selectivity of the Mg-lizardite and Mg-talc phyllosilicates

Select. (%)	Di Gly	Tri Gly	Tetra Gly	Penta Gly
Mg-Liz C	50	27	15	8
Mg-Liz R	53	30	12	5
Mg-Talc	50	25	16	9
Mg-MCM	60	32	8	-

Selectivity ≥ 90%
at 80% conv.
after 4h reaction

Similar selectivity for

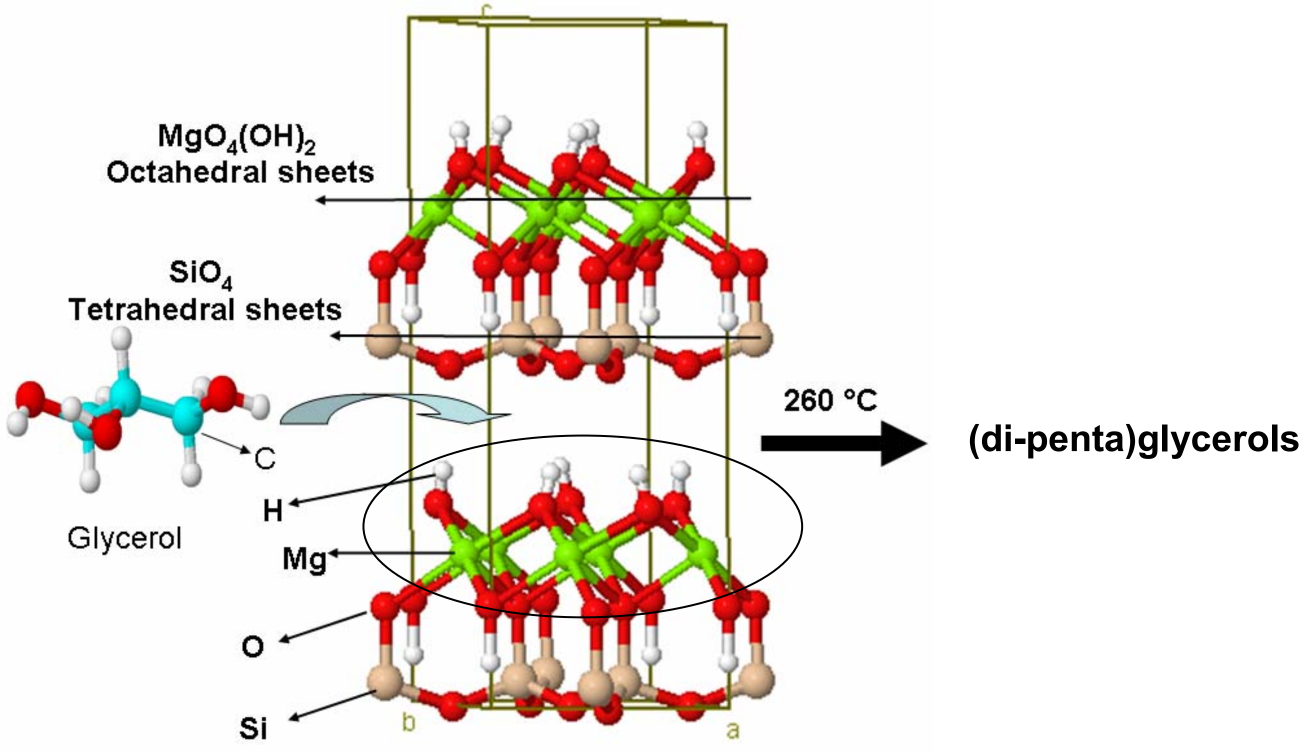
- both Mg-phyllosilicates
- reused Mg-Liz / Mg-Liz

Larger fraction of polyglycerols for Mg-PS compared to Mg-MCM-41

Selectivity to each oligomer ≤ 50%

Selective synthesis of polyglycerols: activity of the Mg-lizardite phyllosilicate (260°C)

TO structure



- **Higher hydrophilicity** of the TO structure than TOT one

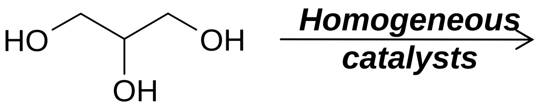
  ⇒ strong interaction with hydrophilic glycerol

- **Higher accessibility** of glycerol to structural Mg species / **higher basicity** of the Mg-Liz

- Key role of **both basic** (deprotonation of glycerol OH group) and **Lewis acid sites** (OH leaving process)

Conclusion (1)

