Gas phase hydroformylation with the post-modified Metal-Organic Framework NU-1000

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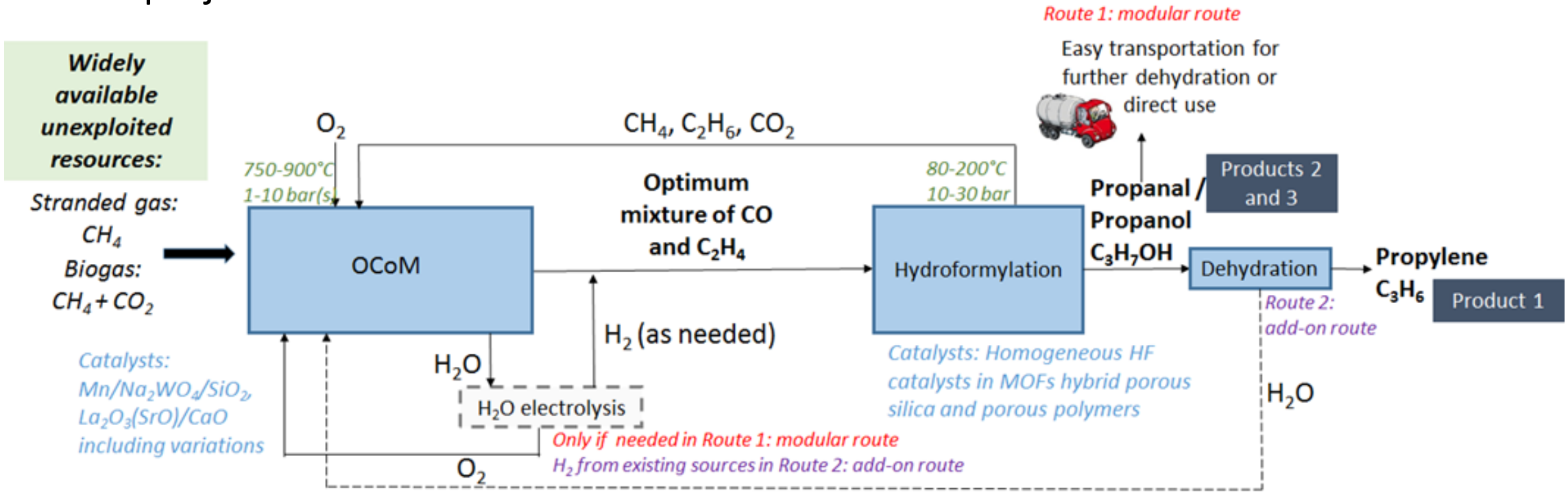
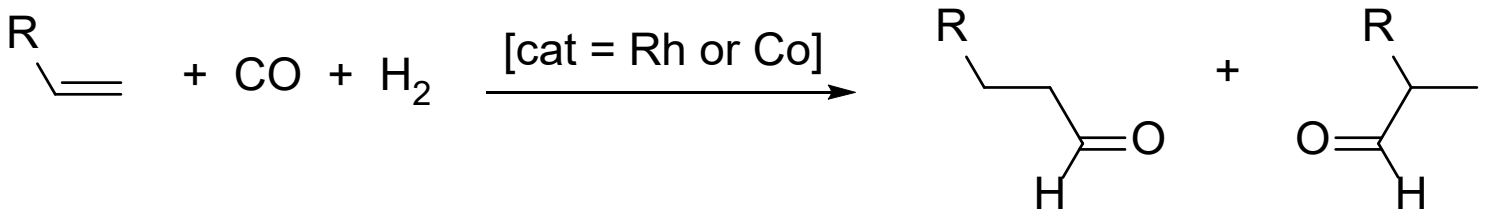
The C123 project

C123 – Methane oxidative conversion and hydroformylation to propylene
H2020 project 01.2019 – 06.2023



Hydroformylation

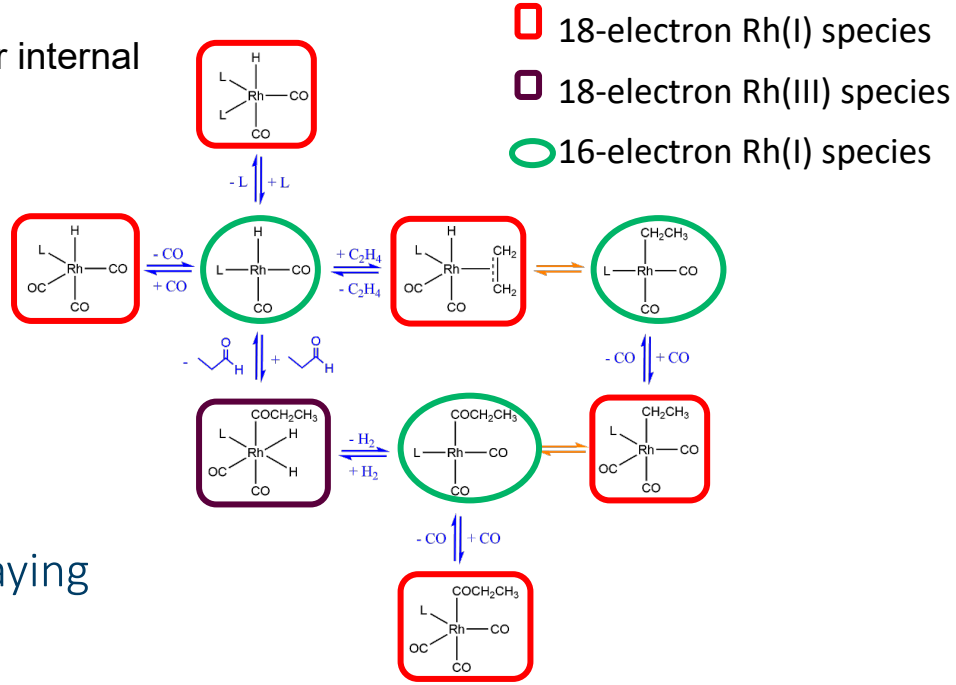
- The world's largest industrial *homogeneous* catalytic process



