

**10th ITALIAN
SOL-GEL
WORKSHOP**

Padova,

15 - 16 September 2025

**SUSTAINABLE SYNTHESIS OF SUPPORTED
TRANSITION METAL PHOSPHATES
WITH ACID CATALYTIC PROPERTIES**

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Elisabetta Finocchio, Gabriella Garbarino, Guido Busca

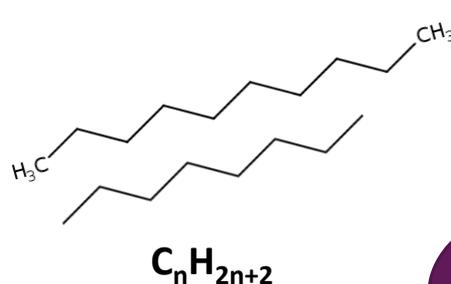
Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova



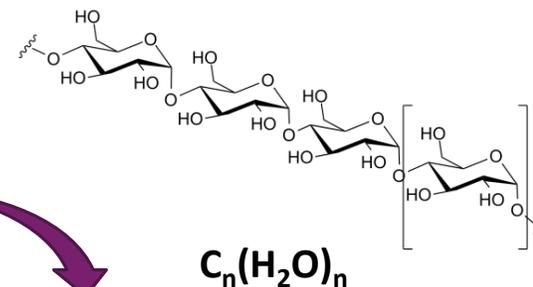
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INTRODUCTION



Hydrocarbon economy
Fossil resources



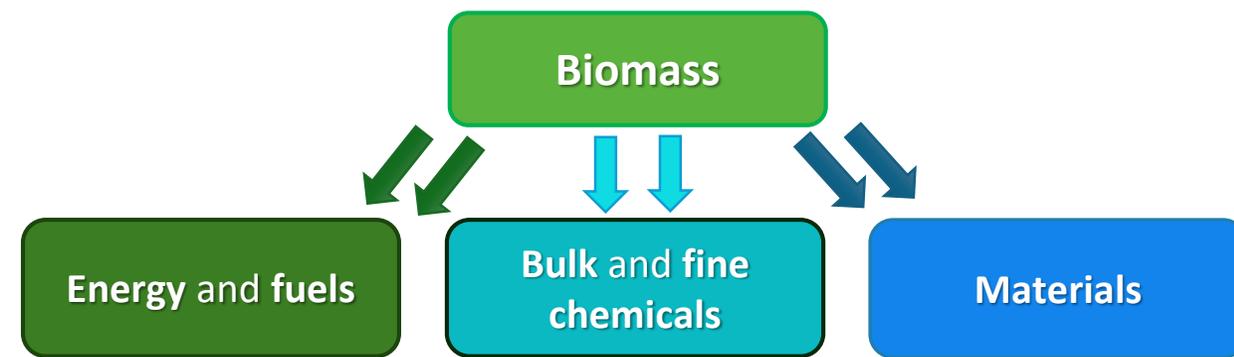
Bio-based economy
Renewable resources



Biorefinery processes for the transformation of biomass into value-added chemicals and biofuels: suitable heterogeneous catalysts with variable characteristics are needed.

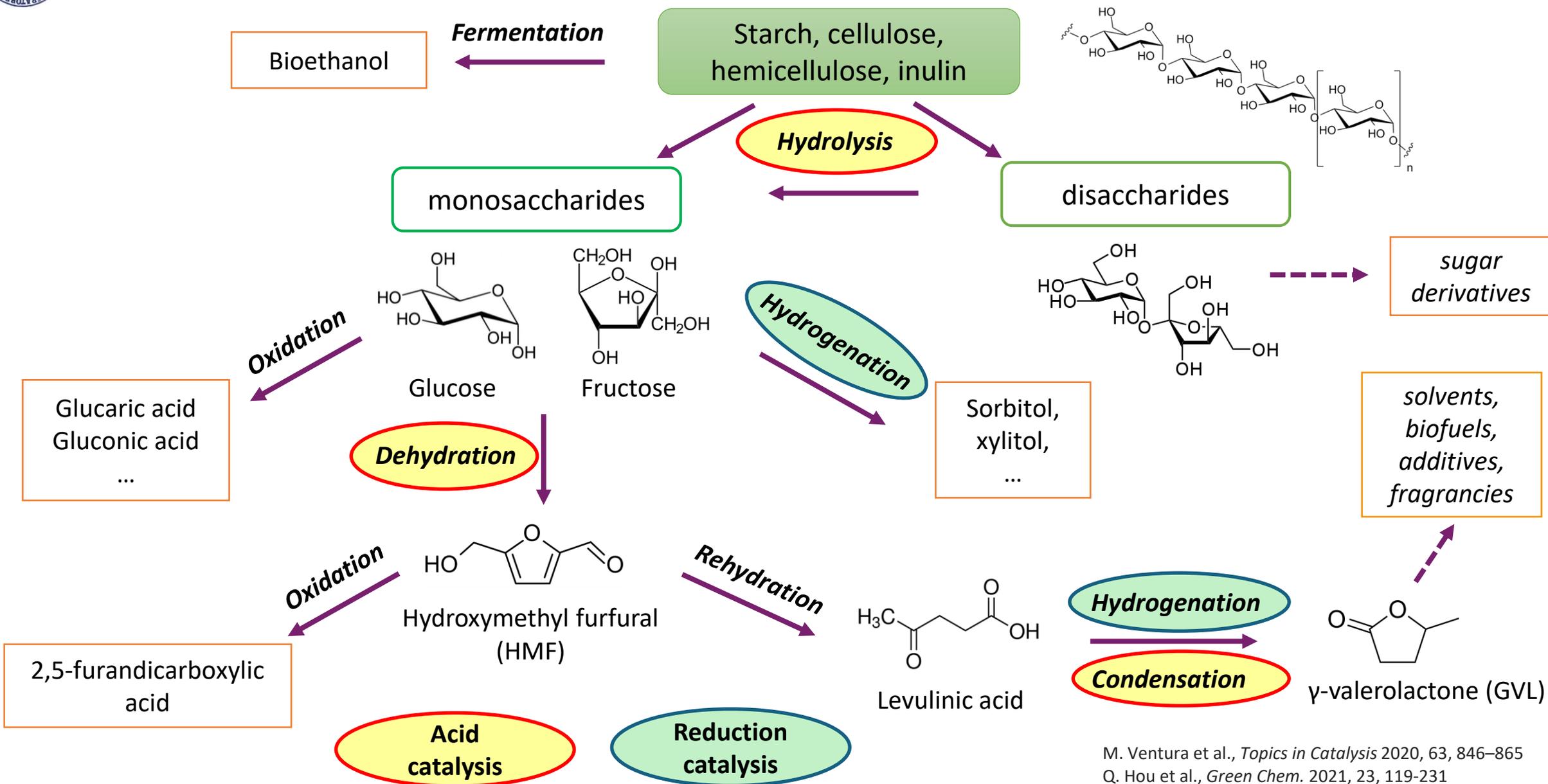
Challenge:

development of **efficient** and **sustainable solid catalysts** with tuneable acid and/or redox activity and high water resistance for the conversion of biomass derivatives.





