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DEVELOPMENT OF BENCHMARK C-BASED ACID CATALYSTS FOR LIGNOCELLULOSIC BIOMASS CONVERSION INTO 5-HMF

PHOSPORE SPRING SCHOOL 14 – 16 April 2024

Presentation by Tonelli Alessia – PhD H WP3

PHOSPORE framework

A brief overview upon the role of PhD student H

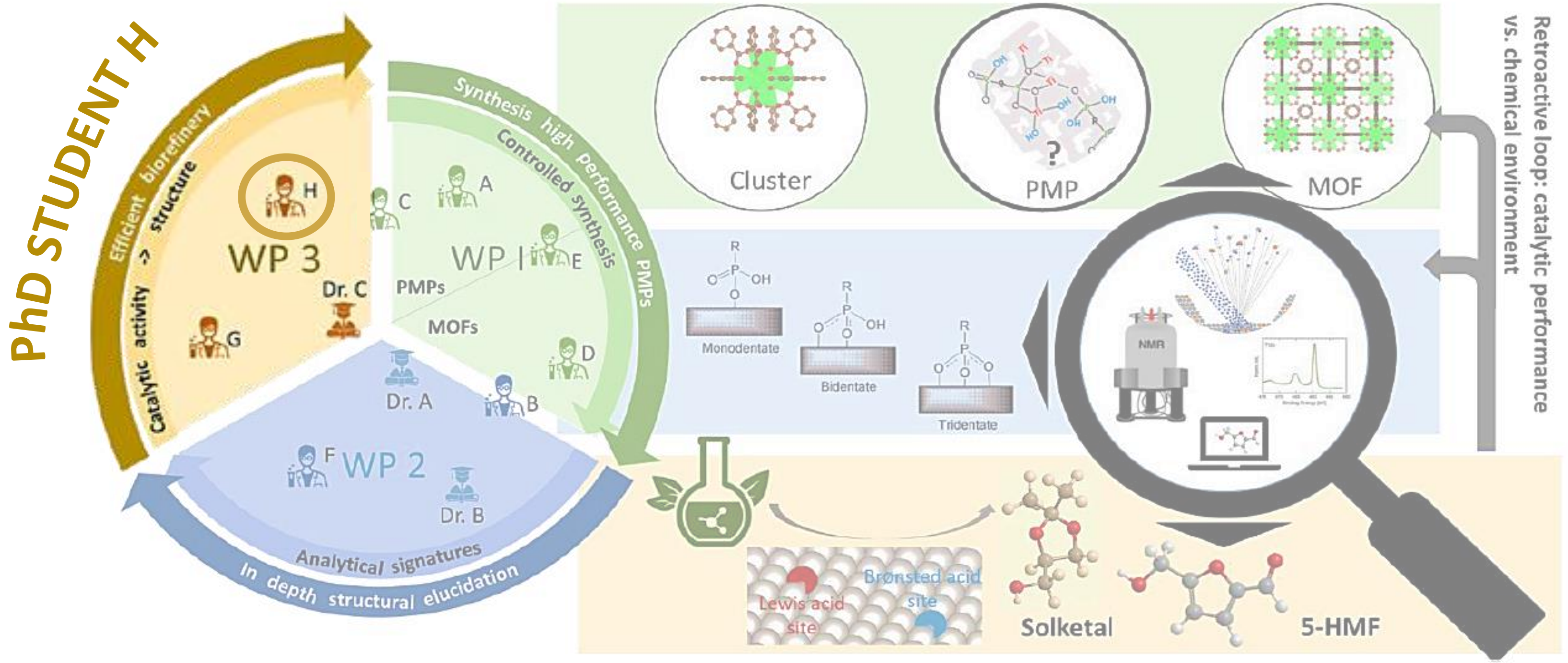
STARTING 01.10.2023

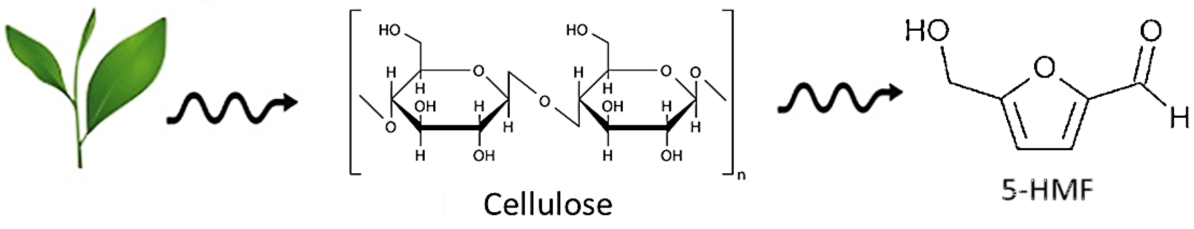
SUPERVISOR: Prof. Sophie Hermans

IMCN UCLouvain

DEVELOPMENT OF BENCHMARK CATALYSTS

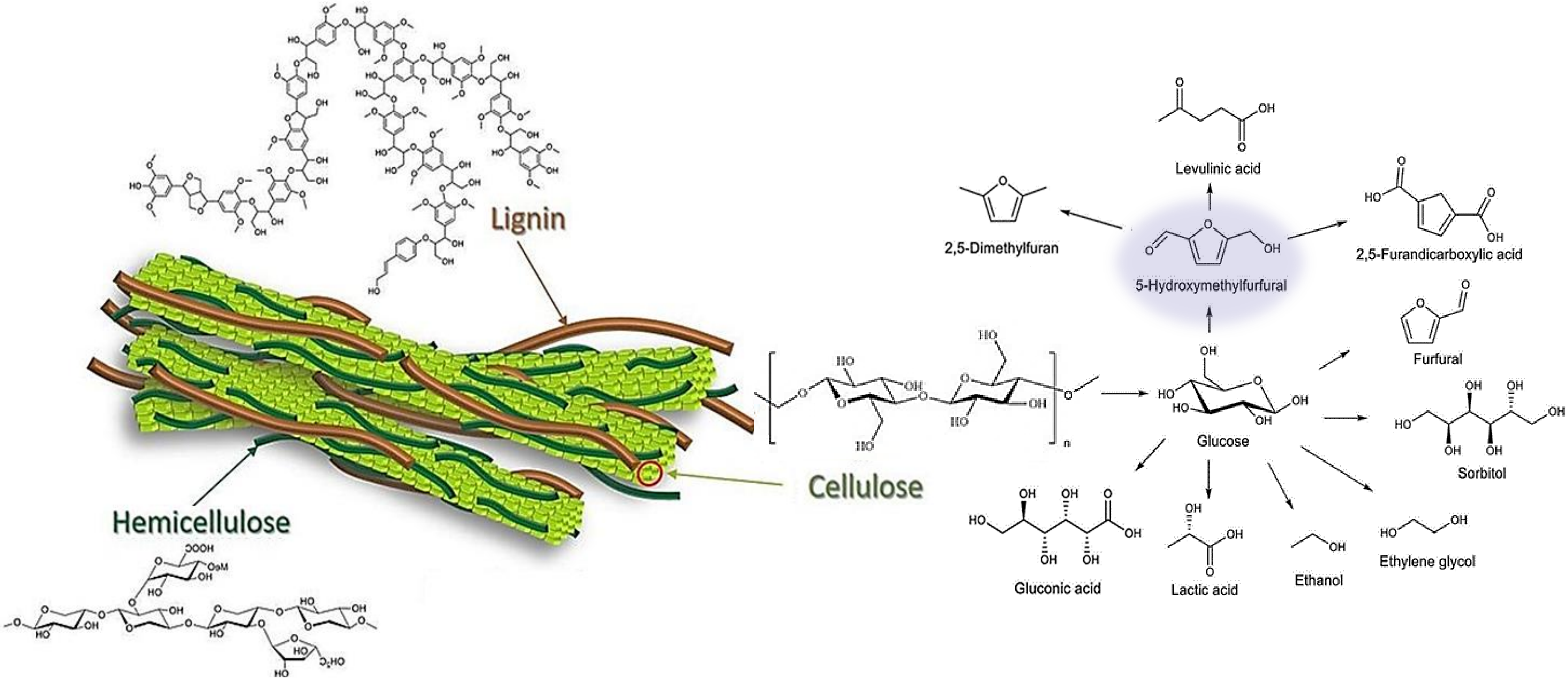
CATALYTIC TESTS ON WP1 MATERIALS





5-hydroxymethylfurfural (5-HMF)

