ADVANCES IN CATALYSIS FOR HYDROCARBONS

RESULTS FROM ZEOCAT-3D, C123 & BIZEOLCAT EU RESEARCH PROJECTS

ZEOCAT-3D

C123
VALORISING METHANE RESOURCES

BiZeolCat

Funded by
the European Union

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Ethylene Hydroformylation Catalysis

Alvaro Amieiro Fonseca

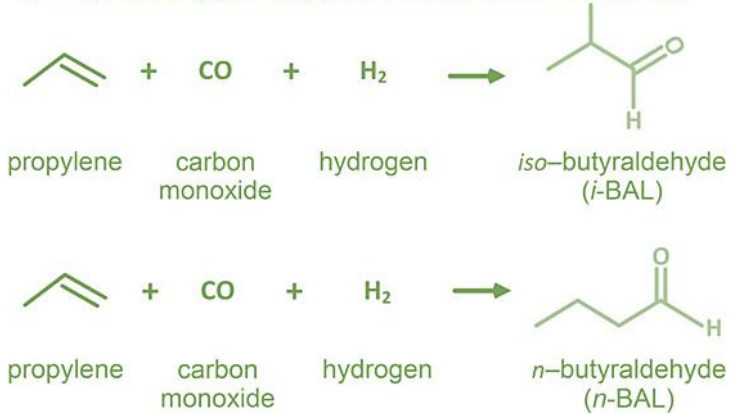
C123
VALORISING METHANE RESOURCES

EU-project Horizon 2020 GA No. 814557 C123 Methane oxidative conversion and hydroformylation to propylene

Hydroformylation

Hydroformylation is the process by which an olefin reacts with syngas to form an aldehyde.

Also commonly known as the "Oxo" process, hydroformylation ***is the first step in the production of oxo alcohols*** *with the intermediate aldehyde converted to an alcohol by hydrogenation.*



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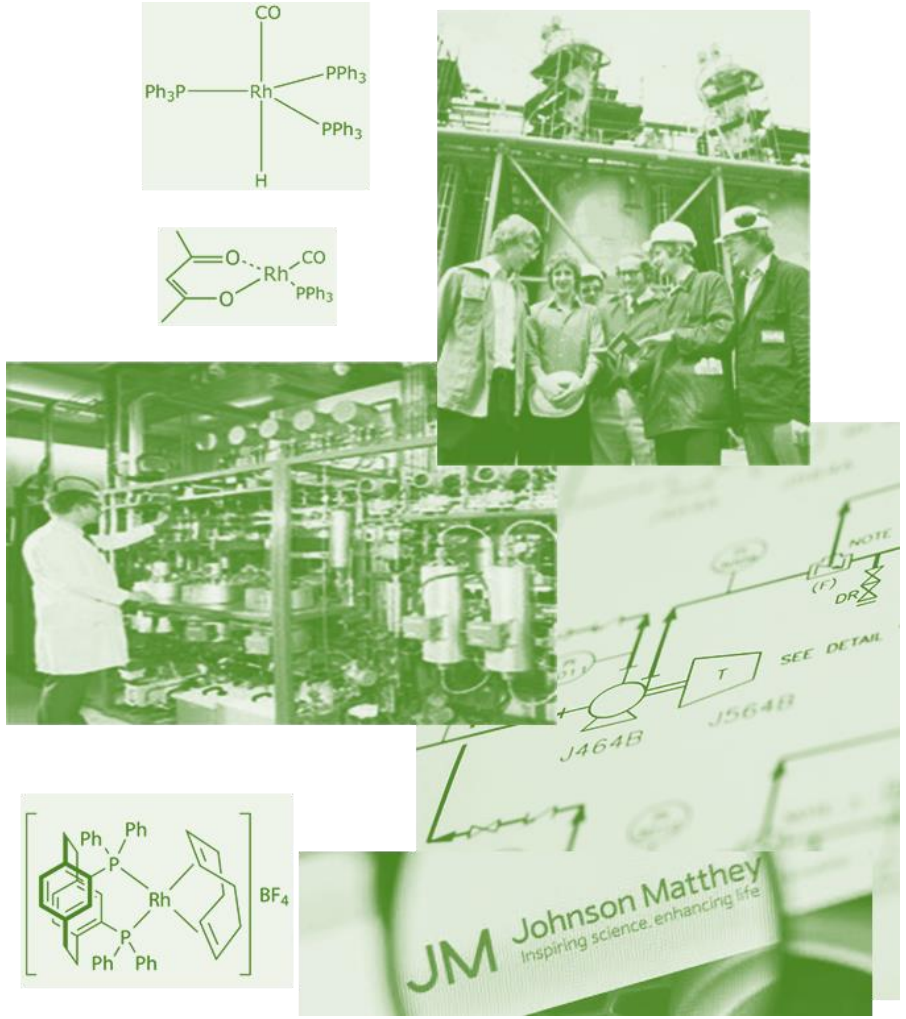
Hydroformylation

Johnson Matthey and Dow LP OxoSM technology is the world's leading process to alcohols from olefins.

The offer to the licensees is a combination of superior catalyst and a simplified flowsheet, which results in lean design , low investment cost, and high feedstock efficiency in a plant that is environmentally compliant and reliable.