POLYSACCHARIDE BIOREFINERY

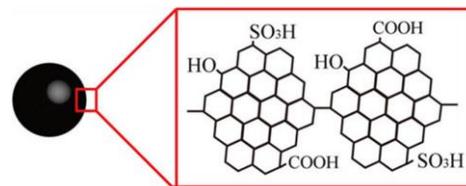




SOLID ACID CATALYSTS

Acid-catalyzed reactions in biorefinery:

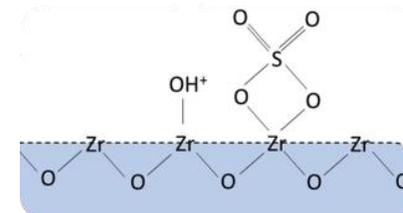
- hydrolysis
- dehydration
- esterification
- transesterification
- epoxide ring opening



Rev. Adv. Mater. Sci. 2024, 63, 20240060

Carbon-based materials

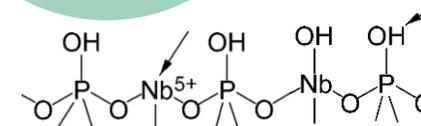
Metal oxides (pure or modified, e.g. sulfated ZrO_2)



Appl. Catal. A 2019, 575, 25-37

Solid acid catalysts

Metal (oxo) phosphates (e.g. $NbOPO_4$)

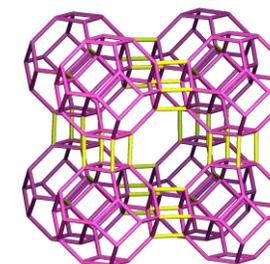


Keggin
{ $XM_{12}O_{40}$ }

Nat. Rev. Chem. 2018, 2, 0112

Heteropoly acids (e.g. polyoxometalates)

Zeolites



Acid sites features:

- nature (Brønsted/Lewis)
- strength
- surface density
- effectiveness in water



SiO₂-P₂O₅ (phosphosilicate) gel glasses:

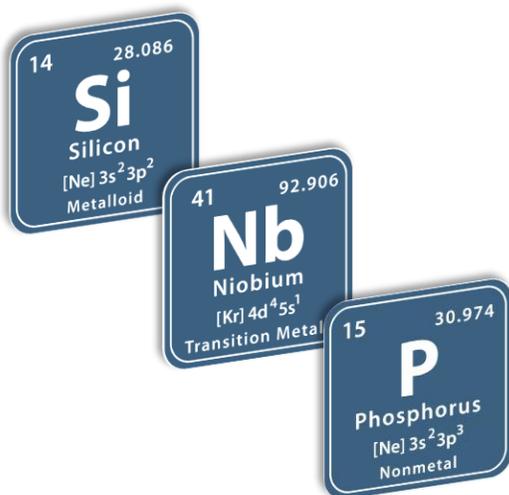
- interesting proton conductivity
 - significant protic acidity
- high affinity to water, low hydrolysis stability

M. D'Apuzzo, A. Aronne, S. Esposito, P. Pernice, *J. Sol-Gel Sci. Technol.* **2000**, 17, 247;
A. Aronne, ..., E. Fanelli, *Chem. Mater.* **2005**, 17, 2081–2090

SiO₂-Nb₂O₅ gel-derived ceramics:

- high surface area, variable acid site strength
- good catalytic activity in epoxidation reactions
- dispersion of NbO_x species leads to high selectivity

A. Aronne, ..., E. Fanelli, *Appl. Catal. A Gen.* **2008**, 347, 179-185;
R. Turco, A. Aronne, ..., M. Di Serio, *Catal. Today* **2015**, 254, 99-103



SiO₂-Nb₂O₅-P₂O₅ ternary systems:

- tuneable Brønsted/Lewis acid site ratio and surface morphology
 - extended activity in acid-catalysed reactions
 - improved stability of P units in water

N.J. Clayden, ..., A. Aronne, *J. Mater. Chem. A* **2015**, 3, 15986; A. Aronne, ..., A. Gervasini, *J. Phys. Chem. C* **2017**, 21, 17378; N.J. Clayden, C. Imperato, ... A. Aronne, *Green Chem.* **2020**, 22, 7140



SiO₂-P₂O₅ (phosphosilicate) gel glasses:

- interesting proton conductivity
- significant protic acidity
- high affinity to water, low hydrolysis stability

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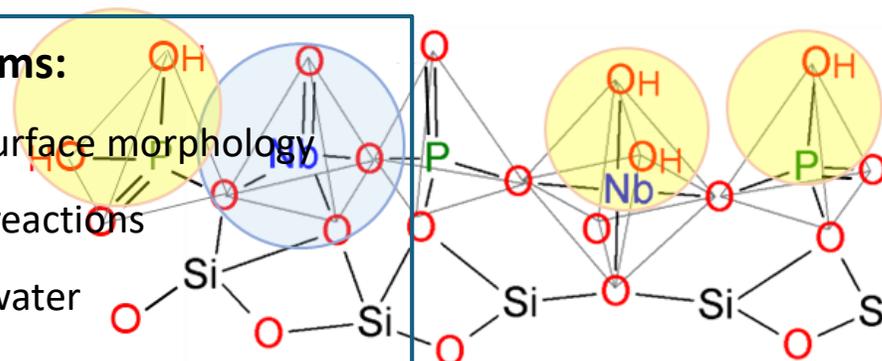
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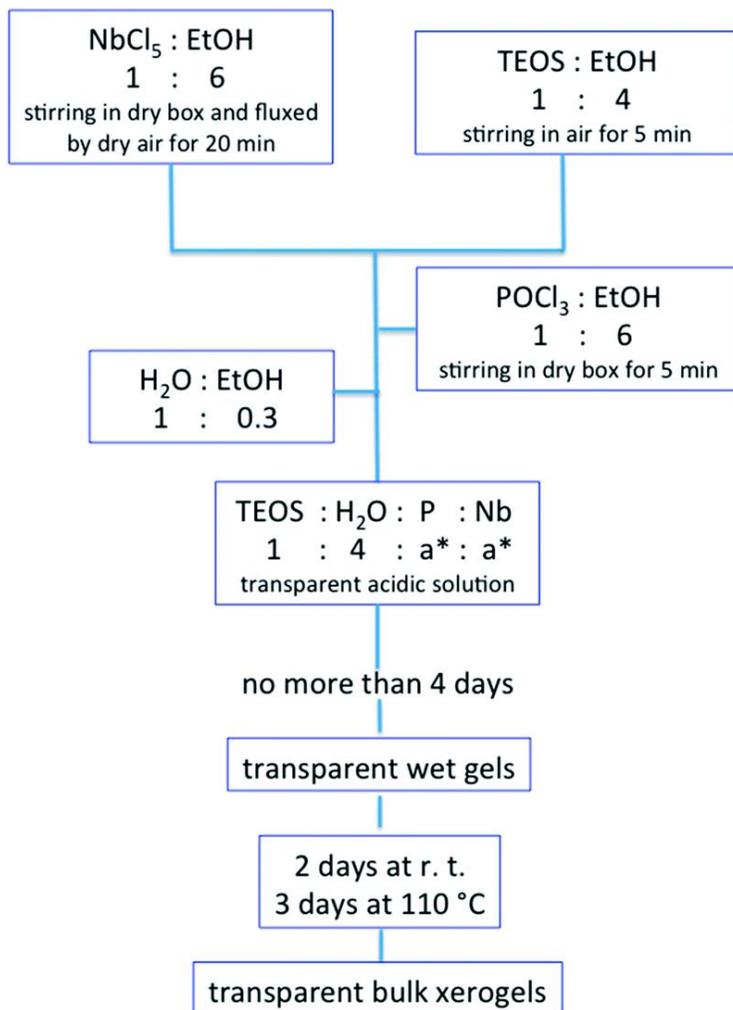
Lewis acid sites