A high added-value platform chemical to be recovered and valorized

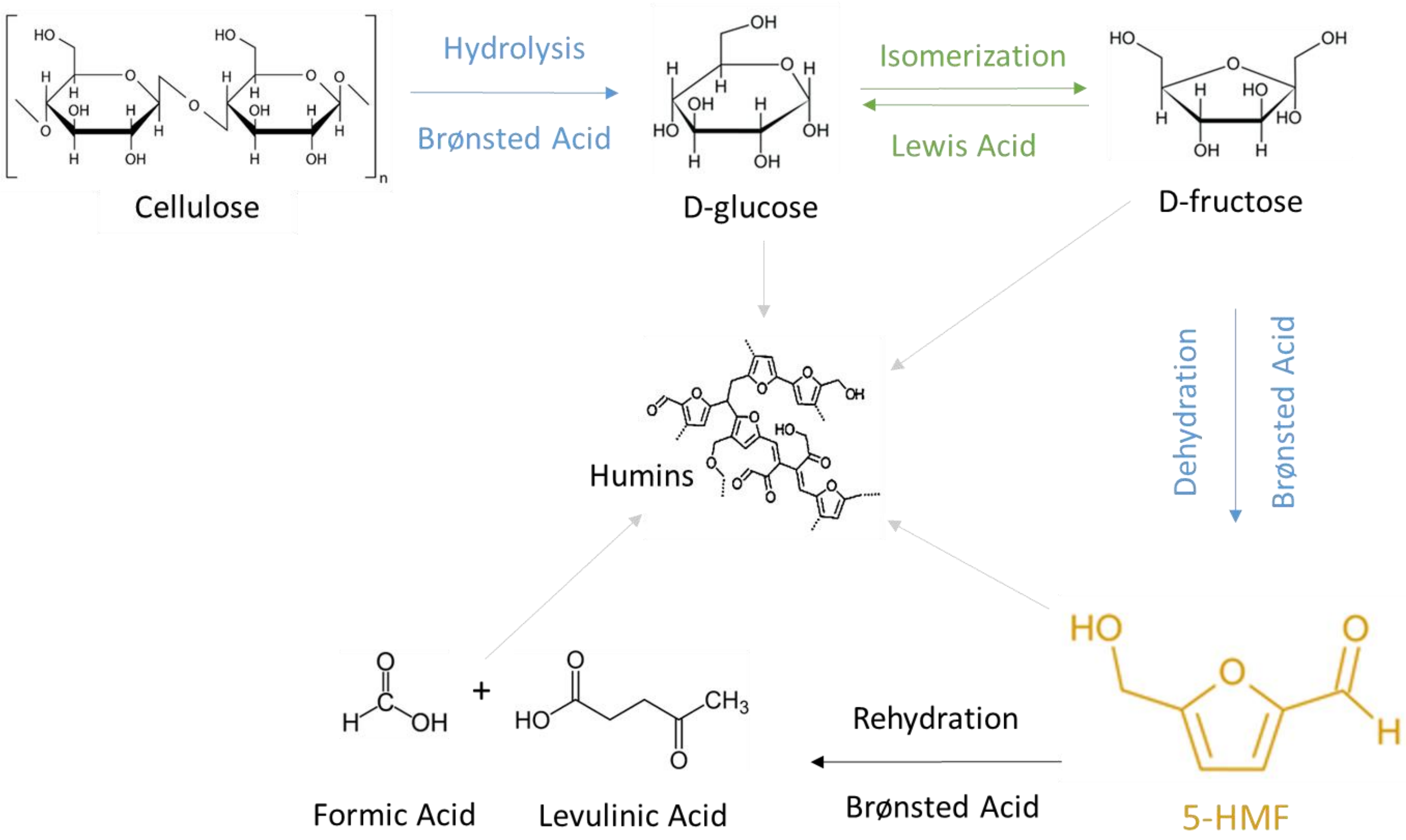


Jensen et al, 2017; 10.1007/s13399-017-0248-8.

5-hydroxymethylfurfural (5-HMF)

A high added-value platform chemical to be recovered and valorized

Three-step conversion enhanced by acid catalysis:



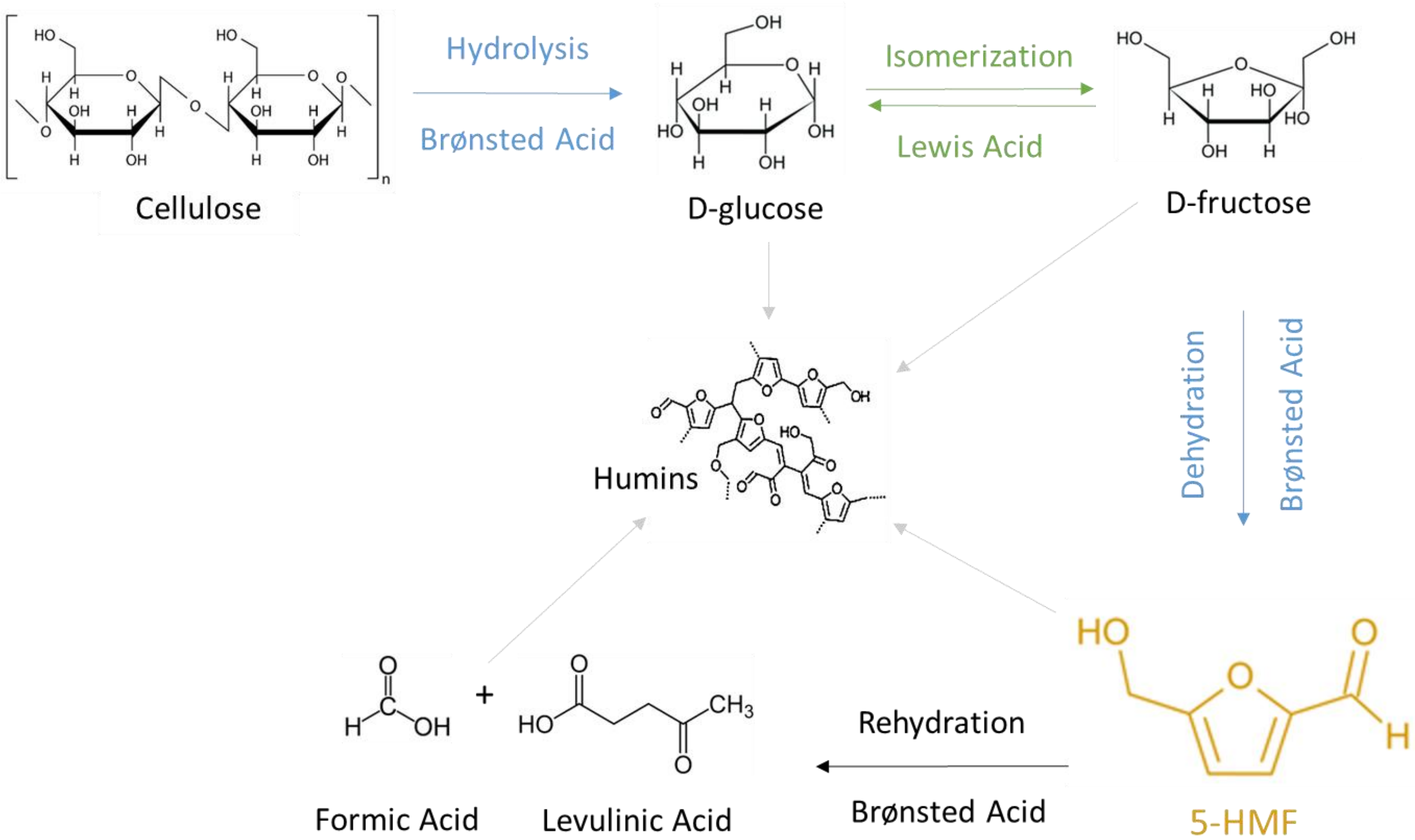
- **Both acidic sites** in a **balanced ratio**;
- **High conversion** and **yield** (avoiding further hydration);
- **High selectivity** (preventing the formation of sugary by-products or humins).