Vegetable oils



glycerol

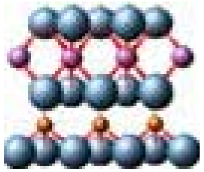
High activity
Non-selective polymerization
Side production of acrolein

ACTIVITY / SELECTIVITY

Organized porous silica-based catalysts

- **Moderate activity**
- **Porosity ⇒ (di-tri)glycerols fraction**

Hydrothermally synthesized Mg-based phyllosilicates



- **Surface hydrophilicity of Mg-Liz**
- **Dispersion/strength of <u>structural</u> active sites**
- **High activity, selectivity (Reach) & stability**

Scaling-up (ANR MATETPRO)

Preparation and shaping of catalyst / Pilot: Synthesis of polyglycerols

Bioproducts

Surfactants, cosmetics, food, pharmaceutical industry

Conclusion (2)
Polyglycerol esters

From **glycerol and methyl esters in a one step process** performed in the same experimental conditions

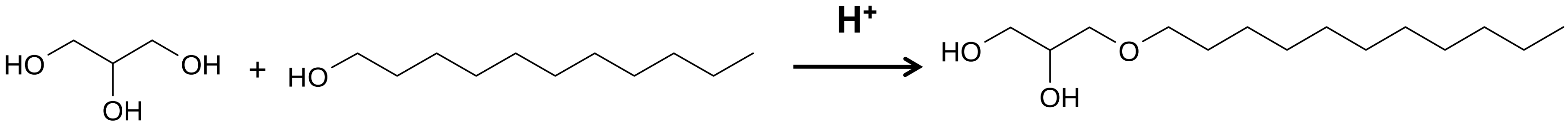
- Over mesoporous and basic MCM 41 catalysts