Brønsted acid sites

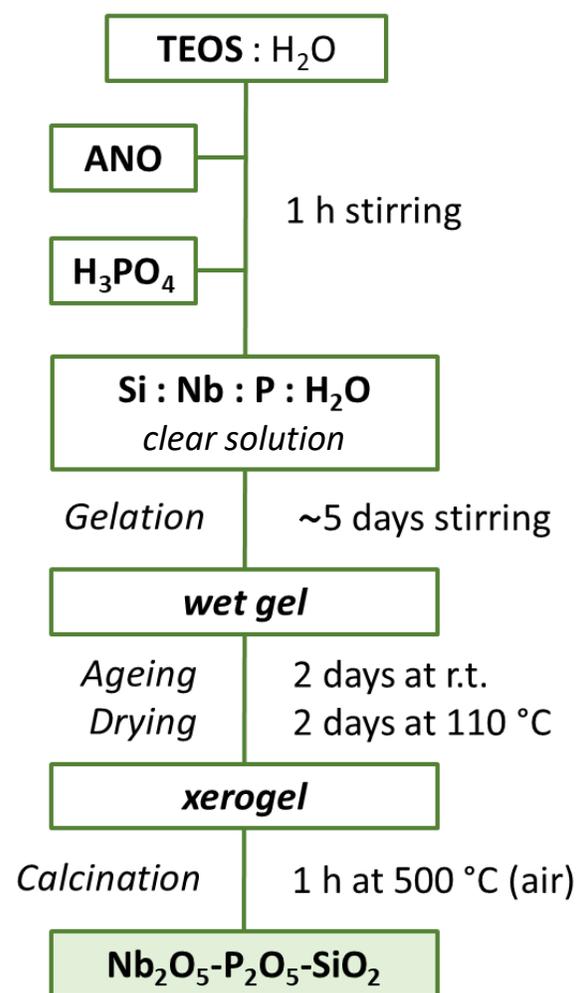


Nb-P-Si mixed oxides: synthesis

First sol-gel synthesis procedure

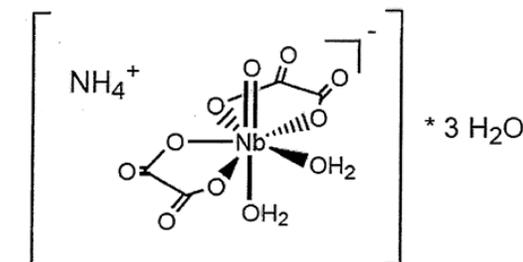
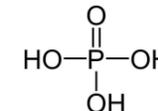
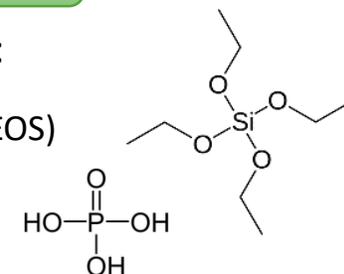


"Chloride-free" sol-gel synthesis procedure



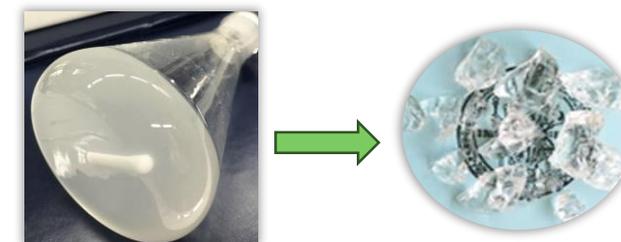
Precursors:

- Tetraethylorthosilicate (TEOS)
- Orthophosphoric acid
- Ammonium Nb oxalate hydrate (ANO)



Solvent: water

No additives or catalysts



Nb-Si-P oxide wet gel and xerogel



Nb-P-Si mixed oxides: characterization

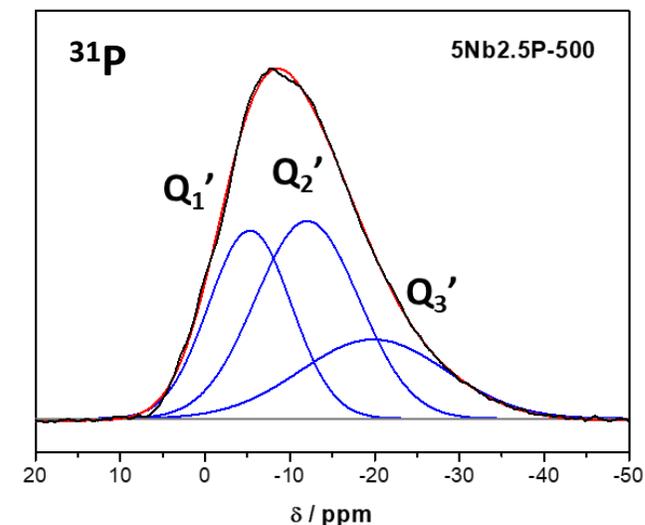
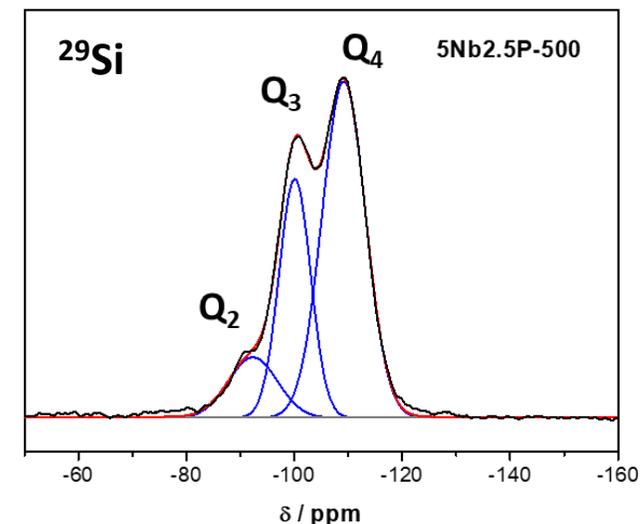
Sample	Nb ₂ O ₅ (mol %)	P ₂ O ₅ (mol %)	Nb/P (mol/mol)
2.5Nb-2.5P	2.5	2.5	1.0
5Nb-2.5P	5.0	2.5	2.0
5Nb-5P	5.0	5.0	1.0