HETEROGENEOUS

5-hydroxymethylfurfural (5-HMF)

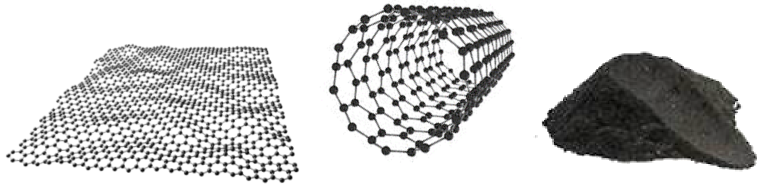
A high added-value platform chemical to be recovered and valorized

Three-step conversion enhanced by acid catalysis:



Carbon-based support:

- Stability in water and O-rich media;
- Good mechanical and chemical resistance;
- Different forms available with **controlled and tuneable porosity**;
- **Easy functionalization**.



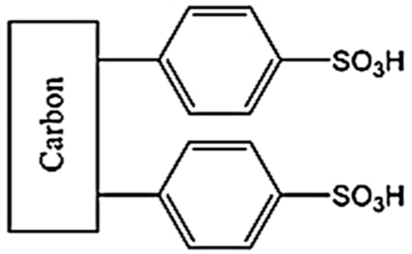
Designed working tasks

Development of bi-functional carbon-based acid catalysts

TASK 1

Preparation and characterization of sulfonated carbons

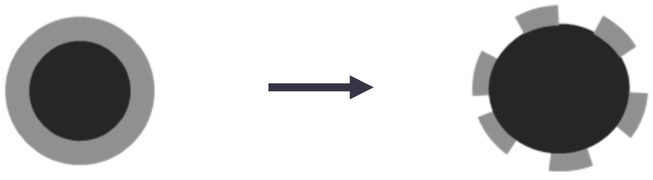
Brønsted acidity



TASK 2

Preparation and characterization of a continuous/discontinuous mesoporous oxide layer on a carbon substrate

Lewis acidity



S. Carlier, Front. Chem. 2020, 8, 347 - T. Haynes, Appl. Cat. B 2019, 241, 196 - T. Haynes, ChemCatChem 2019, 11, 4054

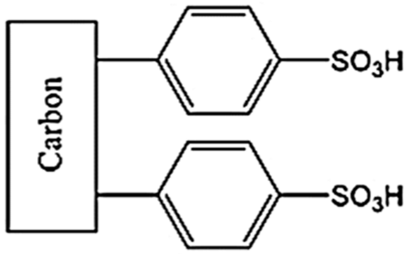
Designed working tasks

Development of bi-functional carbon-based acid catalysts

TASK 1

Preparation and characterization of sulfonated carbons

Brønsted acidity



TASK 2

Preparation and characterization of a continuous/discontinuous mesoporous oxide layer on a carbon substrate

Lewis acidity

PROMOTE ISOMERIZATION
- Aluminium
- Zirconium

PROMOTE DEHYDRATION
- Titanium
- Zinc

Niobium, Hafnium, Tungsten and mixed oxides

Designed working tasks

Development of bi-functional carbon-based acid catalysts

TASK 1

Preparation and characterization of sulfonated carbons

TASK 2

Preparation and characterization of a continuous/discontinuous mesoporous oxide layer on a carbon substrate

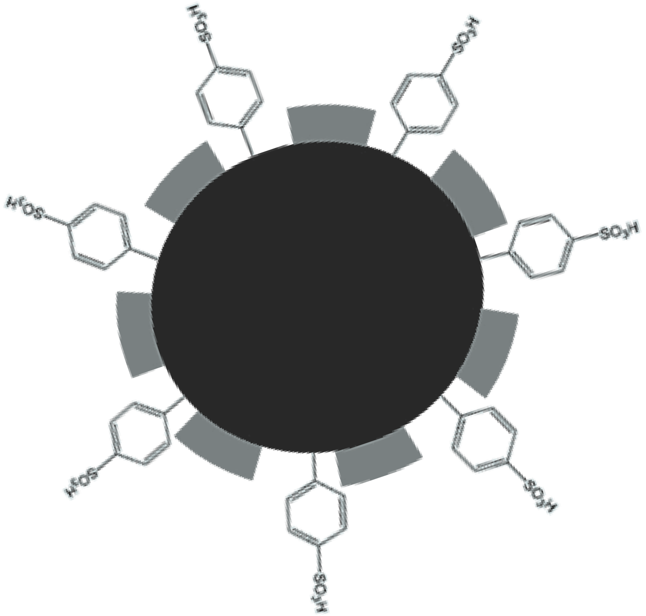
Brønsted acidity

+

Lewis acidity

TASK 3

Synthesis of a bi-functional system: characterization, study of the catalytic performances and optimization.