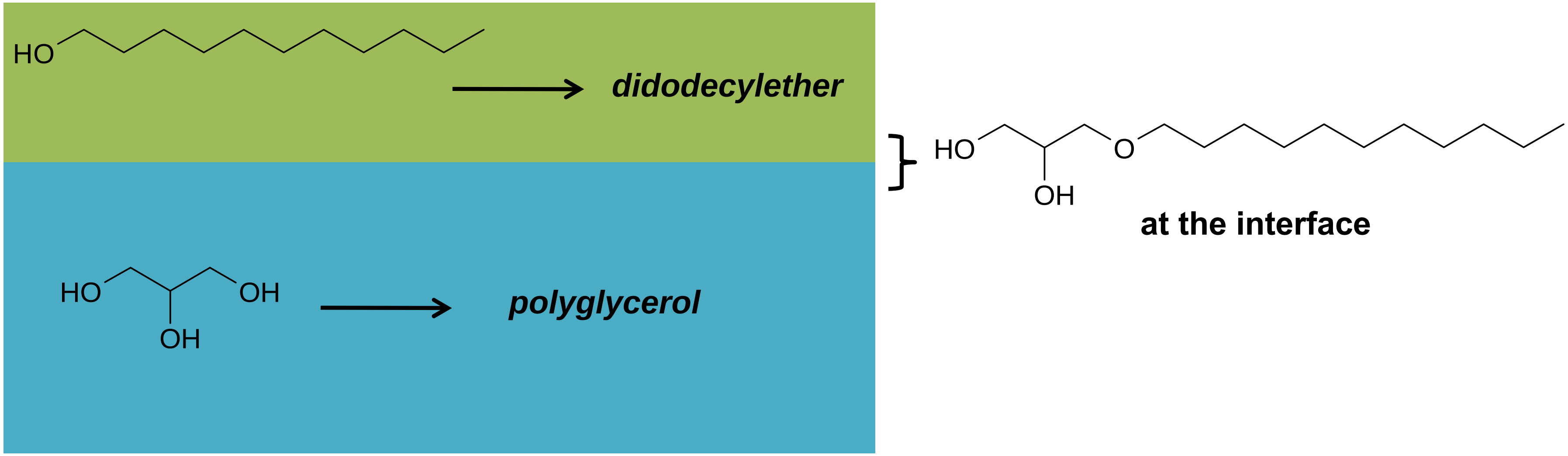
Diglycerol esters are the main products

- Over Mg-based phyllosilicates

Di-and triglycerol esters are mainly obtained

Etherification of glycerol with fatty alcohols





didodecylether

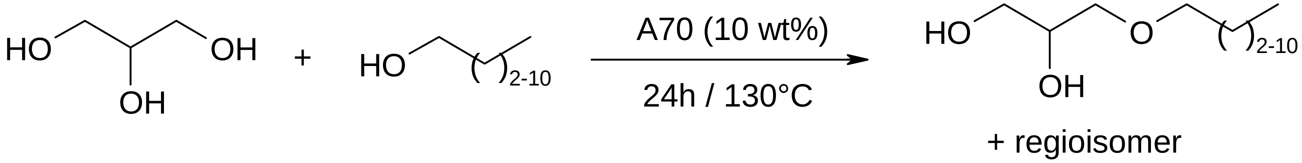
polyglycerol

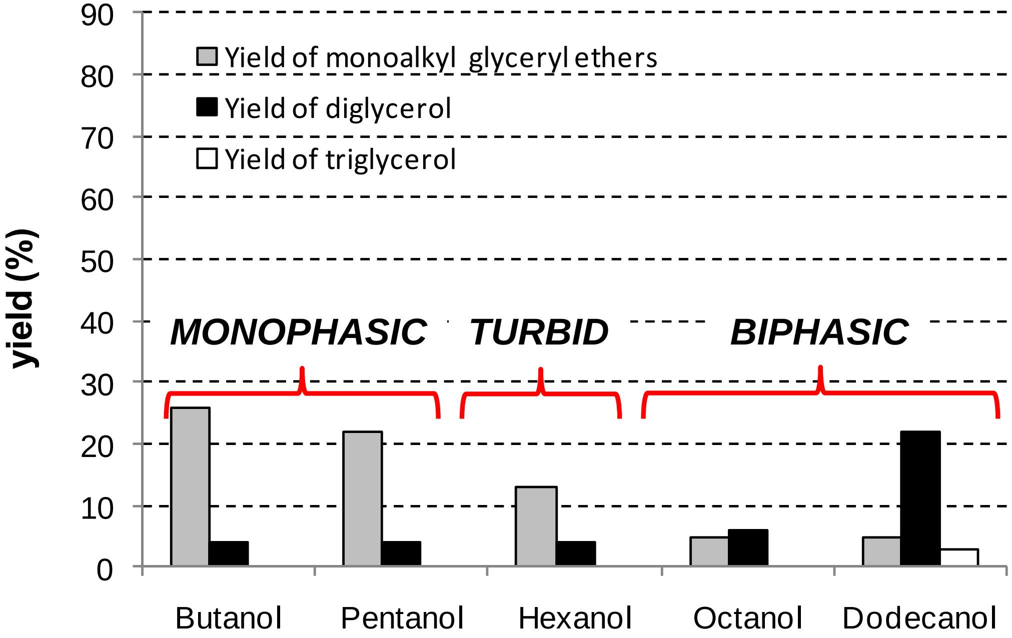
at the interface

1) Glycerol and fatty alcohol are not miscible

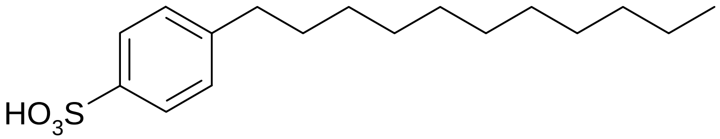
2) Glycerol and fatty alcohol can be oligomerized or dimerized