Linear Branched or internal

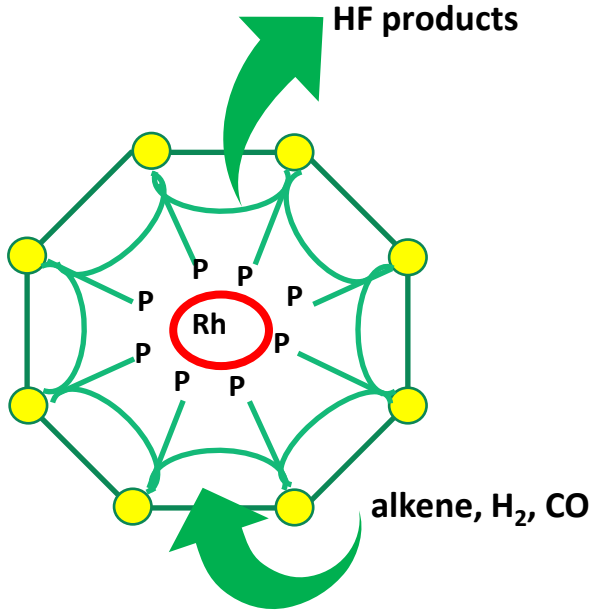
- Propene to butyraldehyde (R = Me) is most common industrial hydroformylation
- For ethene (R = H), only one aldehyde product

- Preferred industrial conditions
  - Rh catalyst
  - Large excess of phosphines
  - High alkene conversions and aldehyde selectivities (> 95 %)
- **No industrial heterogeneous, gas phase process**
  - State-of-the-art gas phase hydroformylation does not provide relevant conversions and selectivities
  - Cannot in general access same homogeneous mechanism
  - Supported metal catalysts in general lack the same electronic playing field as homogeneous catalysts



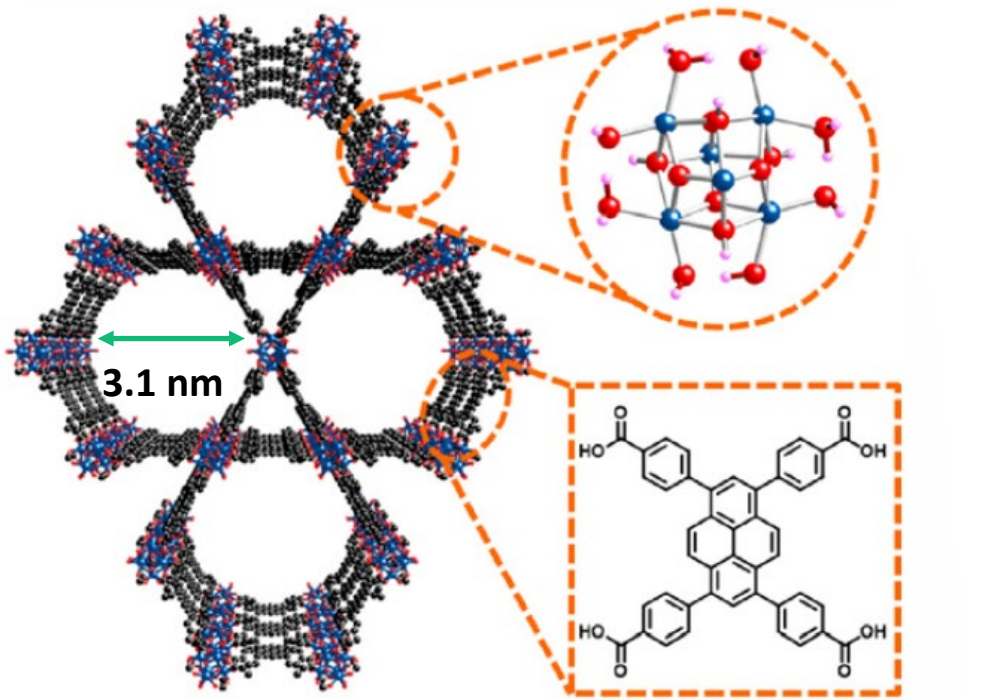
Hypothesis and choice of NU-1000

Our hypothesis for bridging homogeneous and heterogeneous catalysis: Could a MOF with an excess of phosphine ligands in the pores mimic a homogeneous mechanism and provide stable gas phase hydroformylation?



Large, accessible pores

$Zr_6(\mu\text{-}O)_4(\mu\text{-}OH)_4(H_2O)_4(OH)_4$, 8-connected nodes

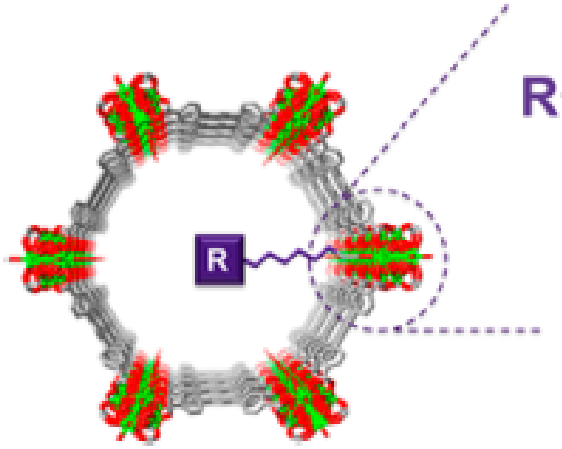


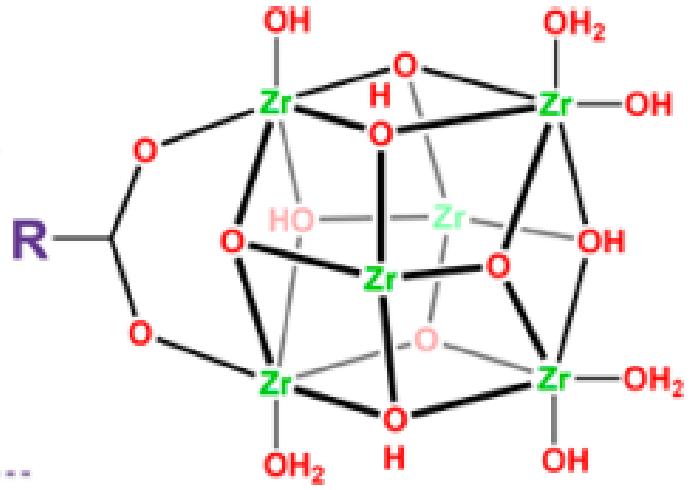
Acc. Chem. Res. **2017**, *50*, 805-813

1,3,6,8-tetrakis(*p*-benzoic acid) pyrene (H_4TBAPy)