- Amorphous micro-mesoporous **structure**
- Silicon:** high degree of cross-linking of Si units (²⁹Si NMR)
- Niobium:** distribution of tetrahedral (NbO₄) and octahedral (NbO₆) units (Raman spectra)
- Phosphorus:** stabilized by (-P-O-Nb-O-Si-) bridges anchoring P units to the silicate matrix (³¹P NMR)

Increase of Nb/P ratio



significant reduction of
P leaching in water

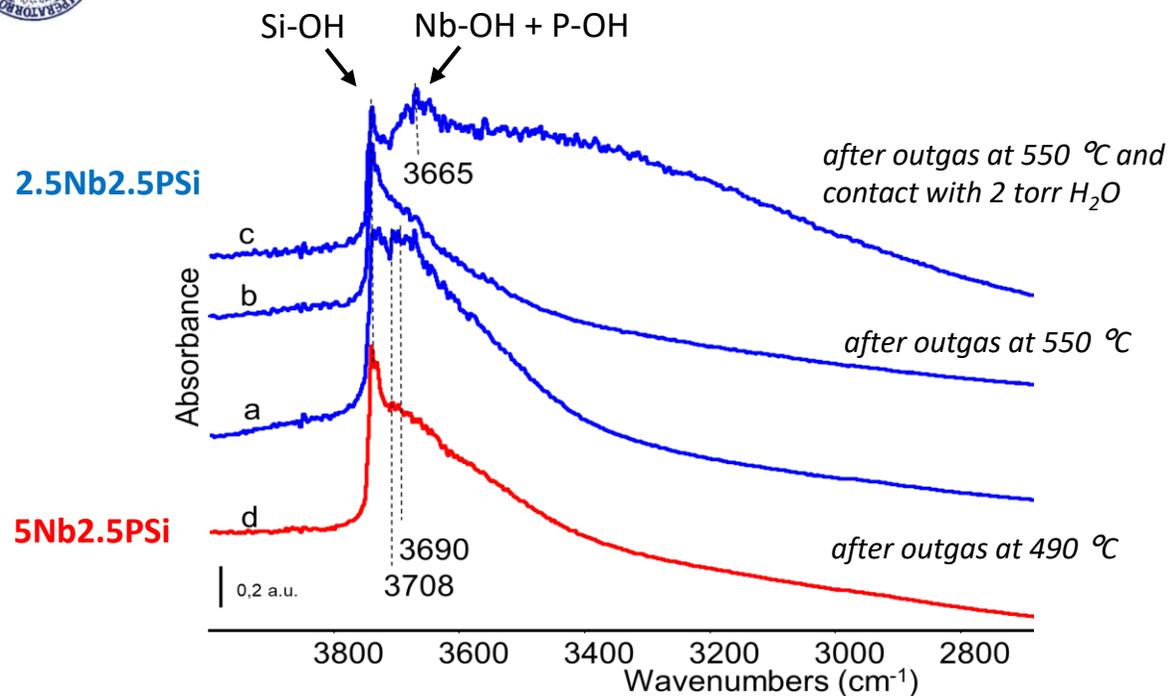


²⁹Si (top) and ³¹P (bottom) MAS NMR spectra of the annealed 5Nb2.5 P sample





Nb-P-Si mixed oxides: characterization



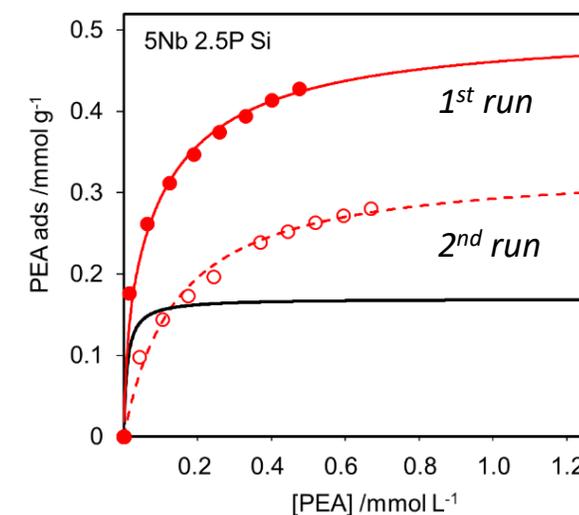
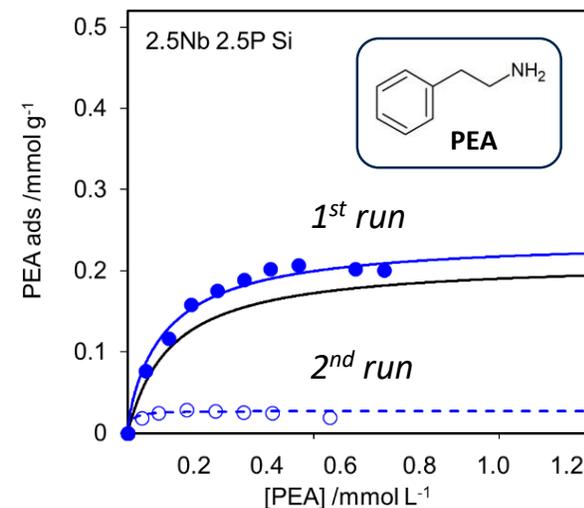
FT-IR spectra recorded in different conditions (O–H stretching region).

Acidity features:

- presence of surface hydroxyl groups (Si-OH, P-OH, Nb-OH)
- relatively strong Brønsted acidity, medium-strong Lewis acidity
- effective acidity partly retained in water
- samples richer in Nb: less and weaker acid sites

Sample	BET SSA (m ² /g)	amount of acid sites	
		meq/g	meq/m ²
2.5Nb-2.5P	408	463	1.1
5Nb-2.5P	366	537	1.5

from NH₃ titration



Adsorption isotherms of PEA probes at 30 °C in cyclohexane (intrinsic acidity determination).