Etherification of glycerol with fatty alcohols

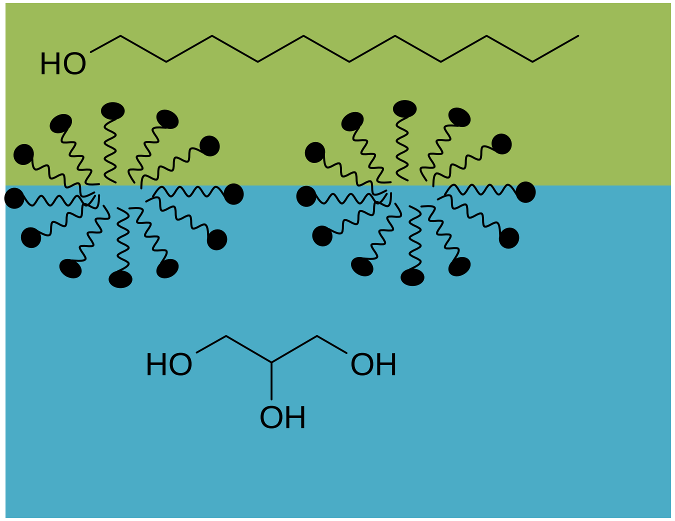


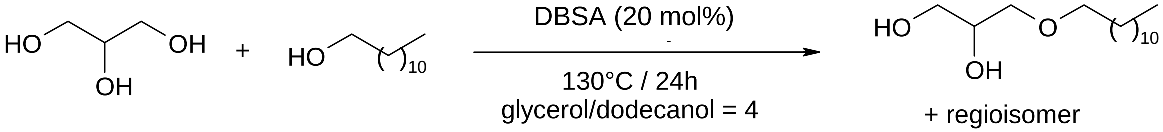


Etherification of glycerol with fatty alcohols



Dodecylbenzene sulfonic acid: **a surfactant-combined-catalyst**

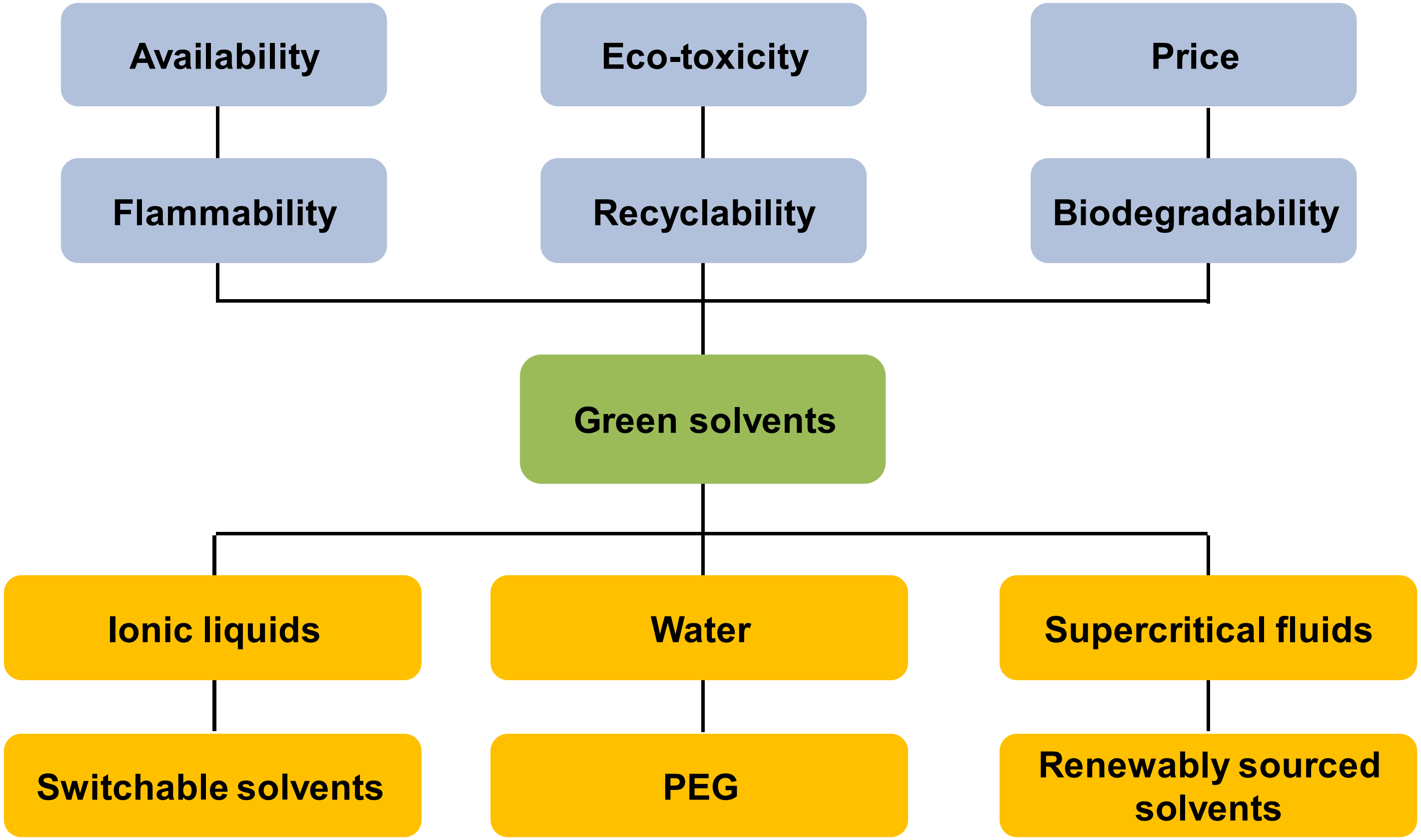




Catalyst	Conv. gly	Conv. dode	Monoether	Diglycerol	Didodecylether
A70	36%	5%	5%	22%	0%
DBSA	59%	50%	**25%**	9%	19%

GLYCEROL: NEW GENERATION OF BIO-BASED SOLVENTS

Green solvents



Availability

Flammability

Eco-toxicity

Recyclability

Price

Biodegradability

Green solvents

Ionic liquids

Switchable solvents

Water

PEG

Supercritical fluids

Renewably sourced solvents

P. G. Jessop, Green Chem. 2011, 13, 1391

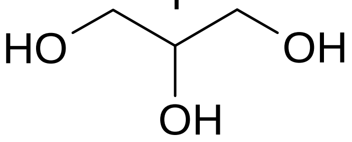
Glycerol

Available in large scale
(□ *2Mt/year*)