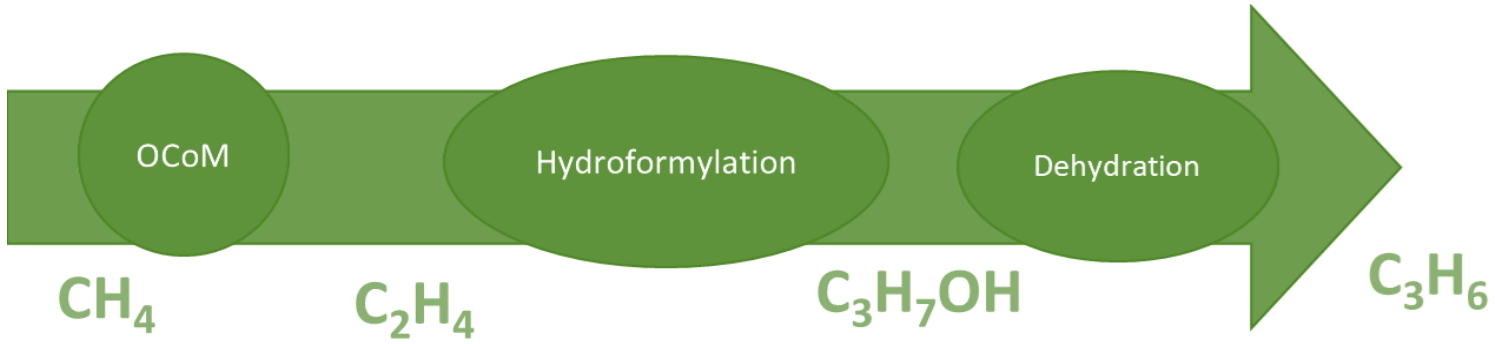


Platinum Metals Rev., 2007, 51, (4), 164
doi: 10.1595/147106707X238211

C123 HF catalyst challenge

Coupling a robust heterogeneous hydroformylation process with oxidative coupling of methane could disrupt the current oxo process technology.

- The **hydroformylation** will require to operate in **gas phase** and operate at lower pressure that usual.
- The traditional **Rh active complexes anchored** with a covalent bond **into traditional carriers**, **polymers and metal organic framework** structures.



EU-project Horizon 2020 CE-NMBP-24-2018 C123 Methane oxidative conversion and hydroformylation to propylene

EU-project Horizon 2020 GA No. 814557 C123 Methane oxidative conversion and hydroformylation to propylene

Anchored catalyst Strategies

Metal Organic Frameworks	• Phosphine modified NU1000 and MOF808. • Rhodium complex inserted.
Polymers	• Polyphos phoshine modified Synthesis metallated with Rh Complexes. • Amine and phosphine Functionalised resin beads.
Silica Functionalization	• Organosilane Chemistry. • Anchor Rh complex over amine or Phosphine group.

Johnson Matthey Technol. Rev., 2021, 65, (2), 311
doi: 10.1595/205651321X16051060155762

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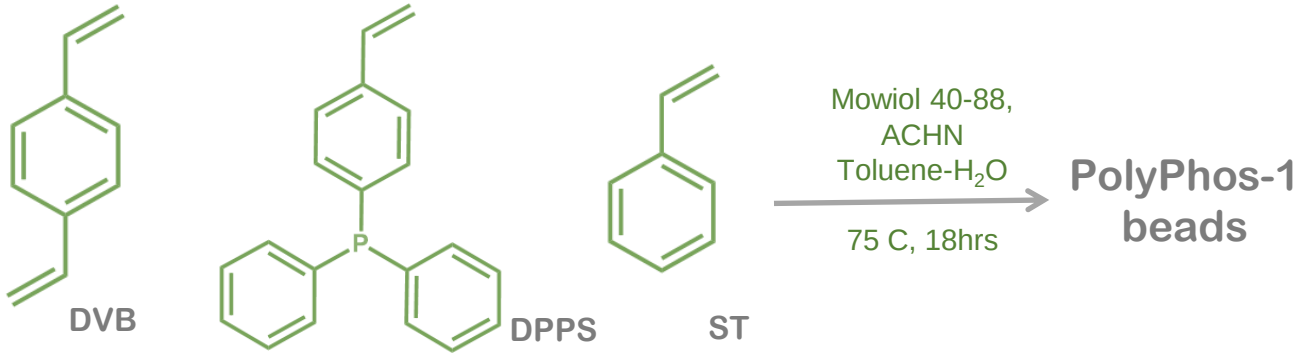
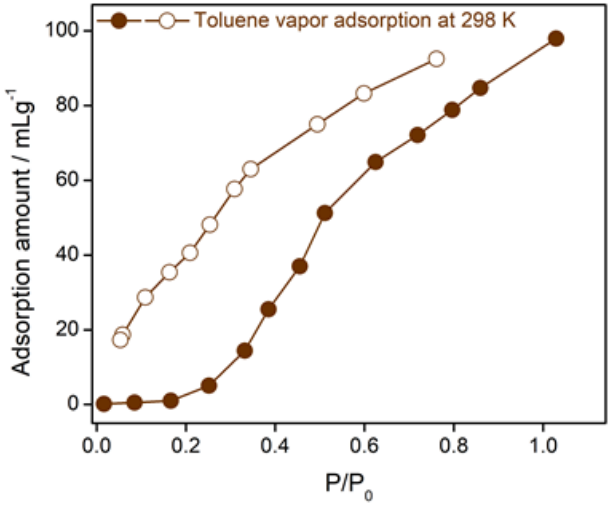
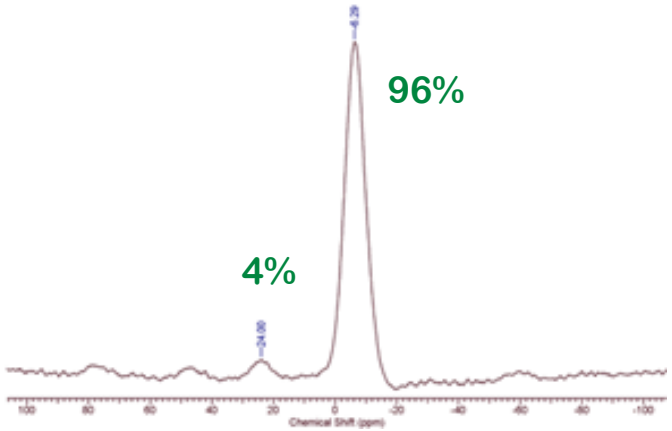
Polymer-based Catalysts:
PolyPhos Beads







