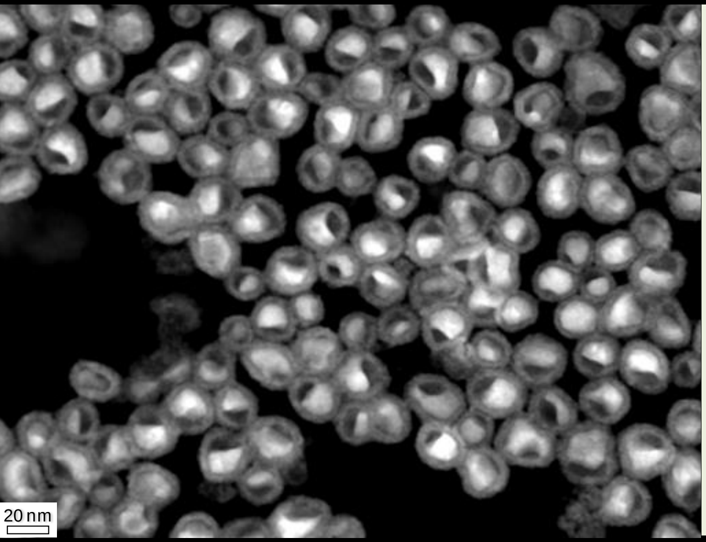
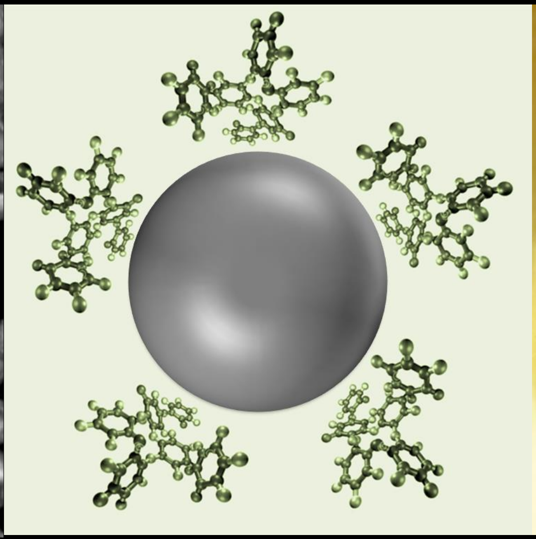
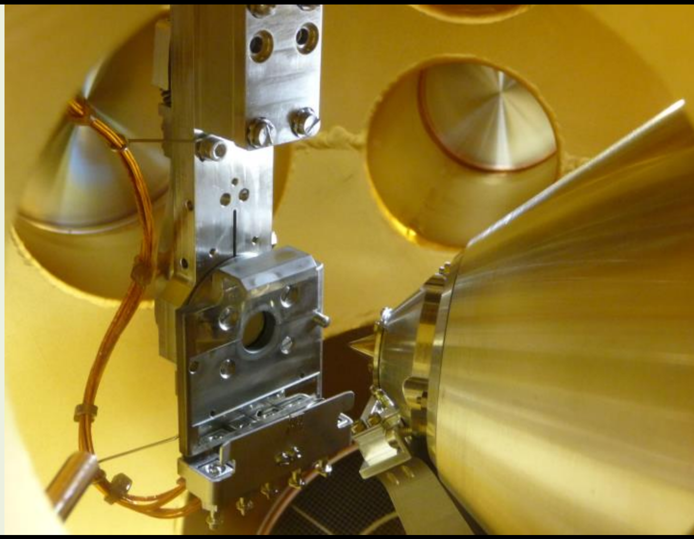
Laboratoire de Chimie de la Matière Condensée de Paris
Sorbonne Université | CNRS | Collège de France



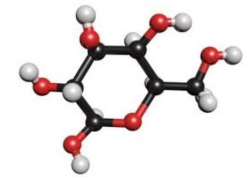
Spectroscopies et microscopies pour l'étude de nanoparticules réactives : un mariage bienvenu

Sophie Carenco

Workshop Science Innov' Carmen Evolution| June 21st, 2022

Research Question

H_2O and CO_2, Sunlight, 25 °C

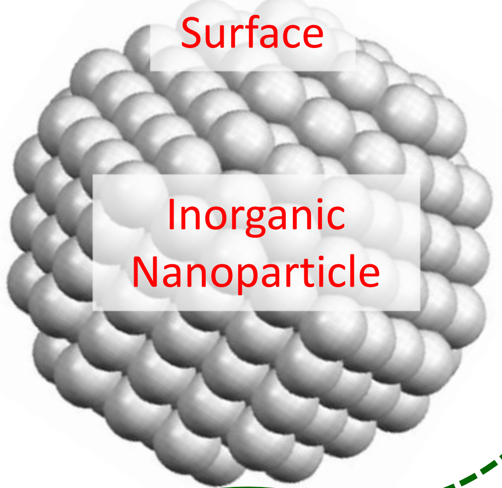


How to boost the surface reactivity of nanoparticles ?