Renewable

Cheap *(<0.5€/Kg)*

Non-toxic
LD50 (oral rat)=12600 mg/Kg



Non-flammable

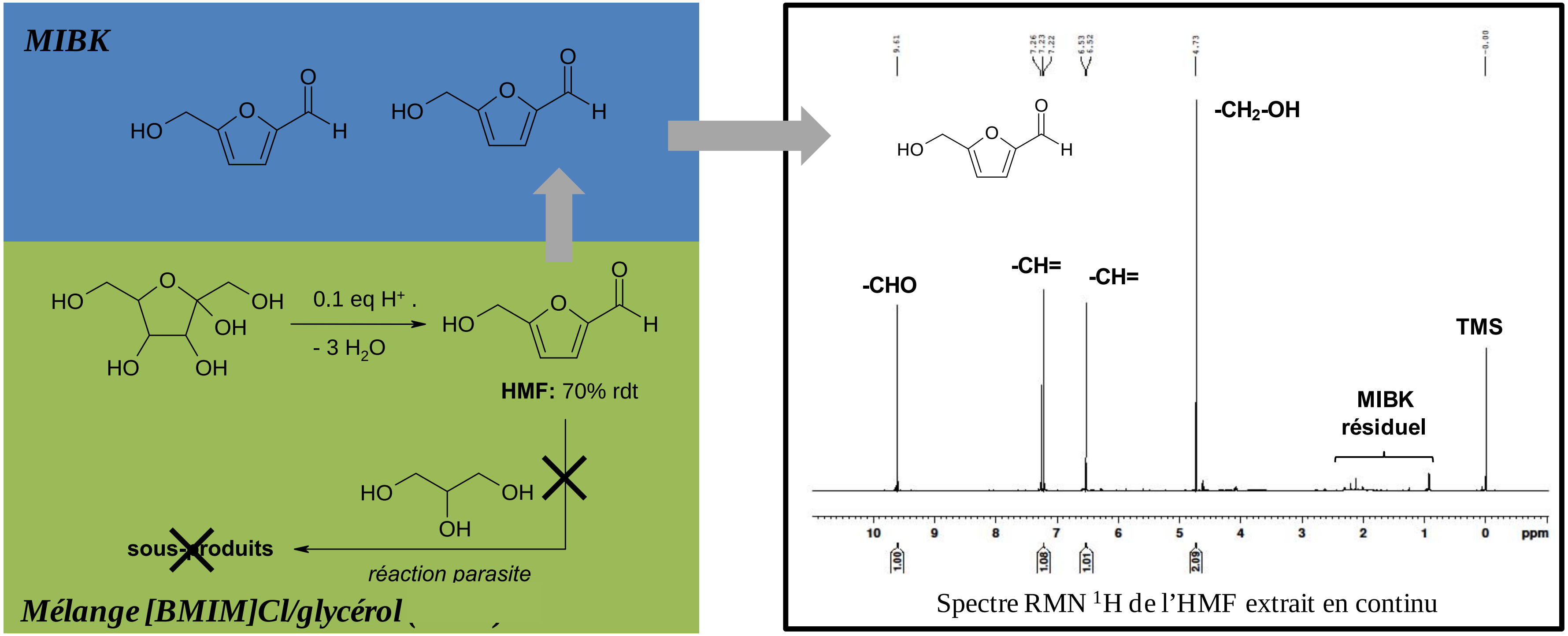
glycerol

Reactivity

Mass transfer

Work-up
Boilling point = 290°C

Glycerol: as a renewably sourced co-solvent



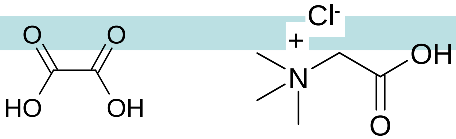
Spectre RMN ^{1}H de l'HMF extrait en continu

1) 50mol % of [BMIM]Cl can be sustituted by glycerol
2) Continuous extraction of HMF with MIBK
3) Isolated yield> 70%, purity 95%