Polymer beads were synthesized with the help of mechanical stirrer

Using Mowiol 40–88 via suspension technique

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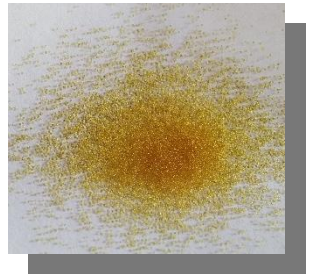
Polymer-based Catalysts:
PolyPhos Beads

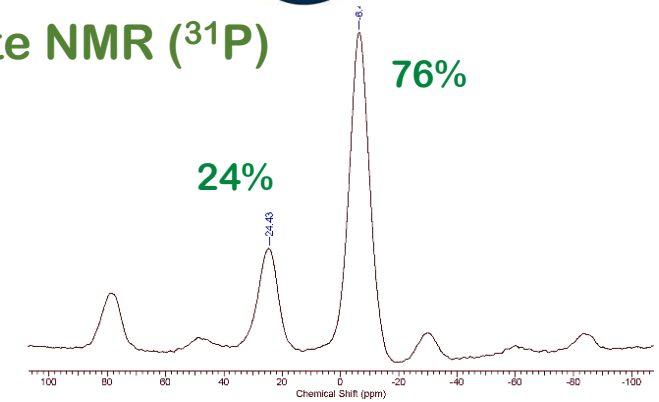
Synthesis

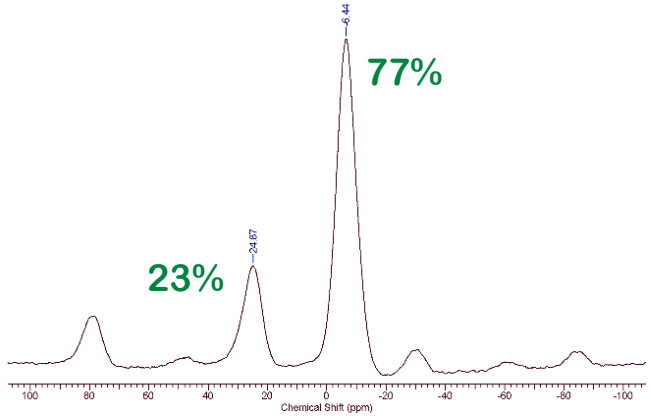
$Rh(CO)_2(acac)$
THF

$RhH(CO)(PPh_3)_3$
THF



Solid State NMR (^{31}P)





ICP-OES

Compounds	Wt % of P	Wt % of Rh
RhH@PolyPhos-1 beads	2.0	0.73
Rh@PolyPhos-1 beads	1.6	0.90

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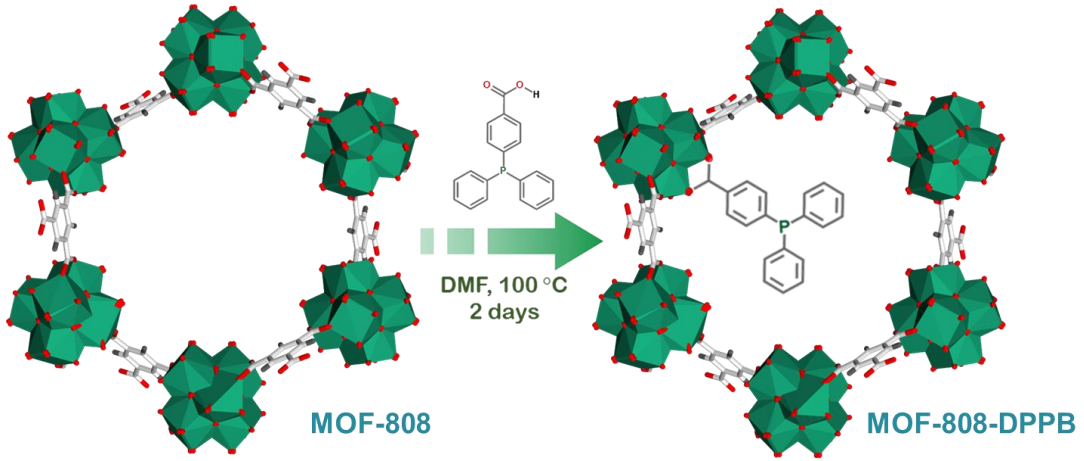
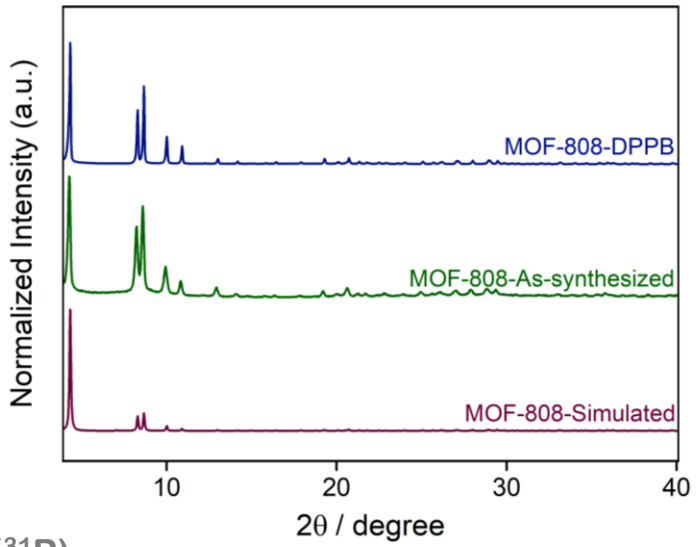
MOF-based Catalysts: Linker grafting in MOF-808