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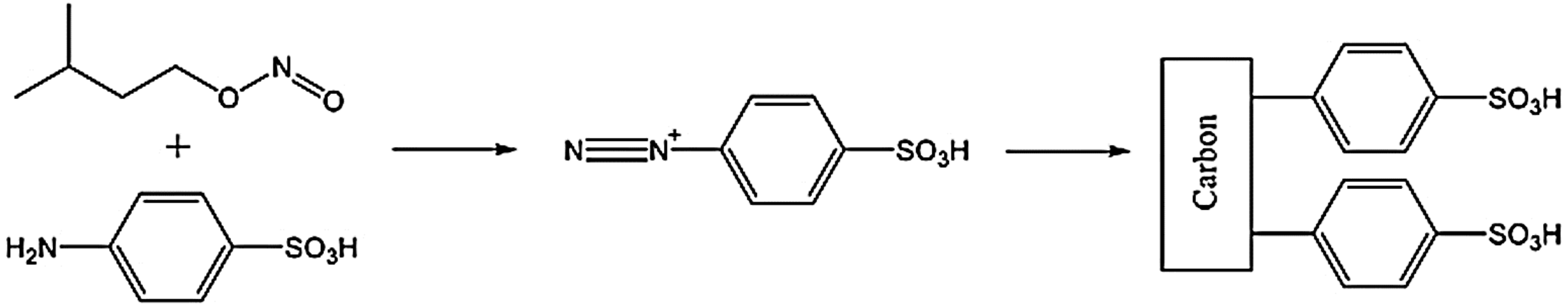
TASK 1: Synthesis of the sulfonated catalysts

Diazonium coupling method on a carbon-based substrate



STEP 1 : 1g C substrate + 1.5g sulphanilic acid in 60mL H_2O (distilled)

STEP 2 : addition of 1.2mL of isopentyl nitrite

S. Carlier, Front. Chem. 2020, 8, 347

TASK 1: Synthesis of the sulfonated catalysts

Diazonium coupling method on a carbon-based substrate

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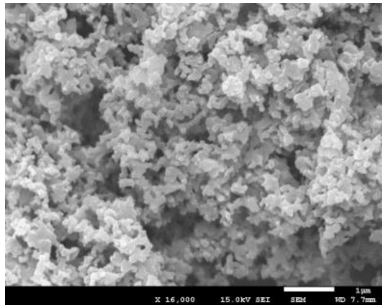
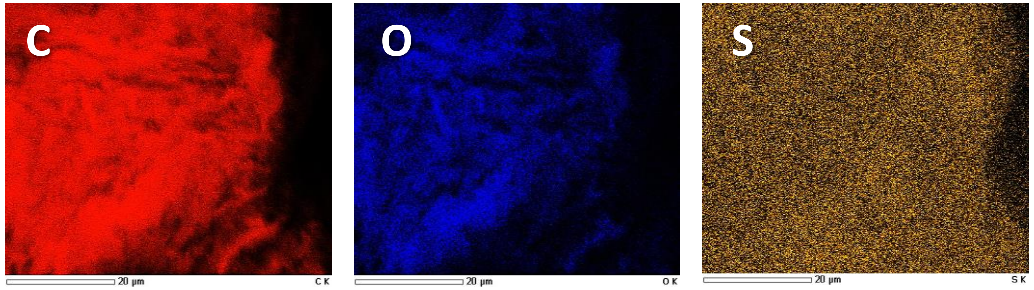
SEM IMAGING + EDX PROBING