Full circles: I run, tot. (reversible+irreversible) adsorption; empty circles: II run, reversible adsorption. Curves: calculated by Langmuir ads. model.

in collaboration with



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Università di Genova

A. Gervasini, ..., A. Rossi, *Appl. Catal. A*, **2019**, 579, 9;

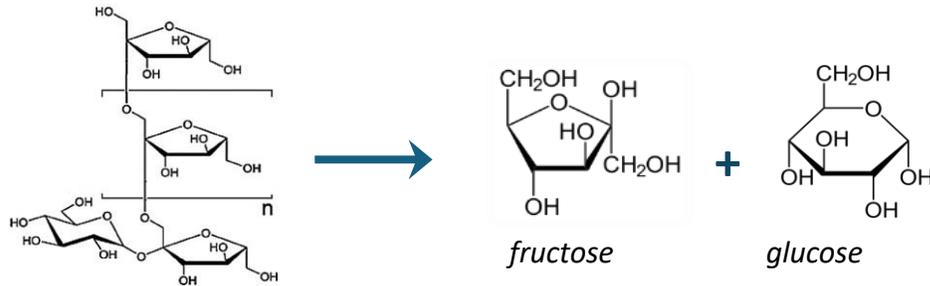
G. Garbarino, ..., A. Aronne, *Microporous Mesoporous Mater.*, **2022**, 343, 112190.



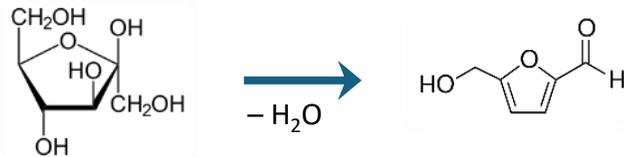
Nb-P-Si mixed oxides: catalytic activity

Activity tests in different **acid-catalysed** reactions:

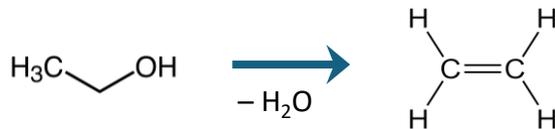
1. hydrolysis of polysaccharides (e.g. inulin) to monosaccharides



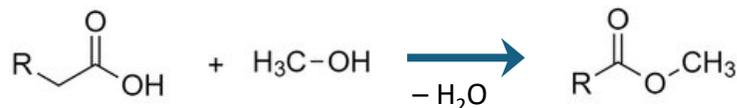
2. dehydration of fructose to 5-hydroxymethylfurfural (5-HMF)



3. dehydration of ethanol to ethylene (gas phase)



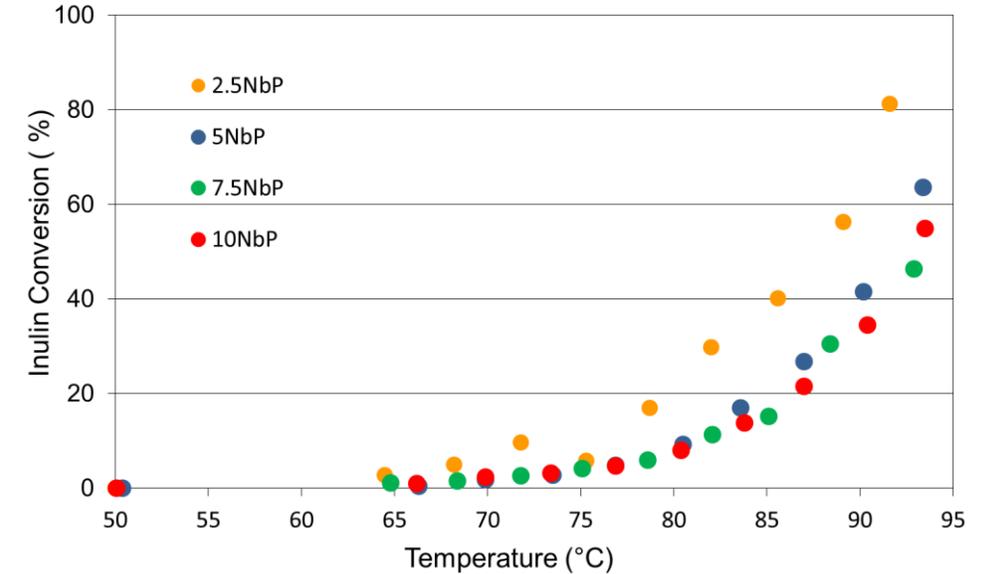
4. esterification of fatty acids with polyalcohols



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Conversion of inulin as a function of temperature (ratio between the reducing sugars produced and those at complete hydrolysis).

- Batch reactor
- water solution
- Temp. ramp 0.12°C/min
- Total time 6 h

A. Aronne et al., *J. Phys. Chem. C* **2017**, 21, 17378;
A. Gervasini et al., *Mol. Catal.* **2018**, 458, 280;
A. Gervasini et al., *Appl. Catal. A* **2019**, 579, 9;
G. Garbarino, et al., *Microporous Mesoporous Mater.* **2022**, 343, 112190

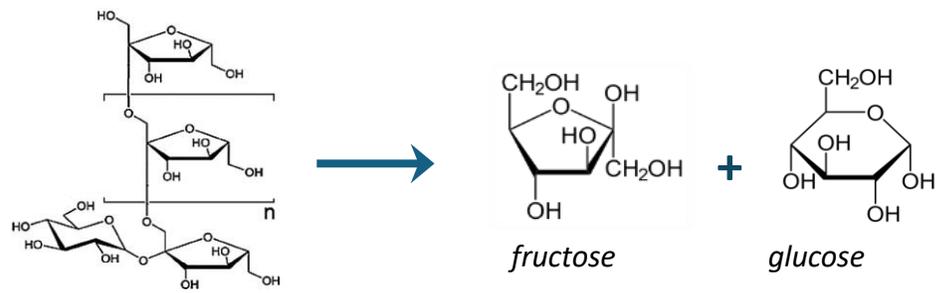


Nb-P-Si mixed oxides: catalytic activity

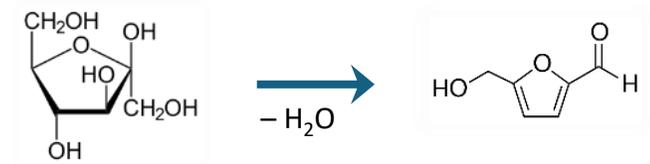
Activity tests in different **acid-catalysed** reactions:

in collaboration with  **Università di Genova**

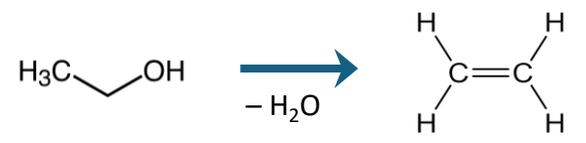
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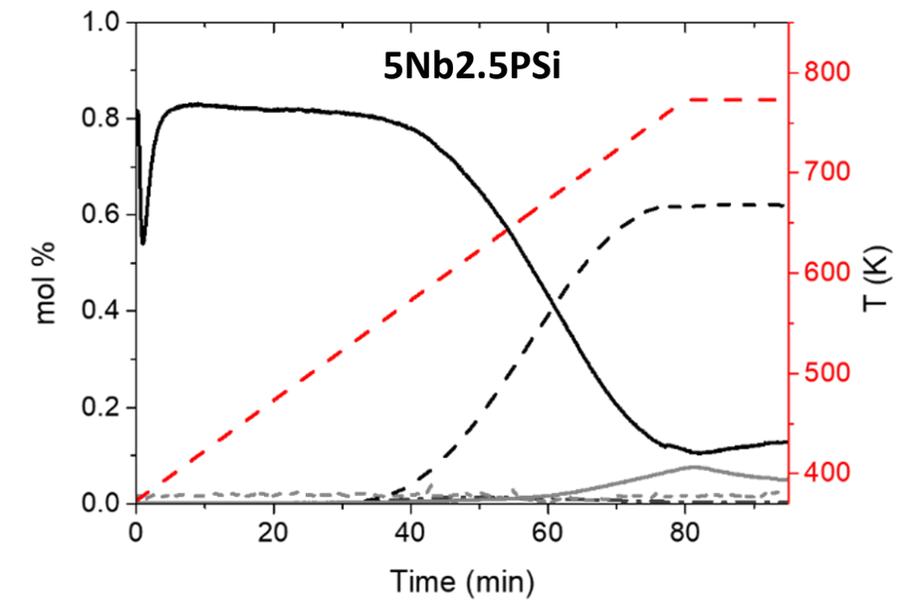
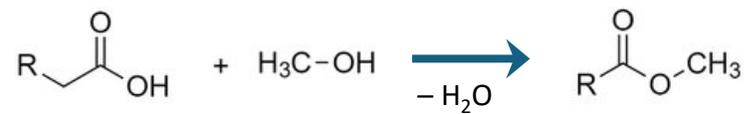
2. dehydration of fructose to 5-hydroxymethylfurfural (5-HMF)



3. dehydration of ethanol to ethylene (gas phase)



4. esterification of fatty acids with polyalcohols



— C₂H₅OH — C₂H₄O --- C₂H₄ - · - C₄H₁₀O - - CO₂ - - - T ramp

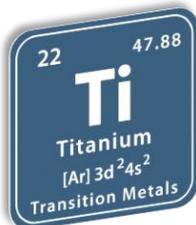
EtOH temperature programmed surface reaction experiment (1% feed).

- EtOH conversion: up to 87%
- high selectivity to ethylene
- tuneable selectivity to acetaldehyde

A. Aronne et al, *J. Phys. Chem. C* **2017**, 21, 17378;
A. Gervasini et al., *Mol. Catal.* **2018**, 458, 280;
A. Gervasini et al., *Appl. Catal. A* **2019**, 579, 9;
G. Garbarino, et al., *Microporous Mesoporous Mater.* **2022**, 343, 112190



Ti-P-Si and Zr-P-Si mixed oxides: synthesis

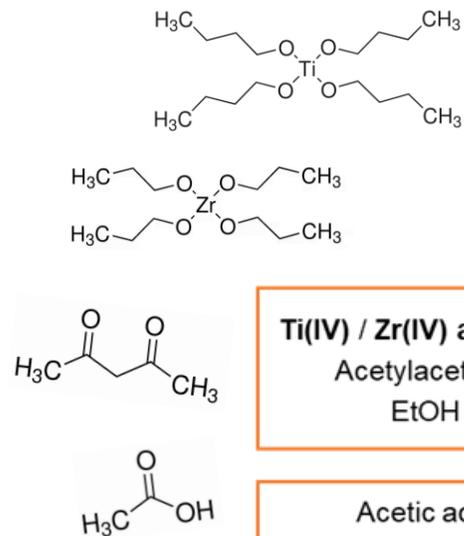


- $\text{TiO}_2\text{-P}_2\text{O}_5\text{-SiO}_2$ (Ti-P-Si)
- $\text{ZrO}_2\text{-P}_2\text{O}_5\text{-SiO}_2$ (Zr-P-Si)

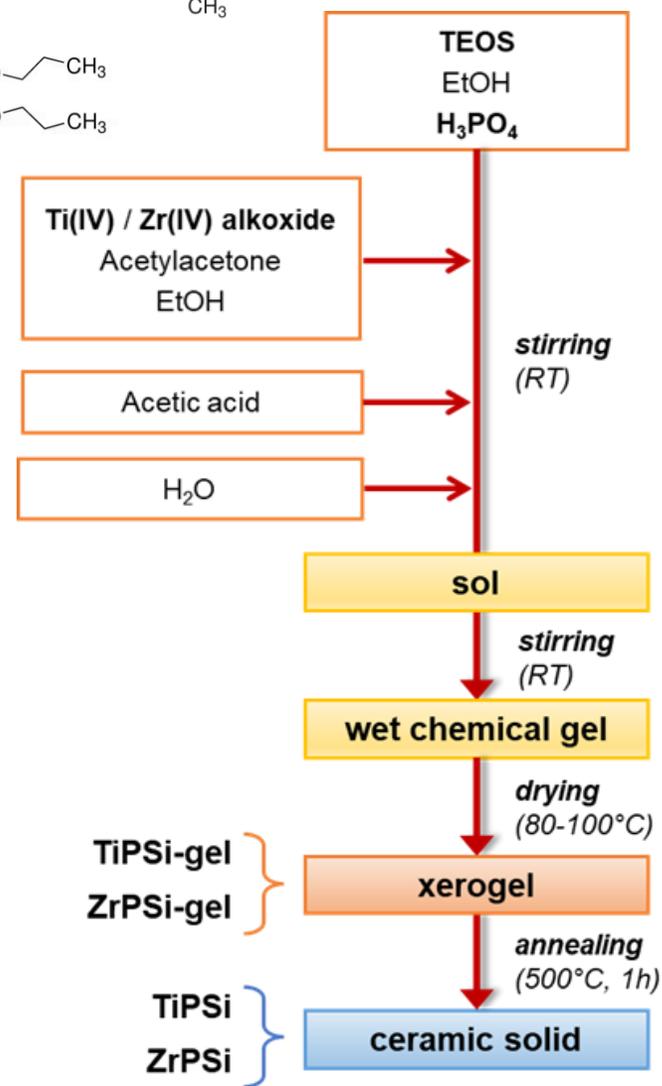
Metal oxo-phosphate active phases
finely dispersed in a large-surface
area porous silica matrix



modulation of acidity and
nanostructure



Sol-gel synthesis procedure



Challenges:

- fast hydrolysis rate of Ti and Zr alkoxides
- high reactivity of H_3PO_4
→ precipitation of Ti/Zr phosphates

Countermeasures:

- ✓ complexation (Hacac + acetic acid)
- ✓ acidic pH (~4)
- ✓ mixing order
- ✓ portionwise addition of water



Me : P : Si = 10 : 5 : 85
(mol/mol)

$(10 \text{ MeO}_2 \cdot 2.5 \text{ P}_2\text{O}_5 \cdot 87.5 \text{ SiO}_2)$

- Amorphous micro-mesoporous **structure**
- Silicon**: high cross-linking degree of Si units (^{29}Si NMR); Si surface enrichment, marked in TiPSi (XPS).
- Phosphorus**: variety of P units connectivity, cross-linking grows during calcination (^{31}P NMR).
- Acidity**: Brønsted + Lewis, slightly stronger in TiPSi.