M. Benoit, Y. Brissonnet, E. Guélou, K. De Oliveira Vigier, J. Barrault, F. Jérôme, *ChemSusChem*, **2010**, *11*, 1298

Green solvents

Oxidation of carbohydrates

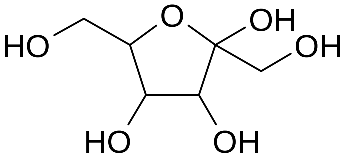


Waste of sugar beet industry

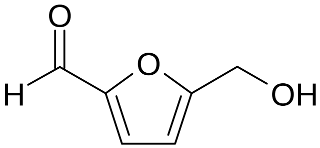
CATALYSTS

S. Hu, Z. Zhang, Y. Zhou, J. Song, H. Fan, B. Han, *Green Chem.*, **2009**, *11*, 873-877

K. De Oliveira Vigier, A. Benguerba, J. Barrault, F. Jerome, ChemSusChem accepted, 2012



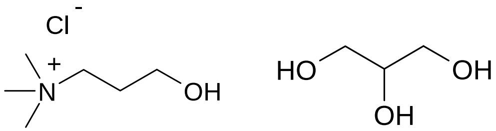
GREEN EUTECTIC SOLVENT « biocompatible ionic liquids »



Yield up to 84%

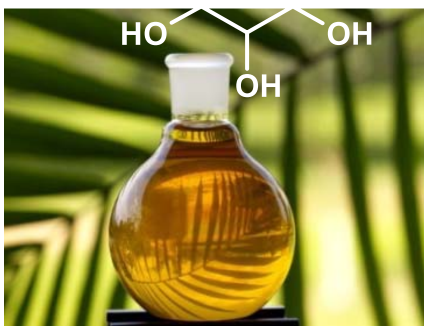
- ❶ ***Recovery by liquid-liquid extraction***
- ❷ ***Recyclable media***

BIOMASS



SAFE DERIVATIVES

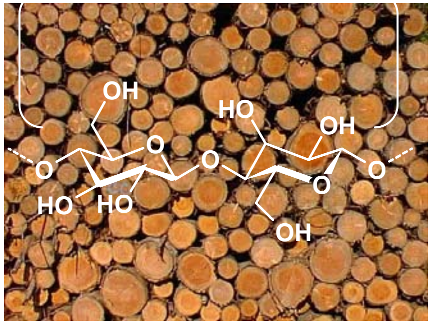
From vegetable oils to lignocellulosic compounds
From glycerol to carbohydrates