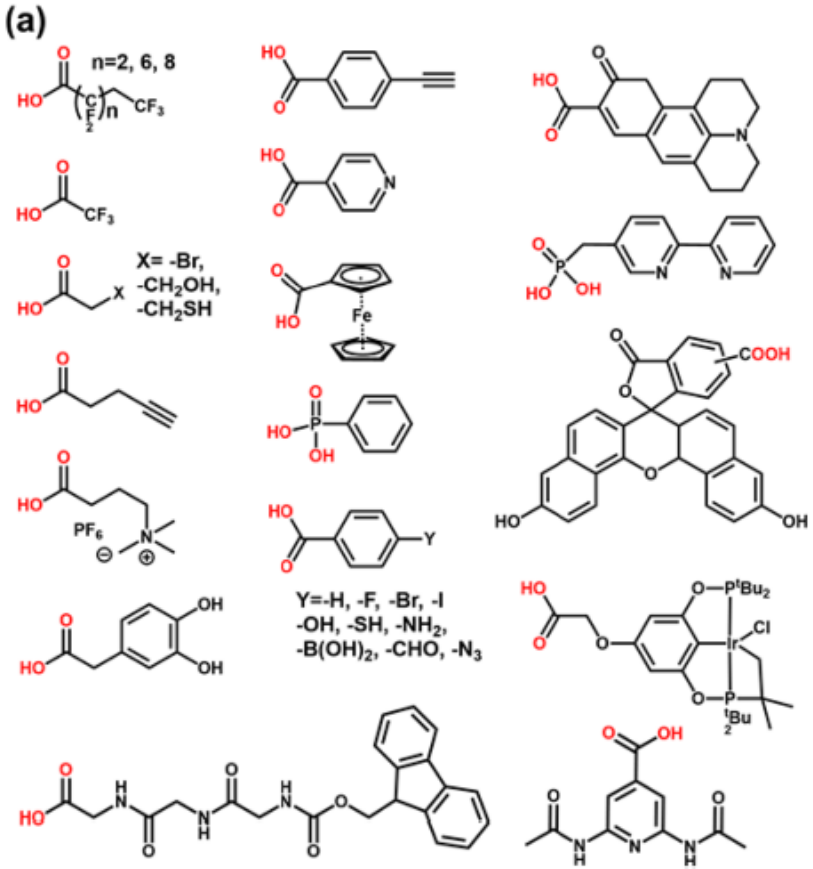
Solvent-Assisted Ligand Incorporation (SALI)

- Reaction of carboxylic or phosphonic acids with OH/H_2O groups on Zr_6 nodes





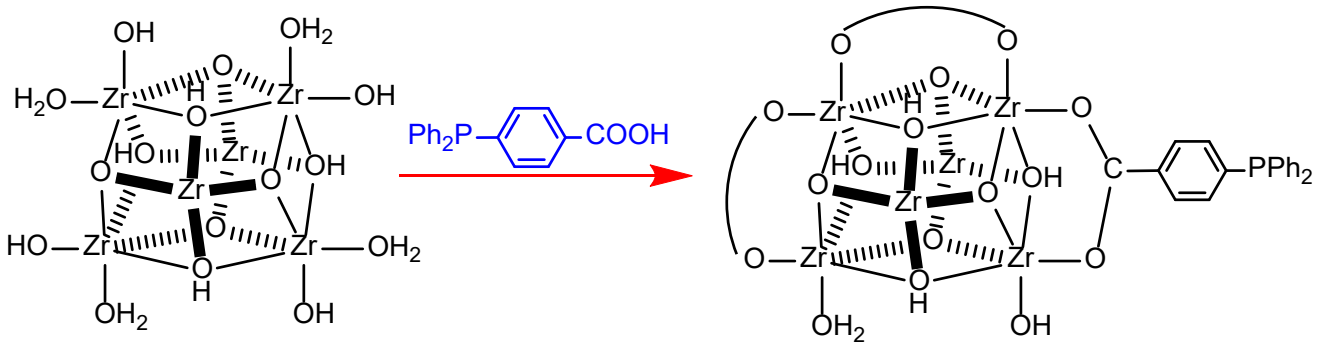
Linkers not shown



Can add up to 4 ligands with this method

Acc. Chem. Res. **2017**, *50*, 805-813

P@NU-1000



Surface area (BET)

NU-1000 (literature)	2220 m^2/g
NU-1000 (synthesized)	2275 m^2/g
P@NU-1000	1456 m^2/g

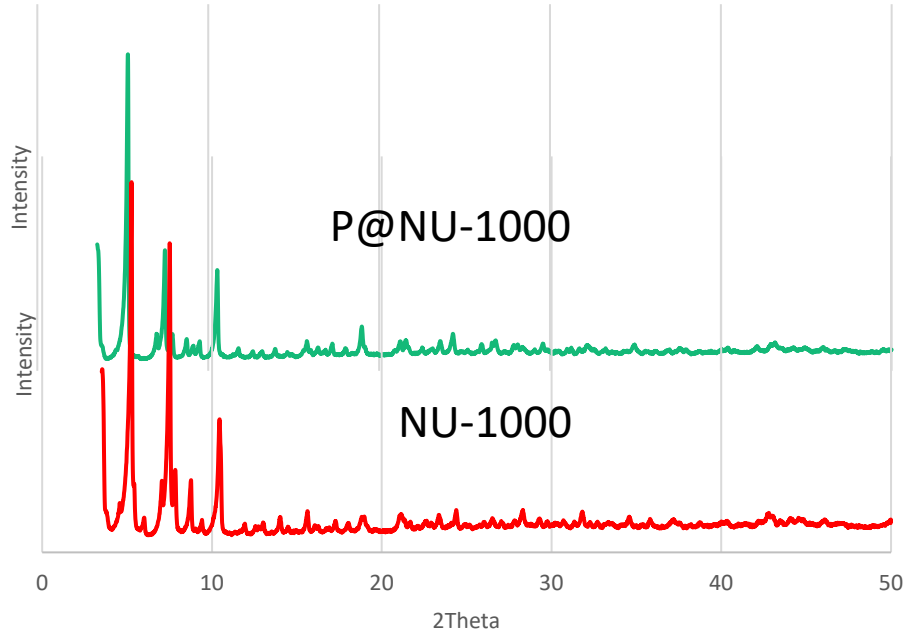
Literature values: 595 m^2/g – 1750 m^2/g