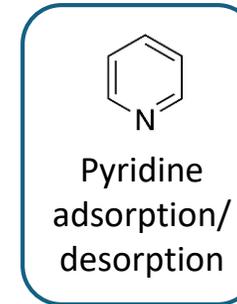
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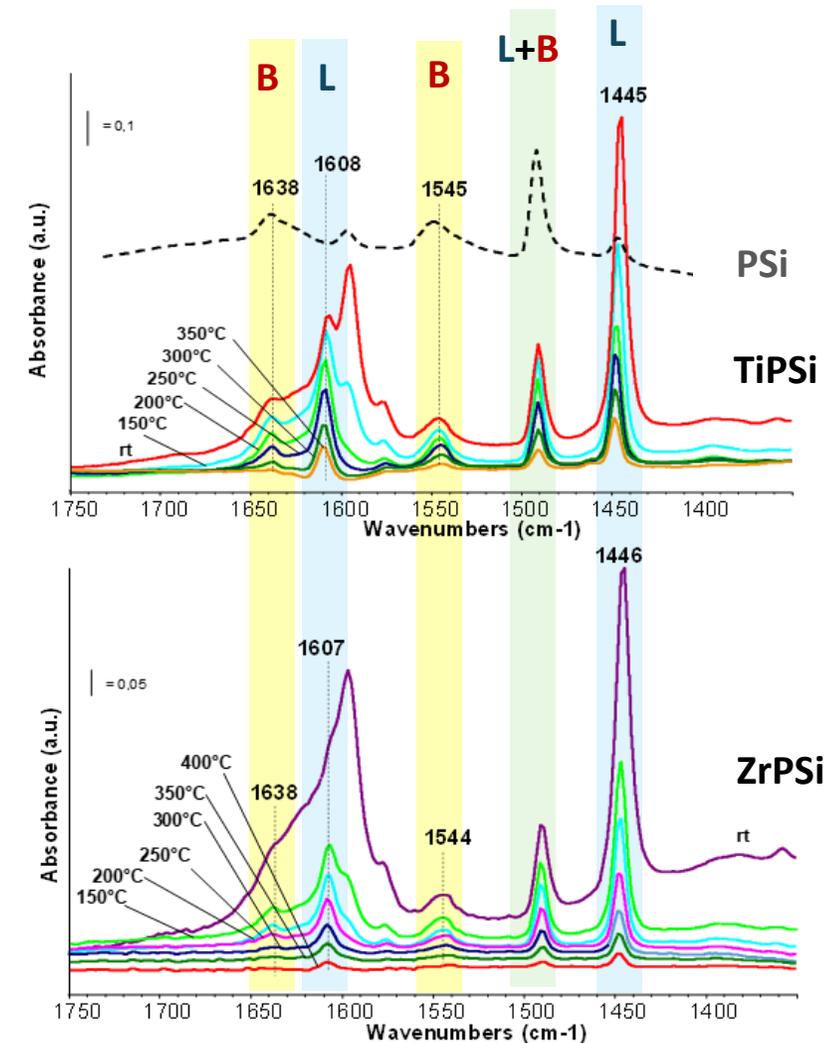
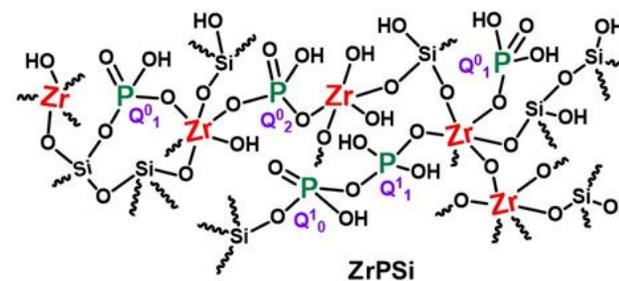
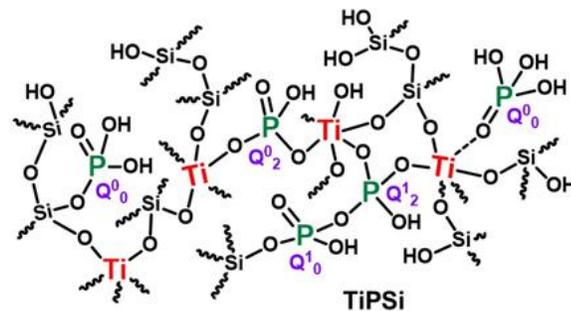
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East Anglia



from NH_3
titration

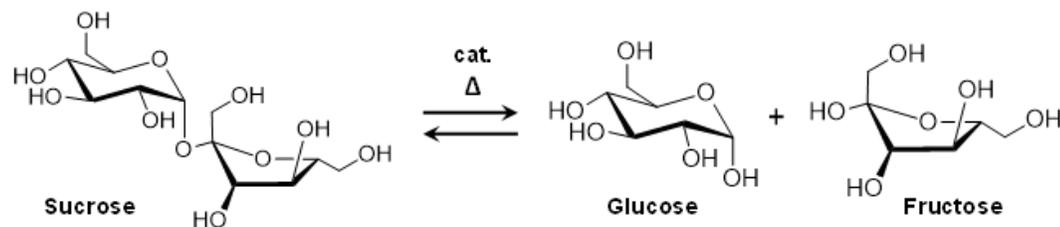
Sample	SSA ($\text{m}^2 \text{g}^{-1}$)		Microporous volume ($\text{cm}^3 \text{g}^{-1}$)	Surface acid sites ($\mu\text{eq g}^{-1}$)	Acid site density ($\mu\text{eq m}^{-2}$)
	BET	Langmuir			
TiPSi	395 ± 11	441 ± 10	0.19 ± 0.02	744	1.7
ZrPSi	346 ± 37	421 ± 20	0.21 ± 0.03	702	1.7



FTIR spectra of surface species arising from adsorption/desorption of pyridine (activated surface subtracted).