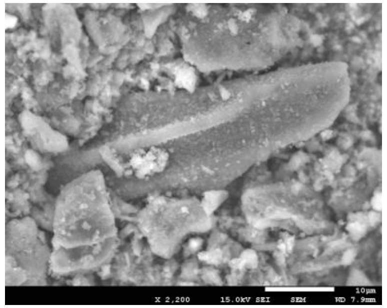
$CB@SO_3H$

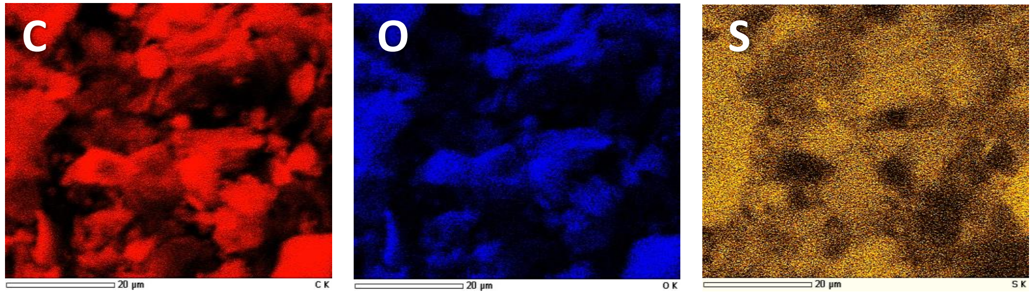




Average **S%** as mass of element = **0.21**

$SX+@SO_3H$





Average **S%** as mass of element = **2.87**

(SX+) >>> CB

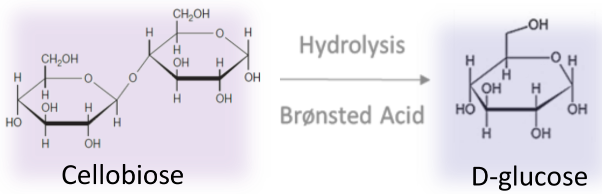
Higher surface area

EASE OF FUNCTIONALIZATION

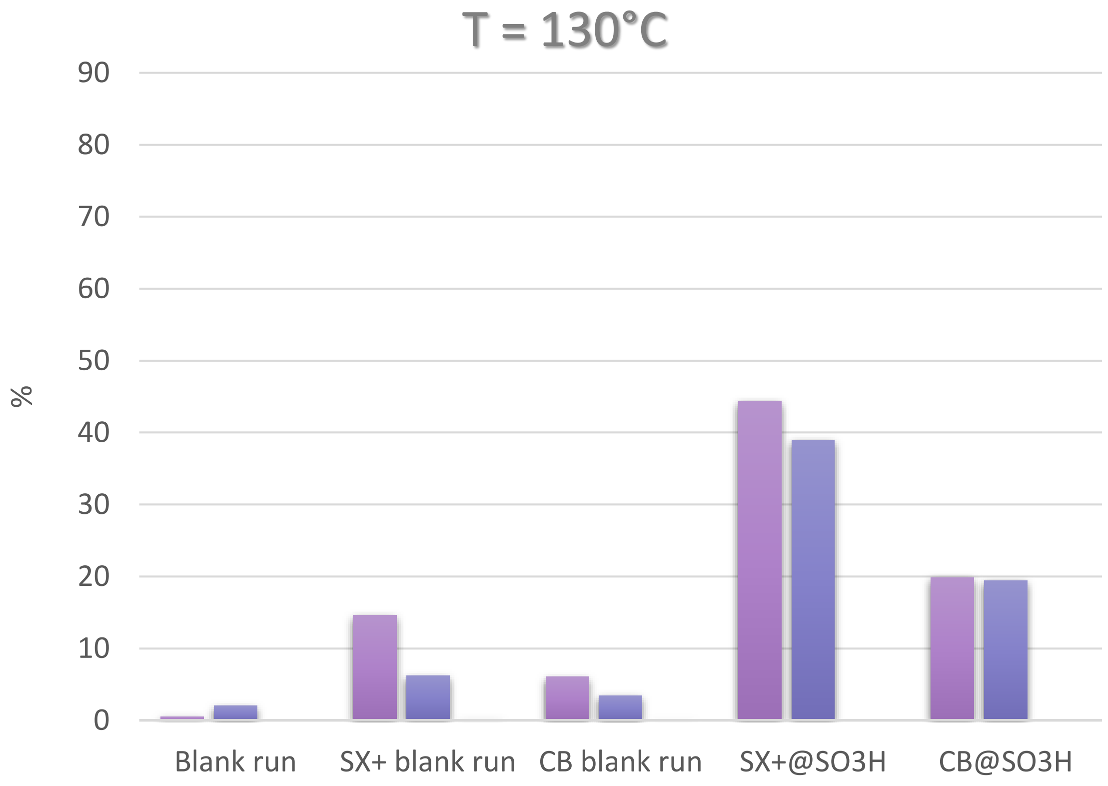
NO. SITE AVAILABLE FOR CATALYSIS

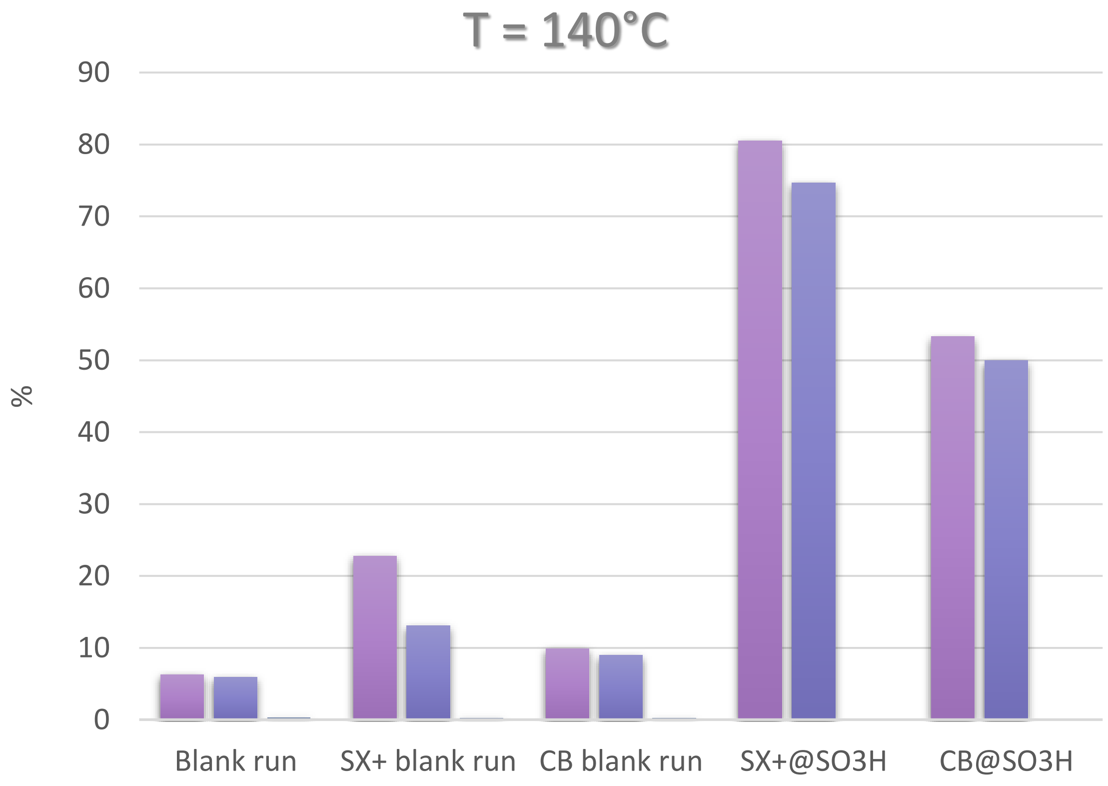
TASK 1: Characterization of the sulfonated catalysts