Ph_2P—COOH

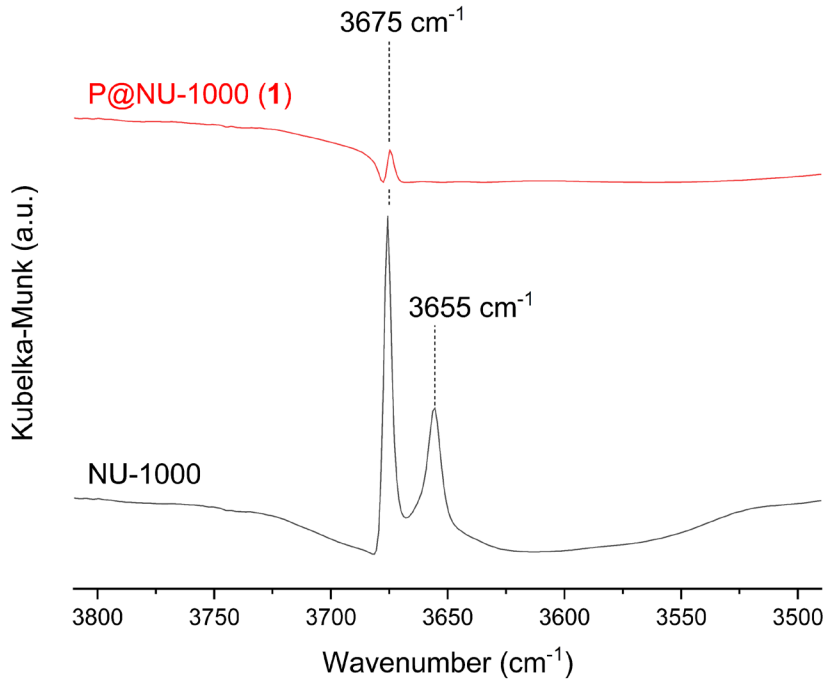
≡ Diphenyl-phosphino-benzoic acid **DPPB**

^{31}P NMR spectrum of digested sample (phosphine oxide observed)
Solid state ^{13}C and ^{31}P NMR spectra

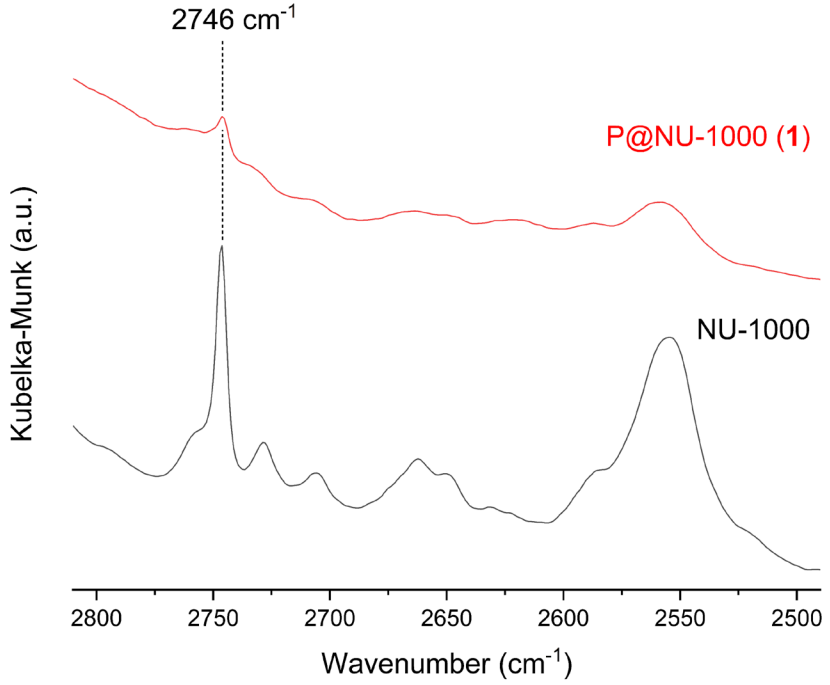
- Integration of ^{1}H NMR spectrum digested P@NU-1000 gives 3 P/Zr_6 cluster
- ICP: 0.56 P/Zr or 3 P/Zr_6



IR spectra of P@NU-1000



-O*H* and H_2O stretch

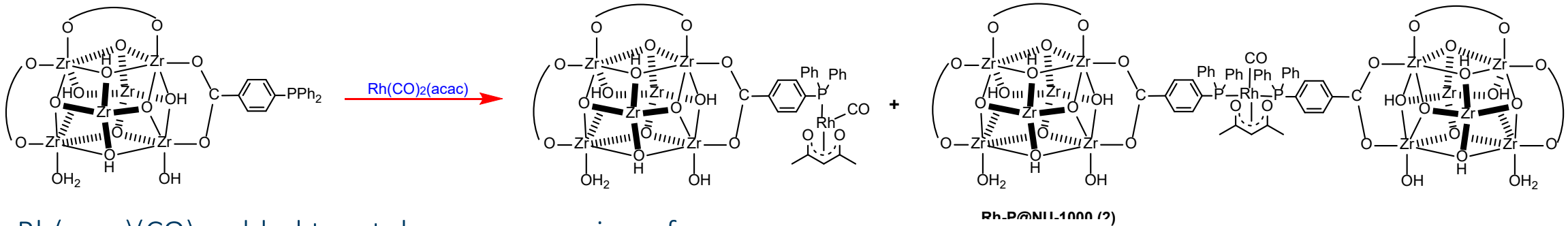


Formate C-H vibration
(from DMF during synthesis)