Catalytic screening:

hydrolysis of disaccharides (model reaction)



- Batch reactor
- Water solution
- T from 50 to 90 °C (0.12 °C/min)
- Total time 4 h

- Better performance by **TiPSi**, attributed to higher **acidity**
- Phosphate leaching due to hydrolysis of P-O-X bonds in hot water

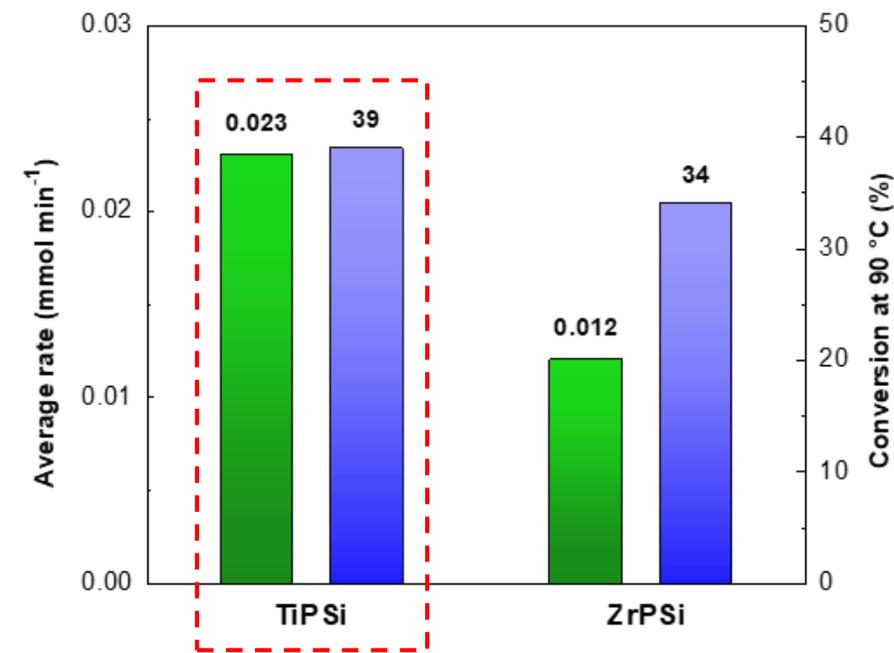
In progress:

- hydrolysis tests with different disaccharides (lactose, maltose, cellobiose) and a trisaccharide (raffinose);
- further stability tests

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Sucrose hydrolysis:

average rate after 240 min at 80 °C;

conversion attained at 90 °C.



Sol-gel: a green chemical synthesis methodology?

Sustainability evaluation of the synthesis process

Environmental (E) factor: accounts for the amount of waste produced in the process

→ the lower, the better!

$$E - factor = \frac{\text{mass of wastes}}{\text{mass of product}}$$

(R.A. Sheldon, *Green Chem.* 2023, 25, 1704)

Metrics	includes:	
	solvents	water
Complete E factor	YES	YES
E factor	YES	NO
Simple E factor	NO	NO



Metrics	NbPSi	ZrPSi	TiPSi
Complete E factor	7.2	7.5	9.4
E factor	2.6	6.6	8.3
Simple E factor	2.6	2.9	3.6

Nr. of steps : methods

2 : sol-gel + impregnation;

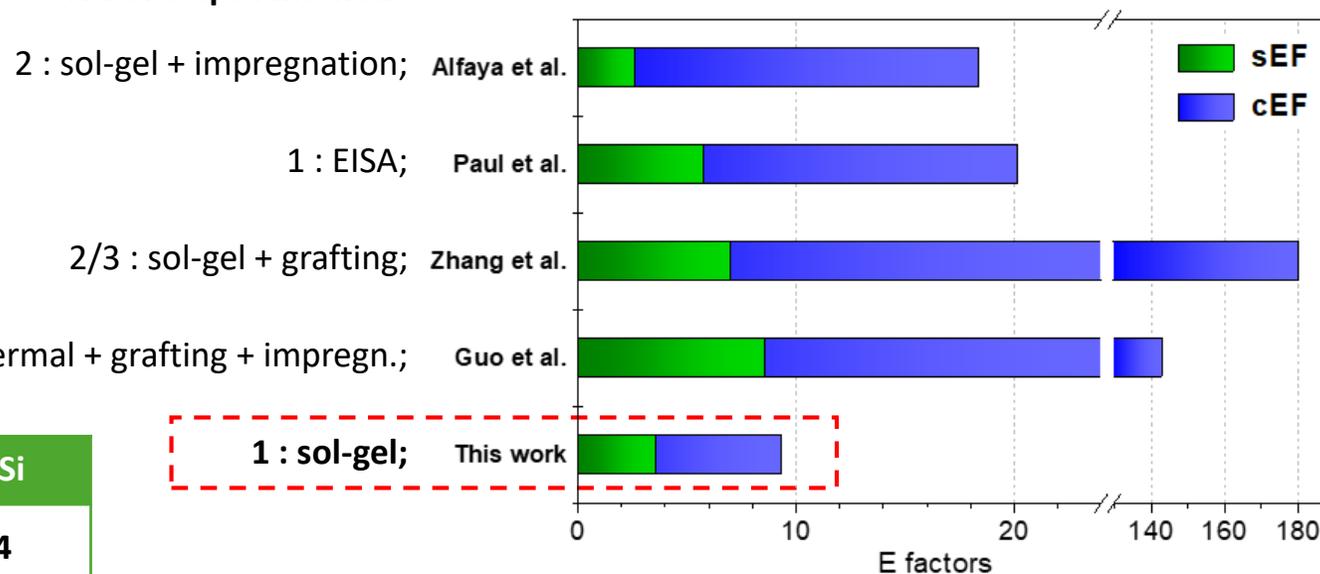
1 : EISA;

2/3 : sol-gel + grafting;

3 : hydrothermal + grafting + impregn.;

1 : sol-gel;

Comparison: synthesis of Ti-P-Si mixed oxides



Simple (sEF) and complete E Factor (cEF) for different synthetic protocols

C. Imparato et al, *Materials Today Chemistry* 2024, 38, 102126



CONCLUSIONS

- ⊕ The **hydrolytic sol-gel method** is a **versatile** and **sustainable** strategy to produce **metal oxophosphates** dispersed in a **silica matrix** with a tuneable porosity and surface properties.
- ⊕ **Nb-P-Si oxides** are effective **solid acid catalysts** active in hydrolysis, dehydration, and esterification reactions (in liquid water and gas phase).
- ⊕ **Ti-P-Si** and **Zr-P-Si oxides** also show promising catalytic activity due to mixed Brønsted/Lewis acid sites.
- ⊕ The materials show **limited structural stability** operating in water at high temperature, due to phosphate reactivity toward hydrolysis.



- ⊕ Further insight into **reaction and deactivation mechanisms** to design more robust catalysts optimized for the desired process.
- ⊕ Focus on other **catalytic reactions** not occurring in water at high temperatures (organic solvents, gas phase).
- ⊕ **New applications**, e.g. multifunctional **additives for recyclable polymeric materials** (dynamic bond exchange **catalysts** and **flame retardants** in covalent adaptable networks).





FUTURE PROSPECTS

Many thanks to...

➤ the Scientific and Organizing Committees

➤ my research group
Materials Chemistry Lab
@ DICMaPI, UniNa



DI
C
Ma
PI
Dipartimento
di Ingegneria Chimica,
dei Materiali e della
Produzione Industriale
Università degli Studi
di Napoli Federico II

➤ everyone who is contributing to
this research activity



Thank you for your attention!

✉ claudio.imparato@unina.it