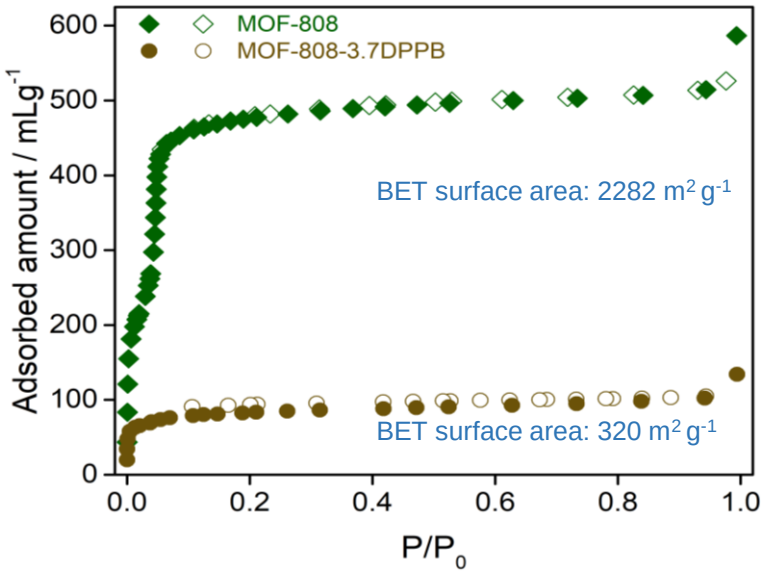
Synthesis



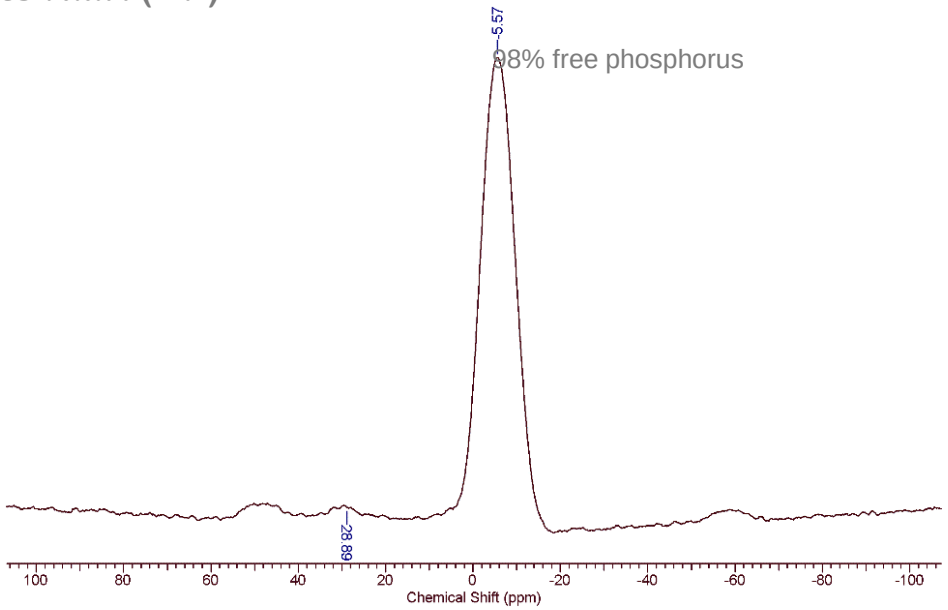
PXRD



N_2 adsorption at 77 K

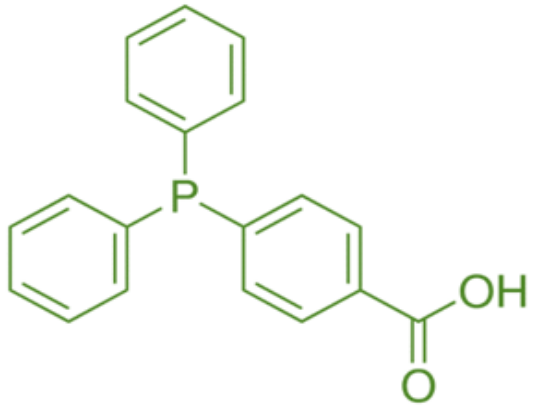


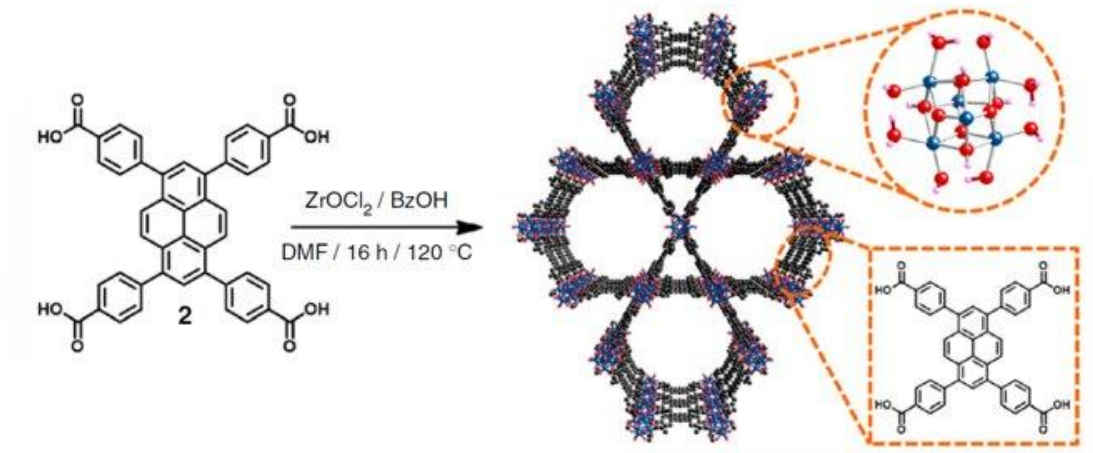
Solid State NMR (^{31}P)