J. Phys. Chem. Lett. **2014**, *5*, 3716-3723

J. Am. Chem. Soc. **2020**, *142*, 21110-21121

Incorporation of Rh



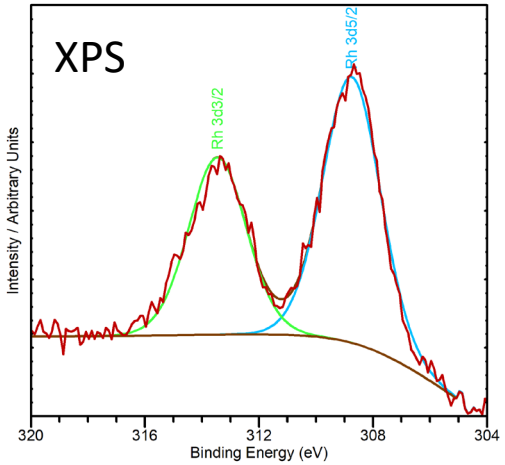
- $Rh(acac)(CO)_2$ added to a toluene suspension of P@NU-1000
- Two targeted Rh concentrations
  - 5 % Rh - **Rh(5%)-P@NU-1000** or **2-5%**
    - Maximum that can be added with one impregnation reaction
  - 1 % Rh - **Rh(1%)-P@NU-1000** or **2-1%**

ICP data

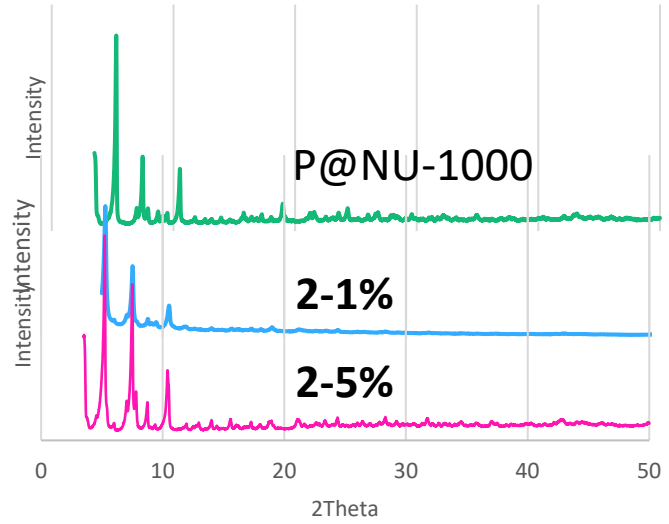
	% P	% Rh	P/Rh
2-5%	2.34	4.24	1.83
2-1%	2.12	0.77	9.1

Surface area (BET)

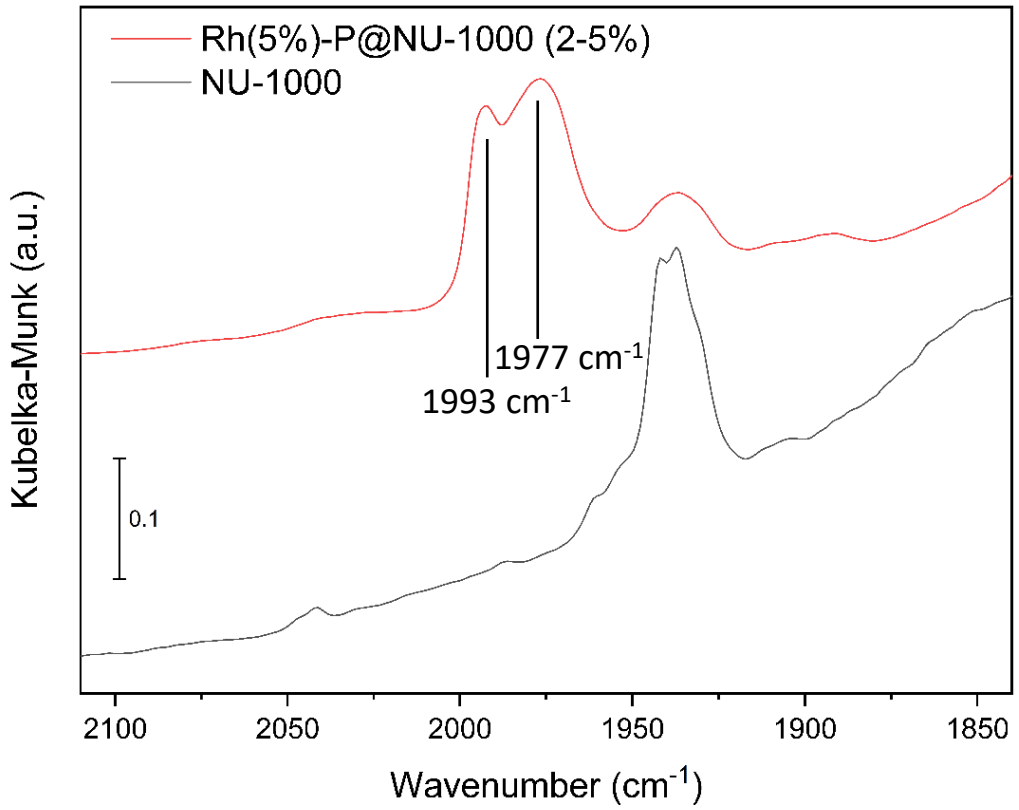
NU-1000 (synthesized)	2275 m^2/g
P@NU-1000	1456 m^2/g
2-5%	1183 m^2/g
2-1%	1232 m^2/g



- Rh $3d_{5/2}$ consistent with Rh(I)-P species
- No Rh(0)



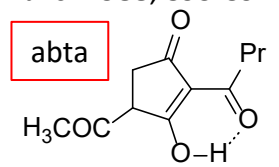
IR spectrum of Rh-P@NU-1000 materials



- Not a $Rh(CO)_2$ species
  - Analogous monomeric dicarbonyl species have two CO stretching frequencies around 2010 cm^{-1} and 2050 cm^{-1}
- $Rh(acac)(CO)(PPh_3)$: ν_{CO} = 1980 cm^{-1} *J. Mol. Catal.* **1993**, *80*, 189-200
- $Rh(O\text{-}acac)(CO)(P^iPr_2Ph)_2$: ν_{CO} = 1954 cm^{-1}