Glycerol

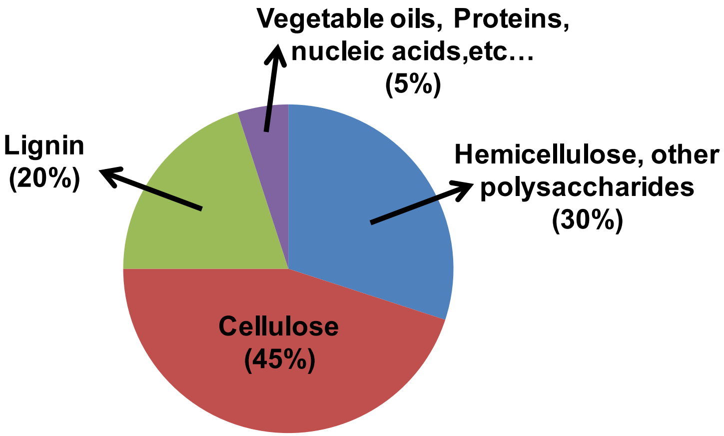
Etherification of disaccharides

J. Mol. Cat. A, **2006**, 259, 67



Cellulose

Biomass



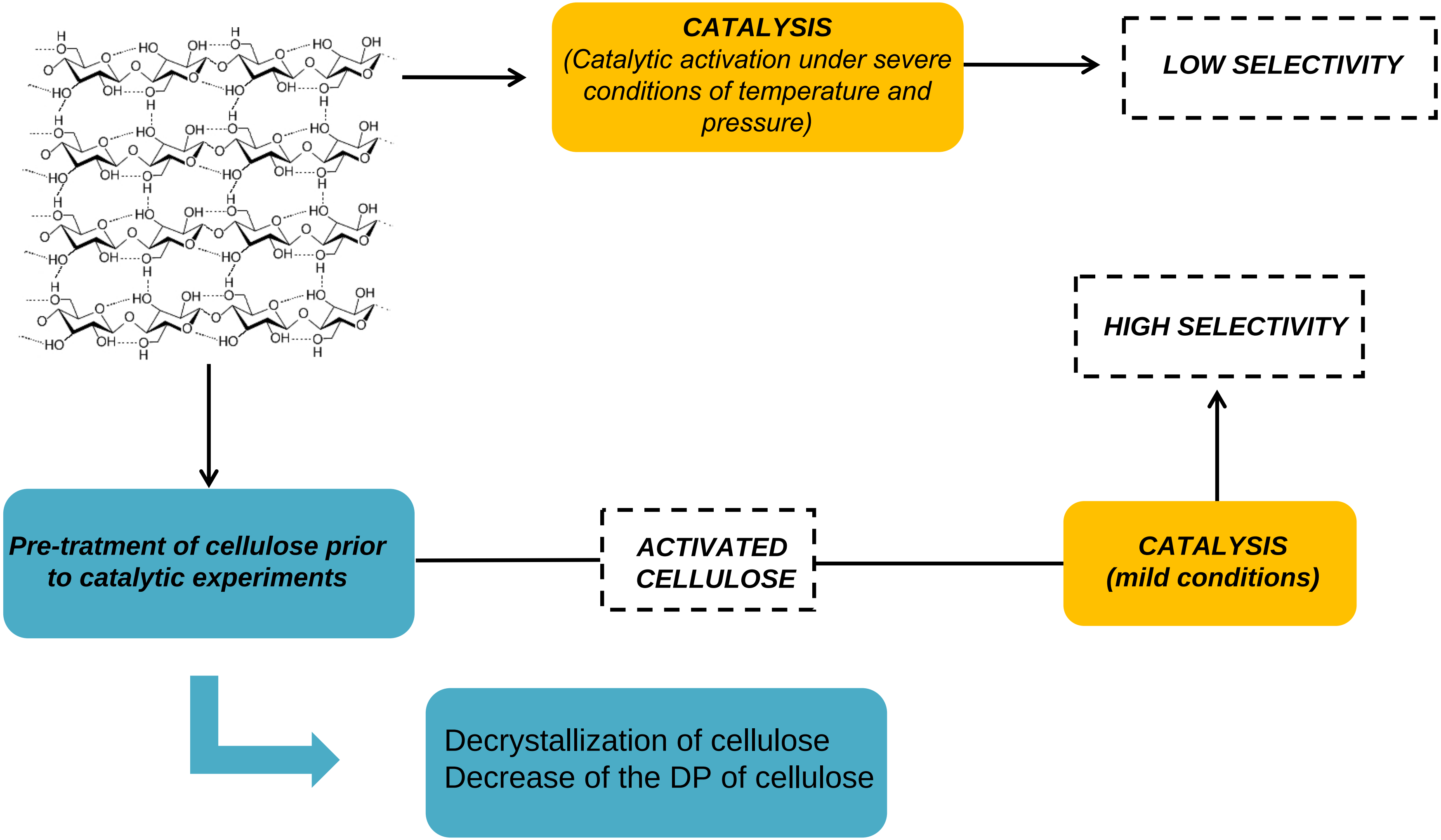
Biomass production: 180 billions t/year

Transportation fuels
(ethanol, hydrocarbons, etc…)

Fine chemicals

CATALYSIS AND LIGNOCELLULOSE

Cellulose: a recalcitrant biopolymer for heterogeneous catalysis



CATALYSIS
(Catalytic activation under severe conditions of temperature and pressure)

LOW SELECTIVITY

Pre-tratment of cellulose prior to catalytic experiments

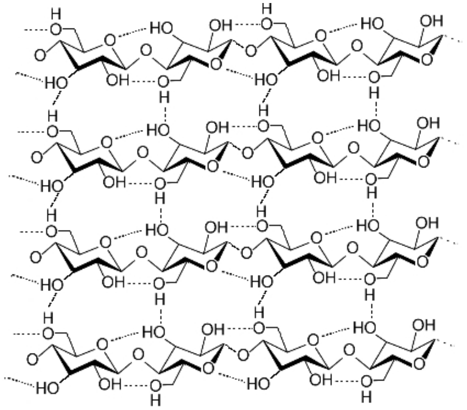
ACTIVATED CELLULOSE

CATALYSIS
(mild conditions)