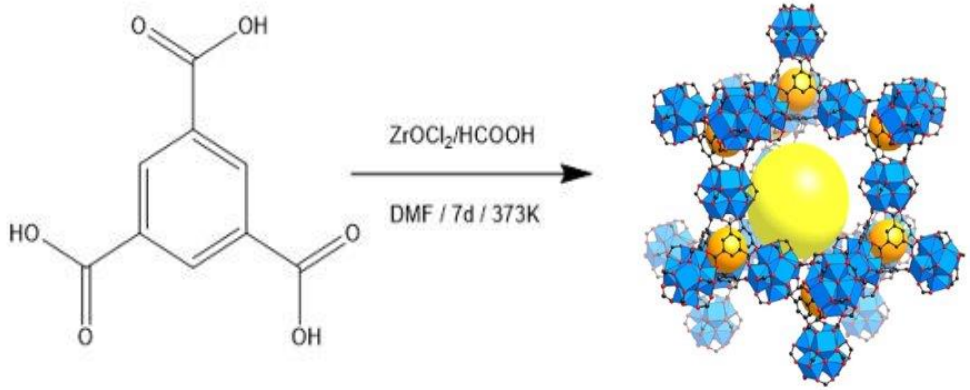


Synthesis of novel MOF based heterogeneous catalysts

- NU1000 synthesis (MOF-808)
- Functionalizing the MOF
- Formulating the MOF
- Testing Heterogenous catalysts







Nature Protocols **2016**, *11*, 149-162
J. Am. Chem. Soc. **2014**, *136*, 4369−4381

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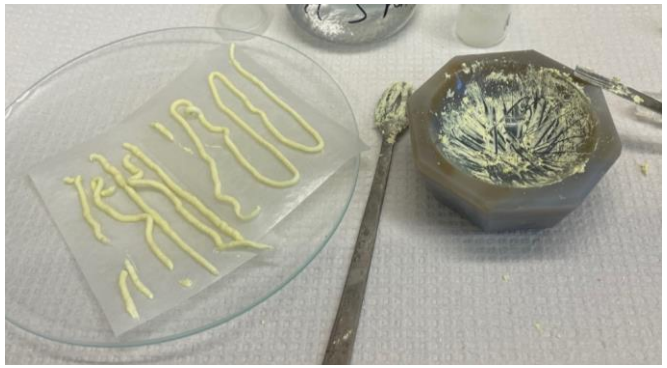
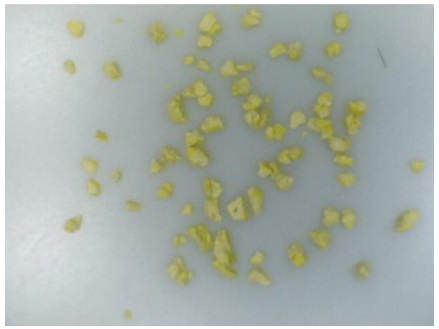
Formulation of functionalized NU-1000

- TRL 5 heterogenous testing requires 500-1.5mm particles
- Previously extruded UTSA-16 by mixing with PVA



Steps PVA-method:

1. PVA solution
2. Mixing PVA with MOF
3. Extruding/milling/sifting
4. Characterization



Pelletising method:

1. Tablets pressed by applying pressure
2. Milling/sifting
3. Characterization

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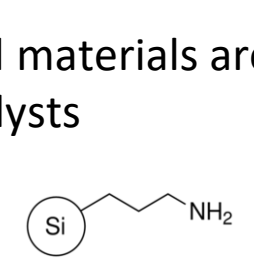
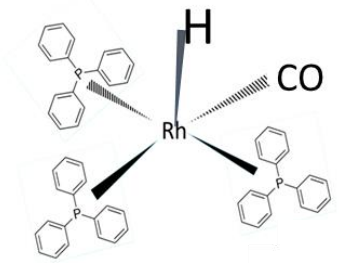
JM Catalyst Strategy:

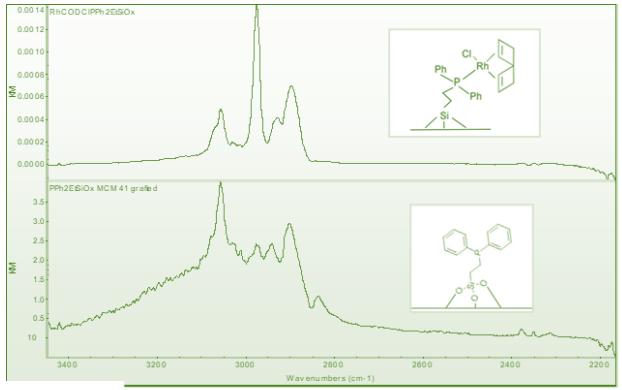
Johnson Matthey
Inspiring science, enhancing life

Material family A:

Amine functionalized materials are reacted with Rh catalysts



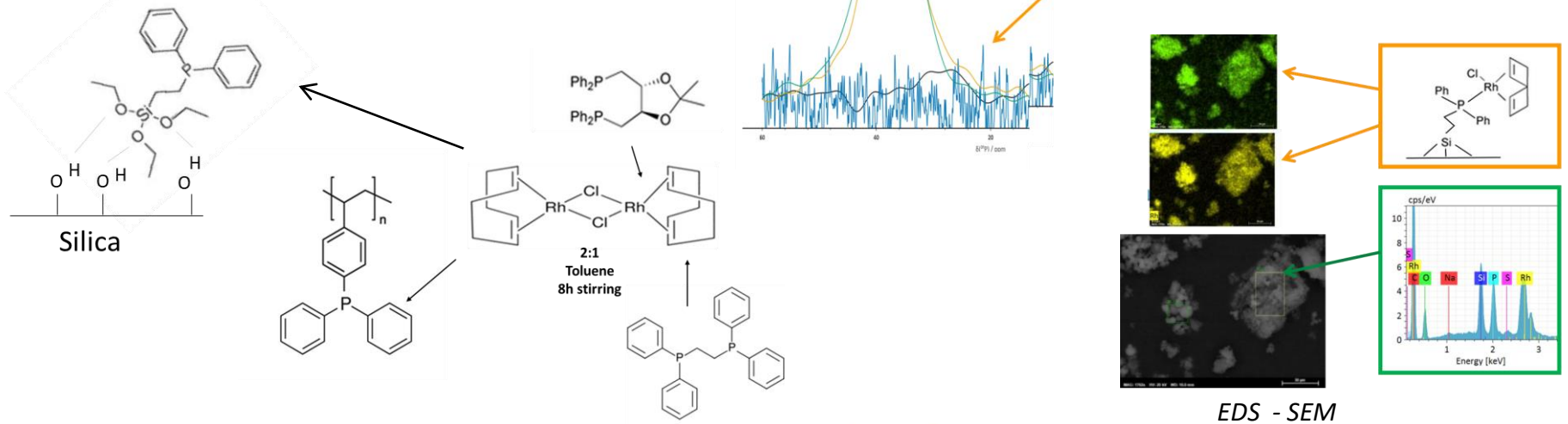




Infrared organic vCH bands

Material family B:

Functionalised TPhP materials react with Rh salts and phosphines



EDS - SEM

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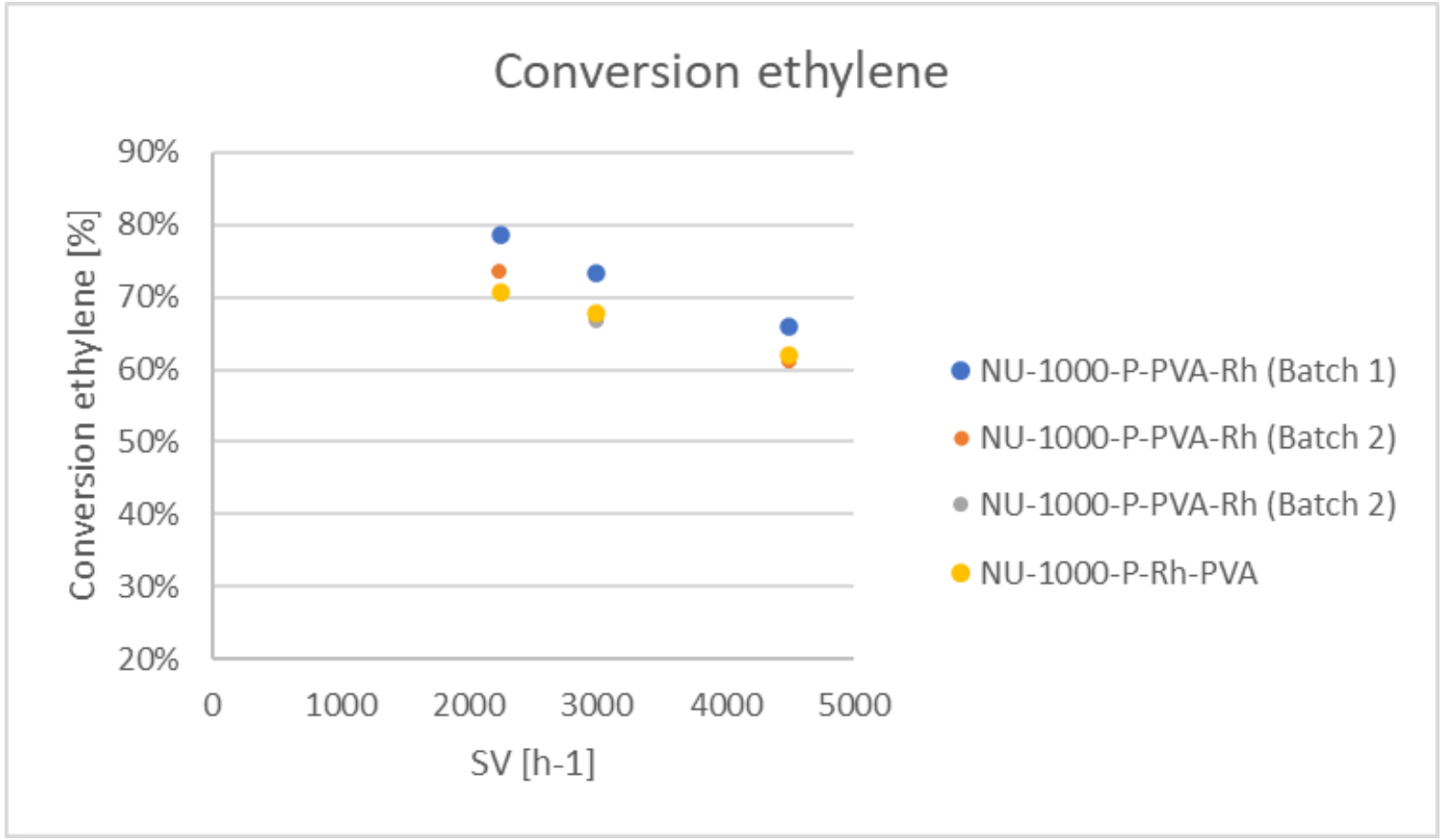
Catalyst Testing:

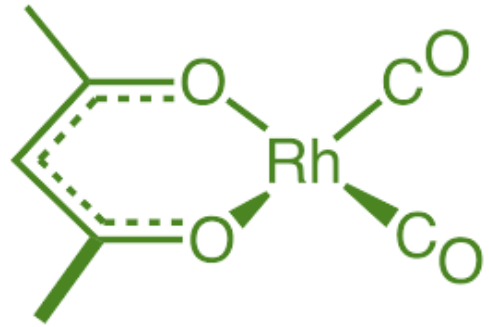
Catalyst	M-complex
NU-1000-P-Rh-PVA	$Rh(acac)(CO)_2$ $Rh(H)(CO)(PPh_3)_3$
RhH@Polyphos-1 beads (400-600 um)	$Rh(H)(CO)(PPh_3)_3$ $Rh(acac)(CO)_2$
MOF-808-P-RhH-PVA	(CO)HRh(PPh3)3

Sample code	Catalyst	Initial conversion [%] TOS = 200 min	Recheck conversion TOS = 2150 min	Propanal selectivity* [%]	Stability	Synthesis reproducibility (first estimate)
Mf-C123-90-21	NU-1000-P-RhH-PVA	57%	75%	95-97%	+++	-
Mf-C123-134-21	NU-1000-P-PVA-Rh(acac)	78%	61%	98%	+	+++
PSM-B-033-10	Rh(CO)2(acac) Polyphos	77%	47%	80-85%	-	++