J. Chem. Soc., Dalton Trans. **1988**, 895-897

abta



- $Rh(abta)(CO)PPh_3$: ν_{CO} = 1990 cm^{-1}
- $Rh(abta)(CO)(PPh_3)_2$: ν_{CO} = 1960 cm^{-1}

J. Chem. Soc., Dalton Trans. **1996**, 1701-1706

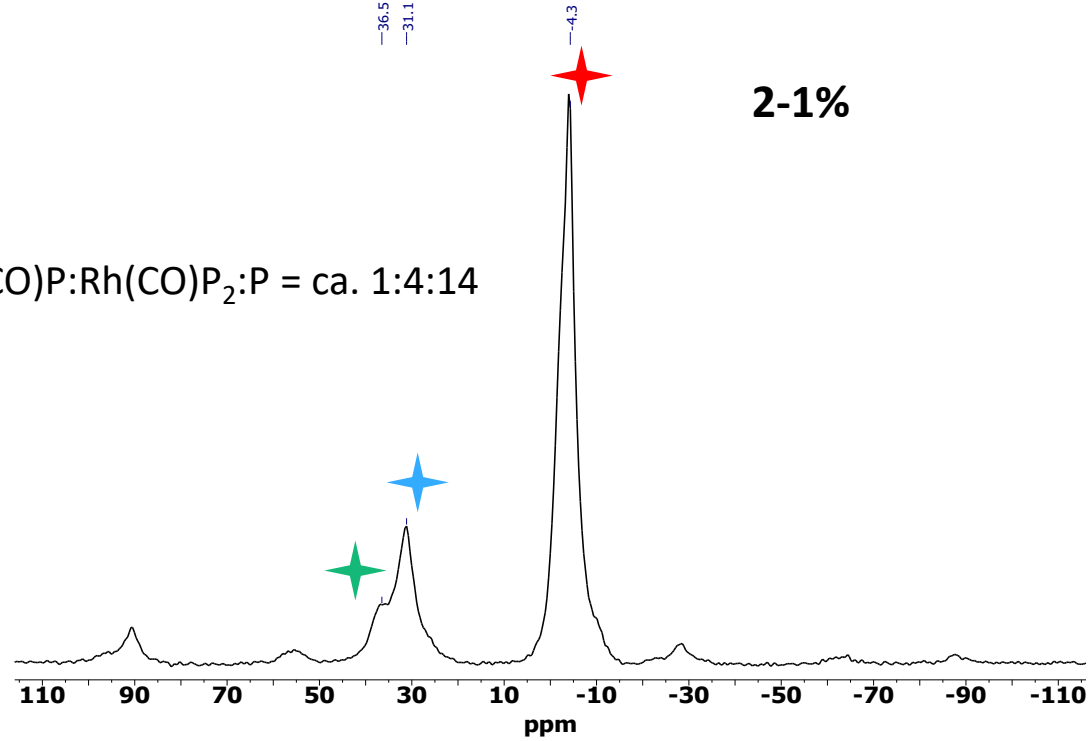
- ν_{CO} = 1977 cm^{-1} = $Rh(CO)(P^*)_2$ species
- ν_{CO} = 1993 cm^{-1} = $Rh(CO)P^*$ species

Node-bound DPPB (P*) is a less electron donating phosphine than PPh_3

^{31}P MAS-NMR spectra of Rh-P@NU-1000

2-1%

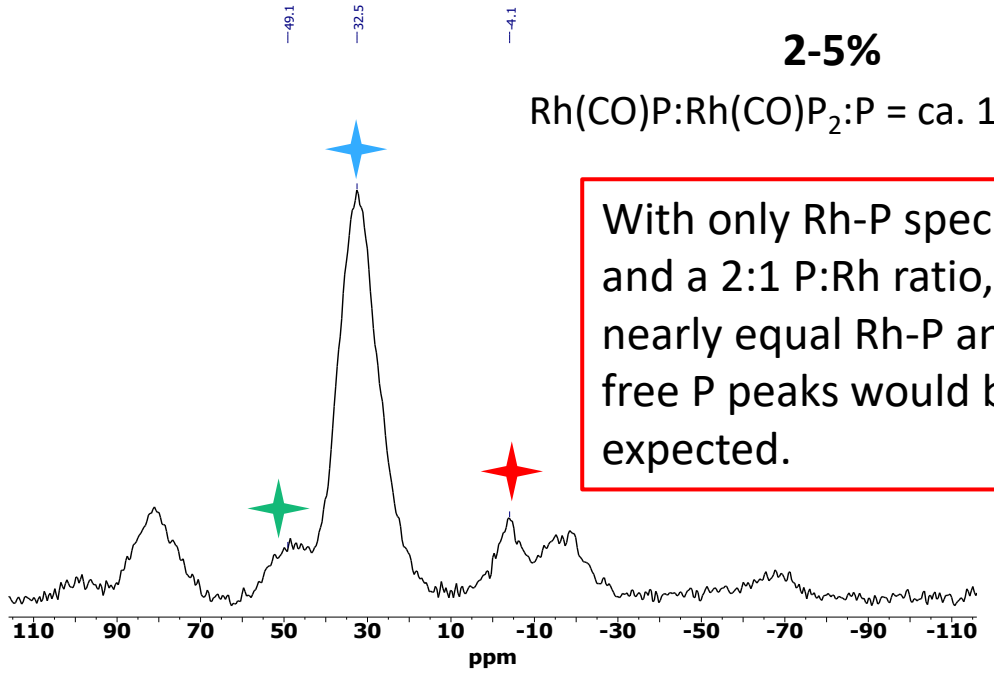
Rh(CO)P:Rh(CO)P_2:P = ca. 1:4:14



- Rh(acac)(CO)(PPh_3): 48.6 ppm
- Rh(abta)(CO)(PPh_3): 47.9 ppm
- Rh(abta)(CO)($PPh_3)_2$: 34.3 ppm

2-5%

Rh(CO)P:Rh(CO)P_2:P = ca. 1:15:1



With only Rh-P species and a 2:1 P:Rh ratio, nearly equal Rh-P and free P peaks would be expected.