Catalytic performance evaluation – from Cellobiose to Glucose



LEGEND: Cellulose Conversion Glucose Yield

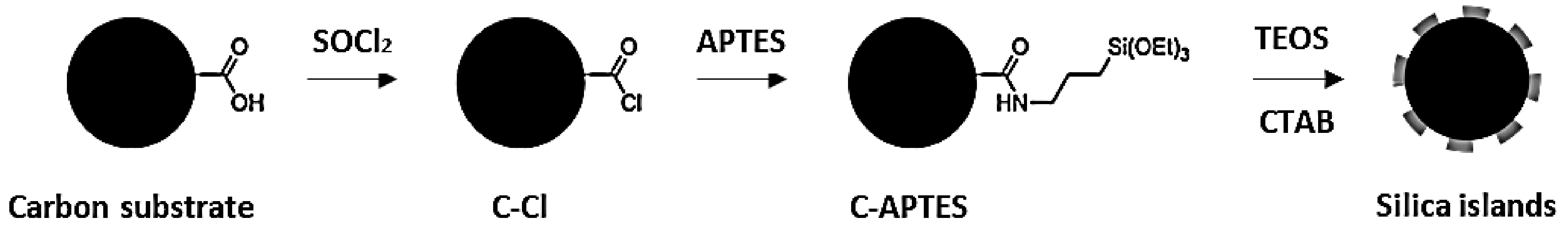




Applied parameters: t = 4h solvent = H_2O (mQ) RPM = 1700 P(N_2) = 4.7 Bar Cellobiose : Catalyst = 2

TASK 2: Preparation of a discontinuous silica layer

Recipe optimization



Amounts based on the optimized ratios

Optimized molar ratio (T. Haynes, Appl. Cat. B 2019, 241, 196)	
TEOS : CTAB	2
TEOS : APTES	0.7
TEOS : SOCl2	0.04

Entry	TEOS [mL]	SOCl2 [mL]	APTES [mL]	CTAB [g]
T0	**0.5**	4.2	0.71	0.4078
T1	**0.4**	3.4	0.57	0.3263
T2	**0.3**	2.6	0.42	0.2447
T3	**0.2**	1.7	0.29	0.1631
T4	**0.1**	0.86	0.14	0.0815

T. Haynes, Appl. Cat. B 2019, 241, 196

TASK 3: Preparation of a bifunctional system

Recipe optimization

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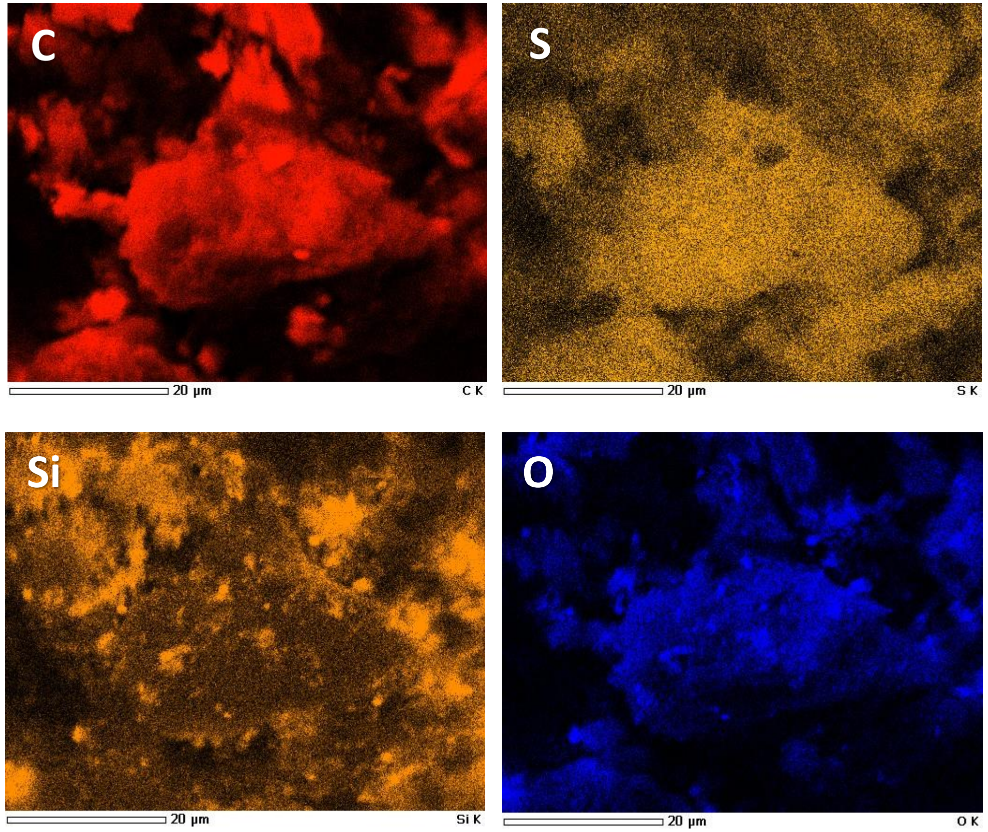
Most promising result attained with T4 SX+@SO_3H