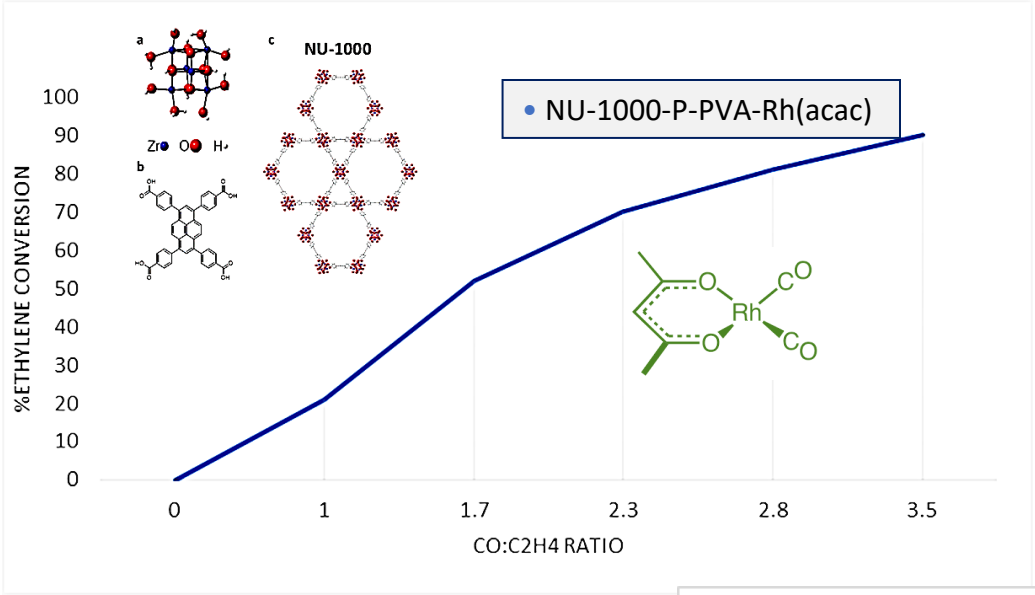
Results and Synthesis reproducibility



NU-1000-P-Rh (5%)
10 bara, 110°C, ethene:CO:H2 = 1:1:2



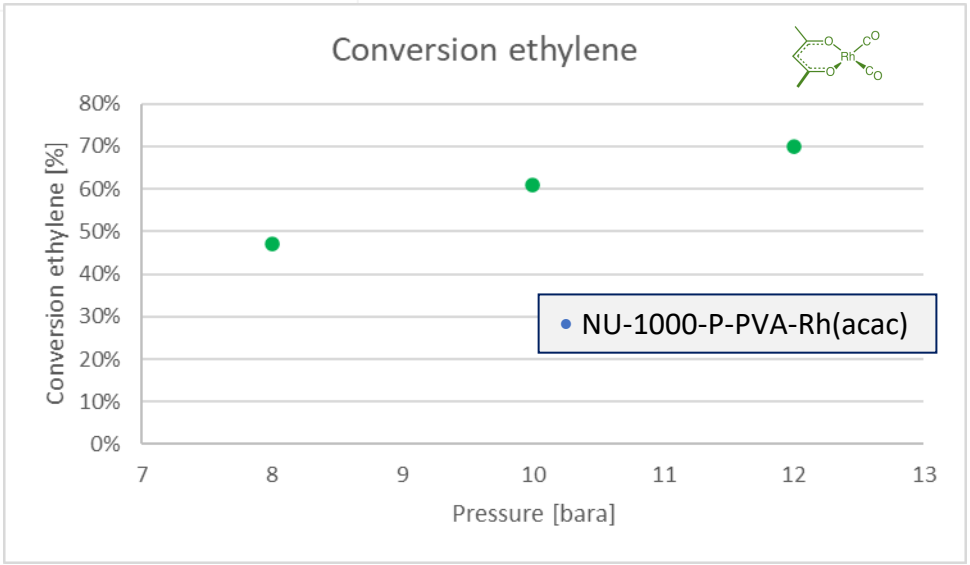
CO ethylene ratio analysis



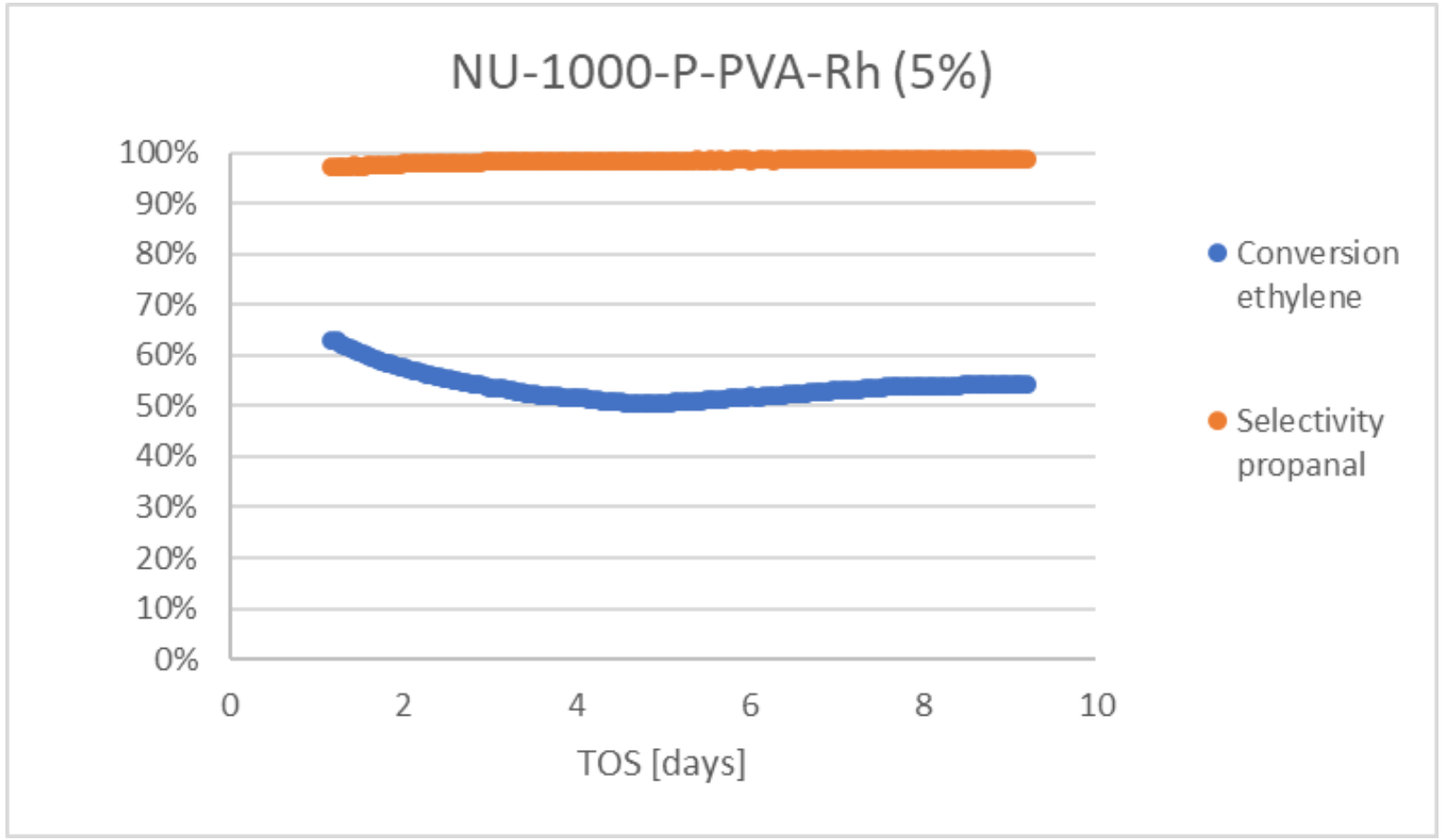
Positive effect of increased CO content in the feed

Pressure effect

As expected positive effect of increased pressure in the conversion



Stability


NU-1000-P-PVA-Rh (5%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
2
4
6
8
10
TOS [days]
Conversion ethylene
Selectivity propanal

Summary

- Several interesting candidates for gas phase HF showing good performance
  - Rh-Polyphos exhibited stability issues
  - Rh functionalised NU-1000 is robust but economically unviable
- $Rh(acac)(CO)_2$ shows overall best performance and is reproducible
- Several attempts of making a Co functionalised NU-1000 not active for HF
- Positive effect of increased CO content in the feed
- Positive effect when pressure is increased as expected
- Small ammounts of O_2 in the feed rapidly deactivates the catalyst
- No negative effect observed with 20 % CO_2 in the feed

Thank you

Acknowledges:

- **Johnson Matthey**
  - Stephen Poulston and Stephen Bennet
- **SINTEF**
  - Richard Heyn (PI) Mortem Frøseth (NU1000 synthesis) Silje Fosse Håkonsen (Catalyst screening).
- **CNRS**
  - Lyon Jerome Canivet (PI) Partha Samantha (Polyphos and MOF 808 Synthesis)
- **Axel One**
- Didier Bonet (PI) Thomas Michon (Shaping and Formulation)

Contacts:

Alvaro Amieiro Fonseca:– C123 WP3 leader-
amieia@matthey.com

Richard Heyn– C123 Project coordinator
Richard.H.Heyn@sintef.no