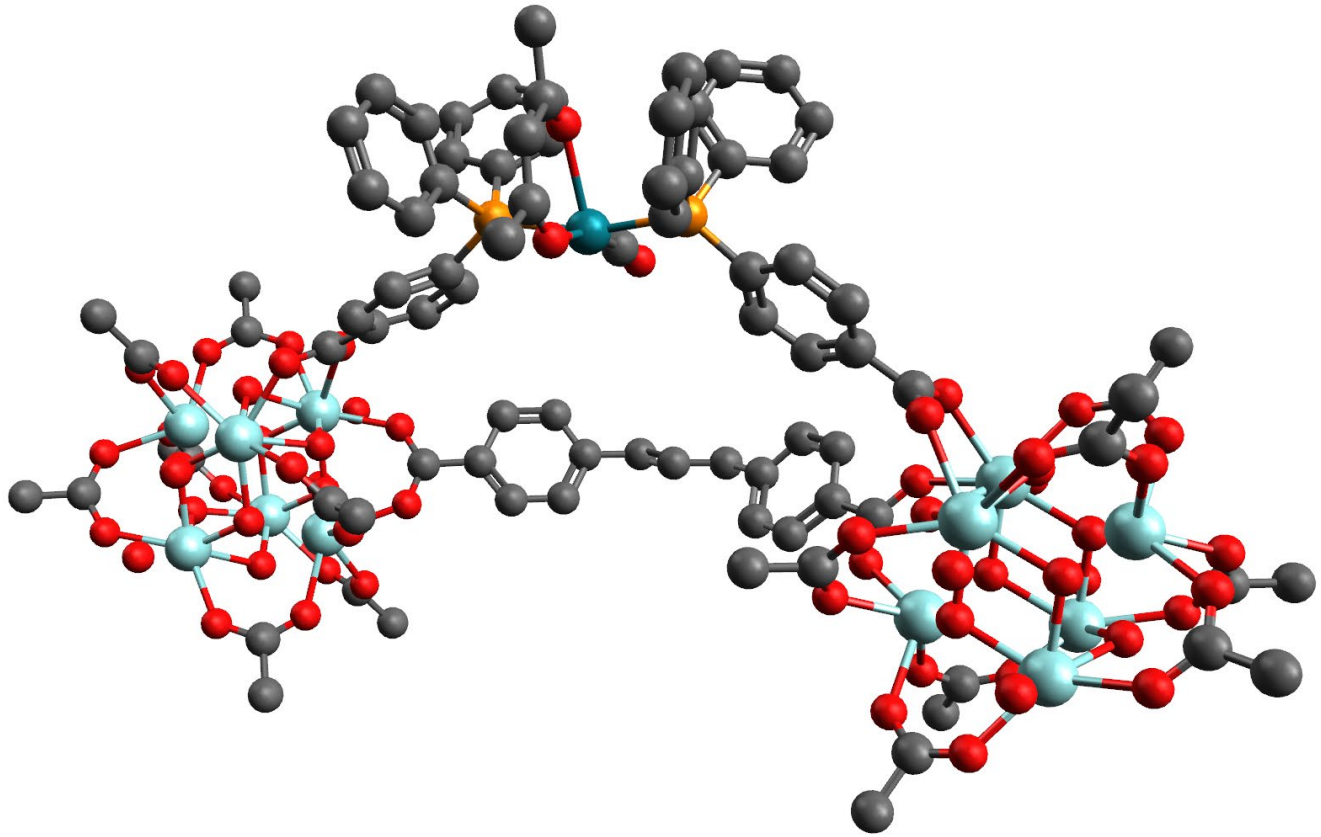
- Uncoordinated DPPB
- Rh(CO)P
- Rh(CO)P_2

Modelled Rh sites

- Calculations with an analogous MOF-808 material (1.8 nm pores) showed diphosphine complex to be less stable than the monophosphine complex.

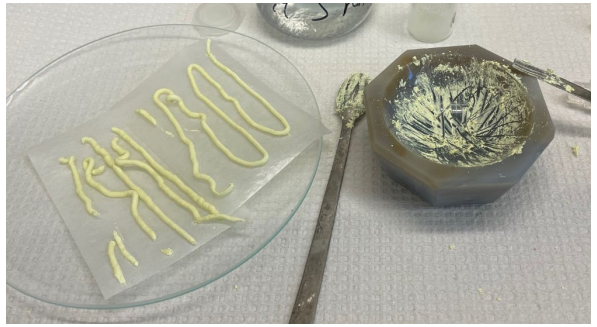
ACS Catal. **2023**, *13*, 4193-4204.

- Lower limit of the bonding energy is 4 kJ/mol.
- Larger pores/longer linker of NU-1000 permit formation of supported diphosphine Rh complexes.



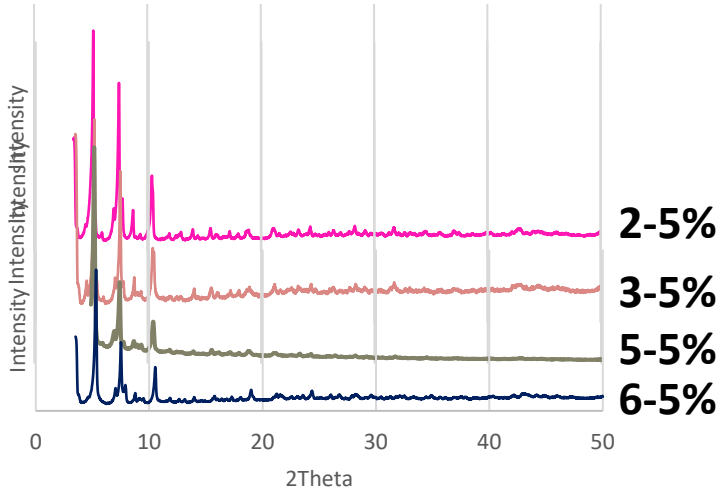
Formulation of Rh-P@NU-1000

- Formulation required for gas phase testing – not straightforward for MOFs
- Two formulation procedures to provide 210 µm – 500 µm particles
  - Pelletization (**3-1%** and **3-5%**)
  - Extrusion from a PVA/H_2O/^{i}PrOH (4:45:45 weight ratio) paste
    - PVA formulation done both before (**5-1%** and **5-5%**) and after Rh addition (**6-5%**)
- No apparent reduction in crystallinity nor significant decrease in surface area or pore volume