Average **S%** as mass of element = **1.89**

ENTRY	%S
(SX+)@SO_3H	2.5
	2.96
	3.13
T4	1.31
(SX+)@SO_3H	1.57
	2.78

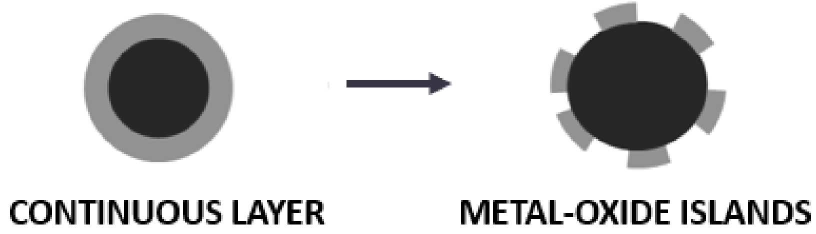
% as mass of element

Local S% detected for T4 is comparable with what found for the sulfonated substrate

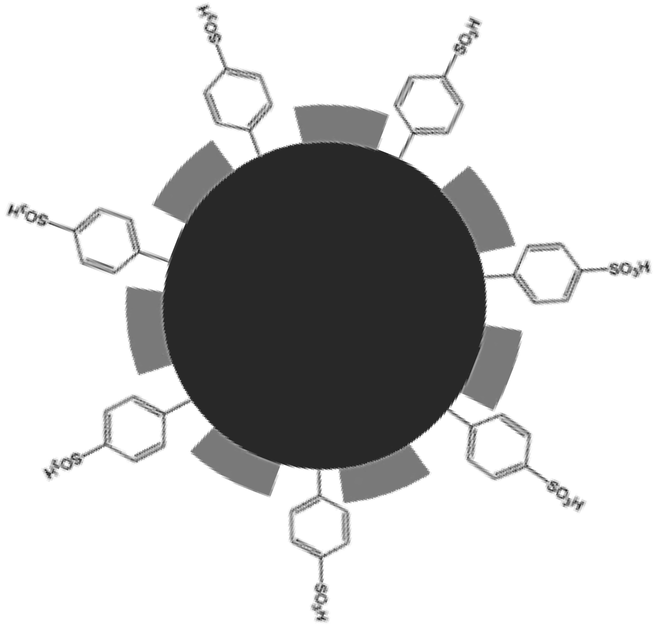
PROMISING FOR THE CATALYTIC ACTIVITY

What has been done so far?

- ✓ A discontinuous silica layer has been produced.



- ✓ A bifunctional system has been synthesized.

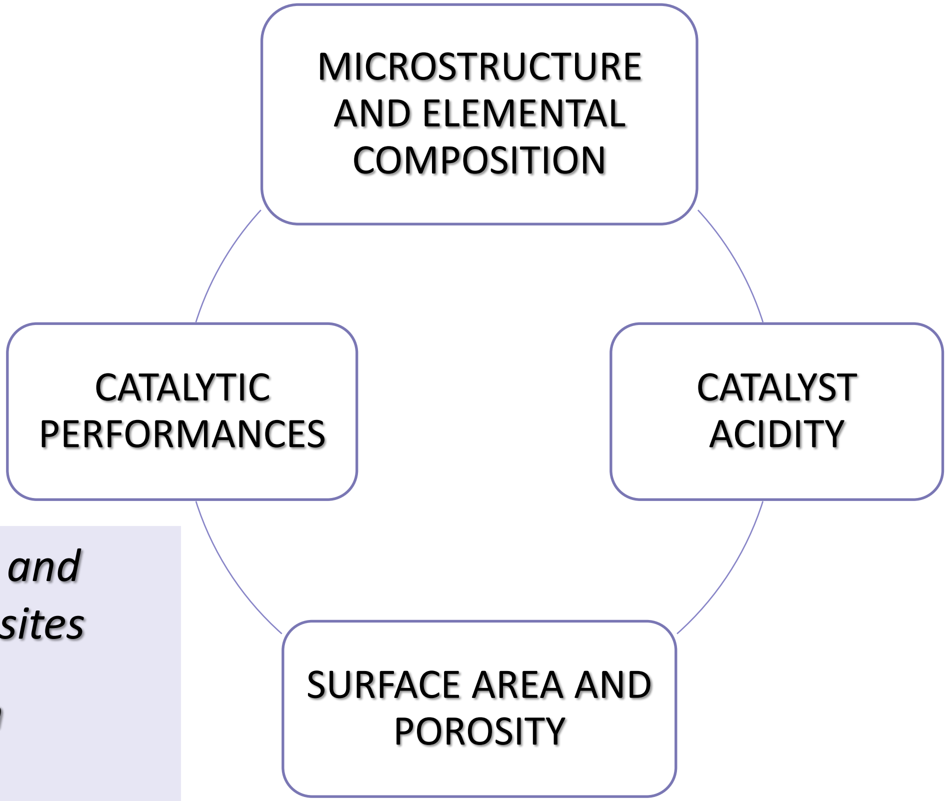


Activity and stability of the attained system

What's next?

- Development of **active metal oxide islands**.
- Reverse the synthetic steps to achieve the bifunctional catalyst.

Structure-Activity relationships



Retroactive Loop

→ *Optimize the amount and accessibility of acidic sites*

→ *Optimize the reaction conditions*

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THANK YOU ALL FOR YOUR KIND ATTENTION

UCLouvain

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