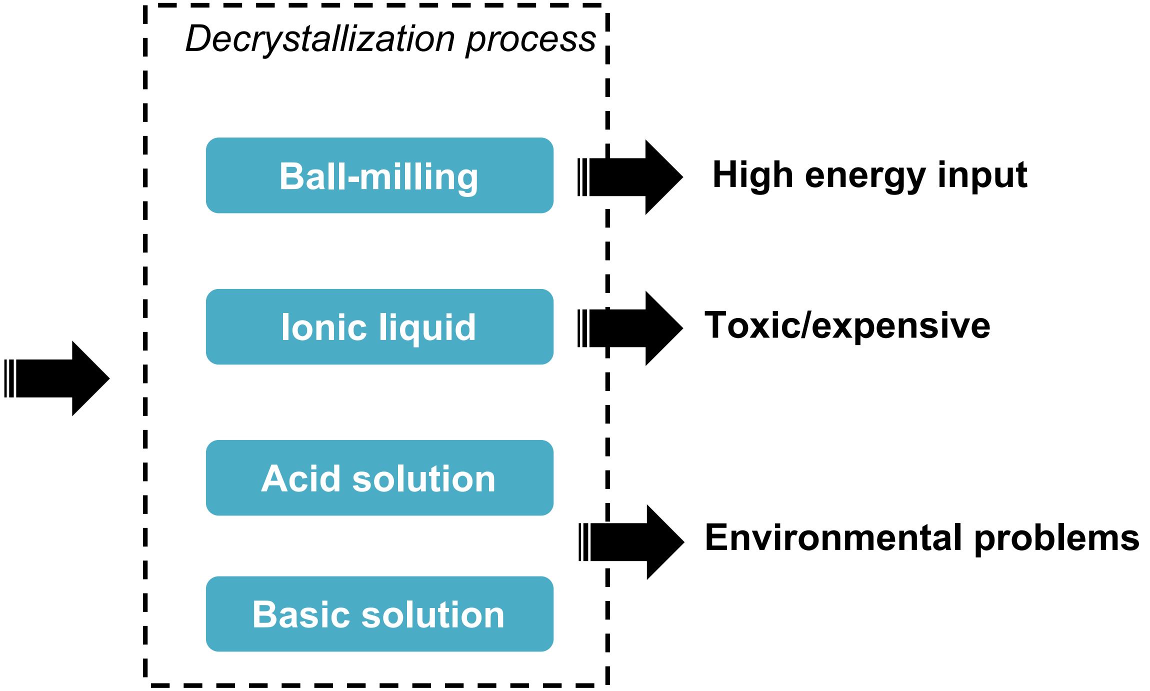
HIGH SELECTIVITY

Decrystallization of cellulose
Decrease of the DP of cellulose

Pre-treatment of cellulose



Microcrystalline cellulose



Decrystallization process

Ball-milling

Ionic liquid

Acid solution

Basic solution

High energy input

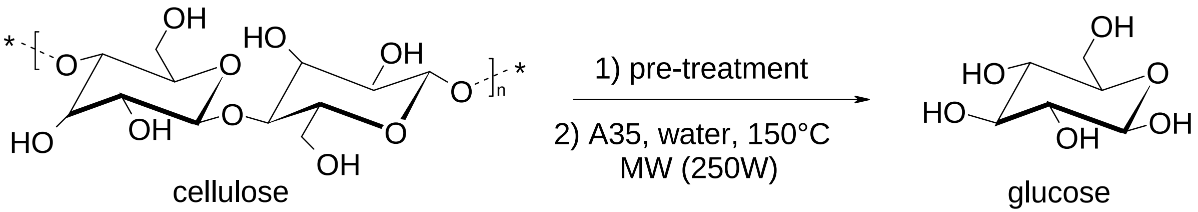
Toxic/expensive

Environmental problems

Physical treatment
Plasma technology

Chemical treatment
Biorenewable ionic liquids

Impact on solid catalyst activity



Pre-treatment	DP of cellulose (%)	Crystallinity of cellulose	Yield of glucose (%)
-	200	Highly crystalline	< 1
[BMIM]Cl	200	amorphous	14
[BMIM]Et_2PO_4	200	amorphous	9
[BMIM]OAc	200	amorphous	3
[Choline]OAc	200	amorphous	9
Ball-milling	200	amorphous	13
Plasma	120	Highly crystalline	22
Ball-milling/Plasma	**40**	amorphous	**58***

* After only 5 min of reaction

Activation of cellulose: low DP>amorphization

Conclusion

Ideal conditions for the heterogeneously-catalyzed hydrolysis of cellulose

Cellulose

Decrease the DP

Decrystallization of cellulose

↓

Dispersion of cellulose in water: better contact with solid catalysts

Solid catalyst

Stability in water

Swelling/dispersion in water

Bifunctional surfaces (acid sites + ionic sites)

Small particle size

Other strategy: combination of heterogeneous and homogeneous catalysis

Main Conclusions

- Multifunctional catalysts are efficient materials for getting activity and selectivity from different renewable ressources (esters, glycerol but also sugars and cellulose as well as lignine compounds)
- But it also appears that the association of homogeneous or/and heterogeneous catalysts to other rather physical techniques (i.e.microwaves, non-thermal plasma, ball-milling) strongly improve the efficiency of some of these reactions.
- Search of specific catalytic materials to increase the performances in these new experimental conditions are on the way