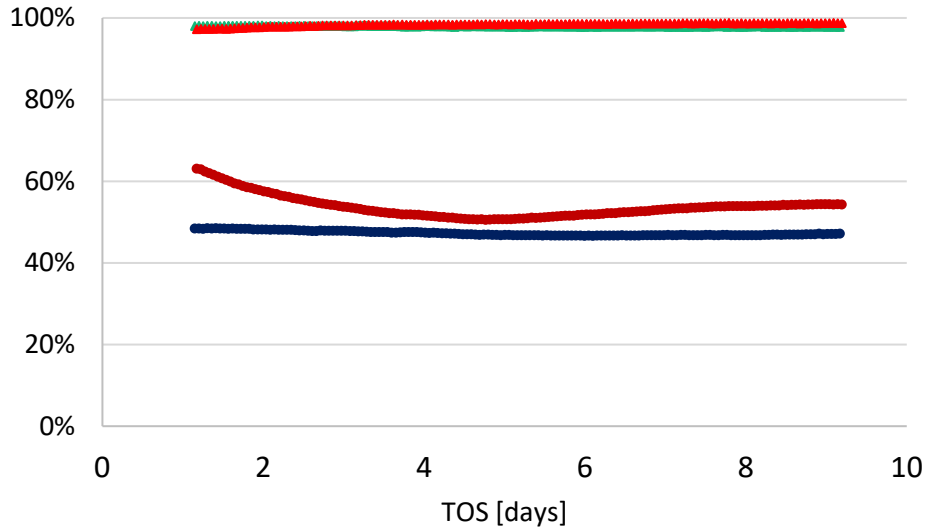


ICP data	% P	% Rh	P/Rh
2-5%	2.34	4.24	1.83
2-1%	2.12	0.77	9.1
5-5%	2.1	3.6	2.0
5-1%	1.4	0.44	10.4
6-5%	2.07	4.04	1.72

	Surface area (BET)	Total Pore Vol
2-5%	1183 m^2/g	0.661 m^3/g
2-1%	1232 m^2/g	0.755 m^3/g
3-5%	1102 m^2/g	0.611 m^3/g
3-1%	1110 m^2/g	0.673 m^3/g
5-5%	1099 m^2/g	0.610 m^3/g
5-1%	1031 m^2/g	0.626 m^3/g
6-5%	1111 m^2/g	0.624 m^3/g



Extended testing and control experiments



Selectivity

Conversion **5-5%**
Conversion **5-1%**

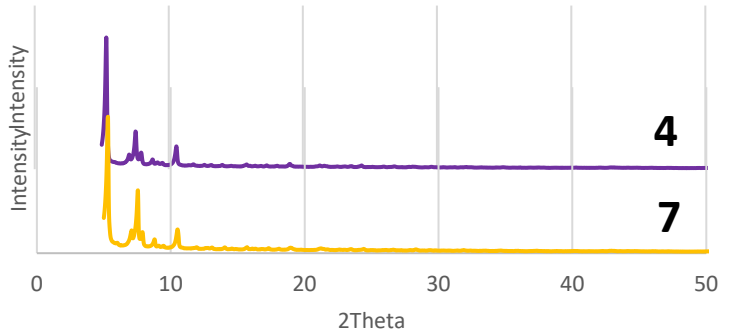
100 °C, 2250 h^{-1}

Neither PVA-P@NU-1000 (**4**) nor Rh(1%)-PVA@NU-1000 (**7**) showed any catalytic activity between 100 °C – 120 °C.

Surface area (BET)	
4	1002 m^2/g
7	1296 m^2/g

ICP data	% Rh
7	0.74

- TOF estimated to be between 100 h^{-1} – 1000 h^{-1}
- **3-1%** is more active than **3-5%** on a Rh wt basis.
- Decrease in activity of **5-5%** hypothesized to be the result of phosphine oxidation/rearrangement



Significance and outlook

- One of the most stable and active heterogenous catalysts for gas phase hydroformylation
  - Ethene conversion only exceeded by a Rh-loaded polymer made from vinyl-functionalized PPh_3
  - Not that different from Fibercat

J. Mol. Catal A **2015**, *404-405*, 211-217

- Despite promising results, industrialization will require dramatic decrease in the cost and environmental impact of NU-1000
  - H_4TBAPy linker very expensive
  - NU-1000 synthesis requires large amounts of solvent
- The most active and stable catalyst requires further research
  - Best use of Rh
  - Better understanding of changes in phosphine structure
  - Minimization of aldol condensation – what is acid or base catalyst?

Conclusions

- Post-modified NU-1000 materials have been synthesized via SALI addition of a PPh_3 analogue and impregnation with $Rh(CO)_2(acac)$.
- IR, NMR and modelling data support the formation of a unique $Rh(CO)(acac)(P^*)_2$ moiety in the pores, that is the likely catalytic site for gas phase hydroformylation.
- Material can be readily formulated via either pelletization or extrusion without loss of structural integrity, surface area or pore volume.
- Material is a stable catalyst for gas phase hydroformylation for up to 9 days with ethene conversions of $\geq$ 50 % and propanal selectivities over 97 %.
- Post-reaction characterization shows changes in the ^{31}P MAS spectrum, consistent with either some phosphine oxidation or formation of other catalytic Rh-P sites, without structural degradation or significant loss in activity and selectivity.

Acknowledgements

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- C123 partners
  - CNRS Lyon (Jerome Canivet) – Similar concept with MOF-808 (*ACS Catal.* **2023**, *13*, 4193-4204)
  - Univ. Gent (Joris Thybaut) – Microkinetic modelling of gas phase hydroformylation
  - Johnson Matthey – Hydroformylation Work Package Leader
  - Arkema (Jean-Luc Dubois) – Discussions and suggestions

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