Costly/Heavy setup

Reactivity at T > 150°C
Pressure > 10 bar

Low complexity of formed molecules

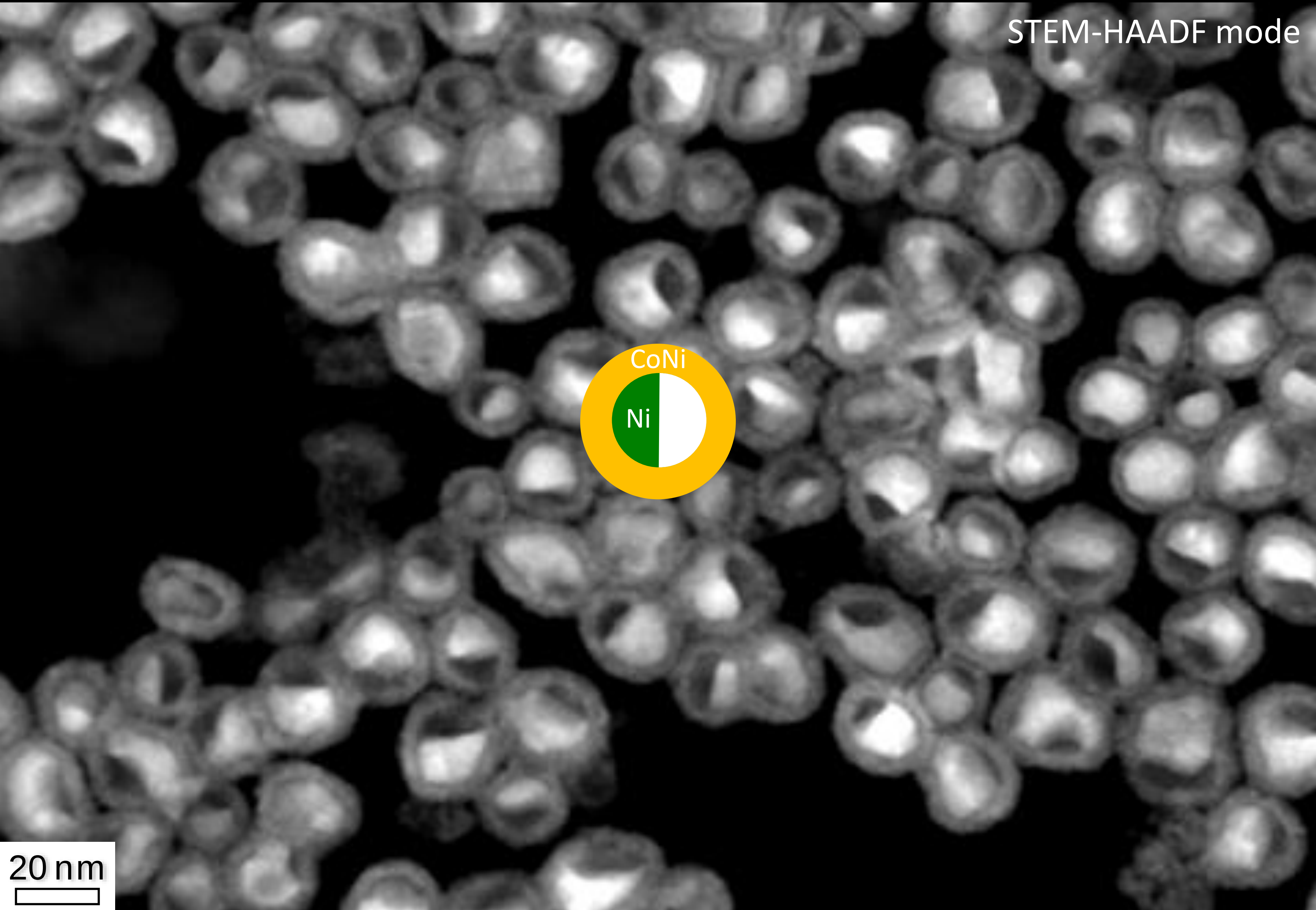


Functional molecules?
Alcohols, amines, etc.

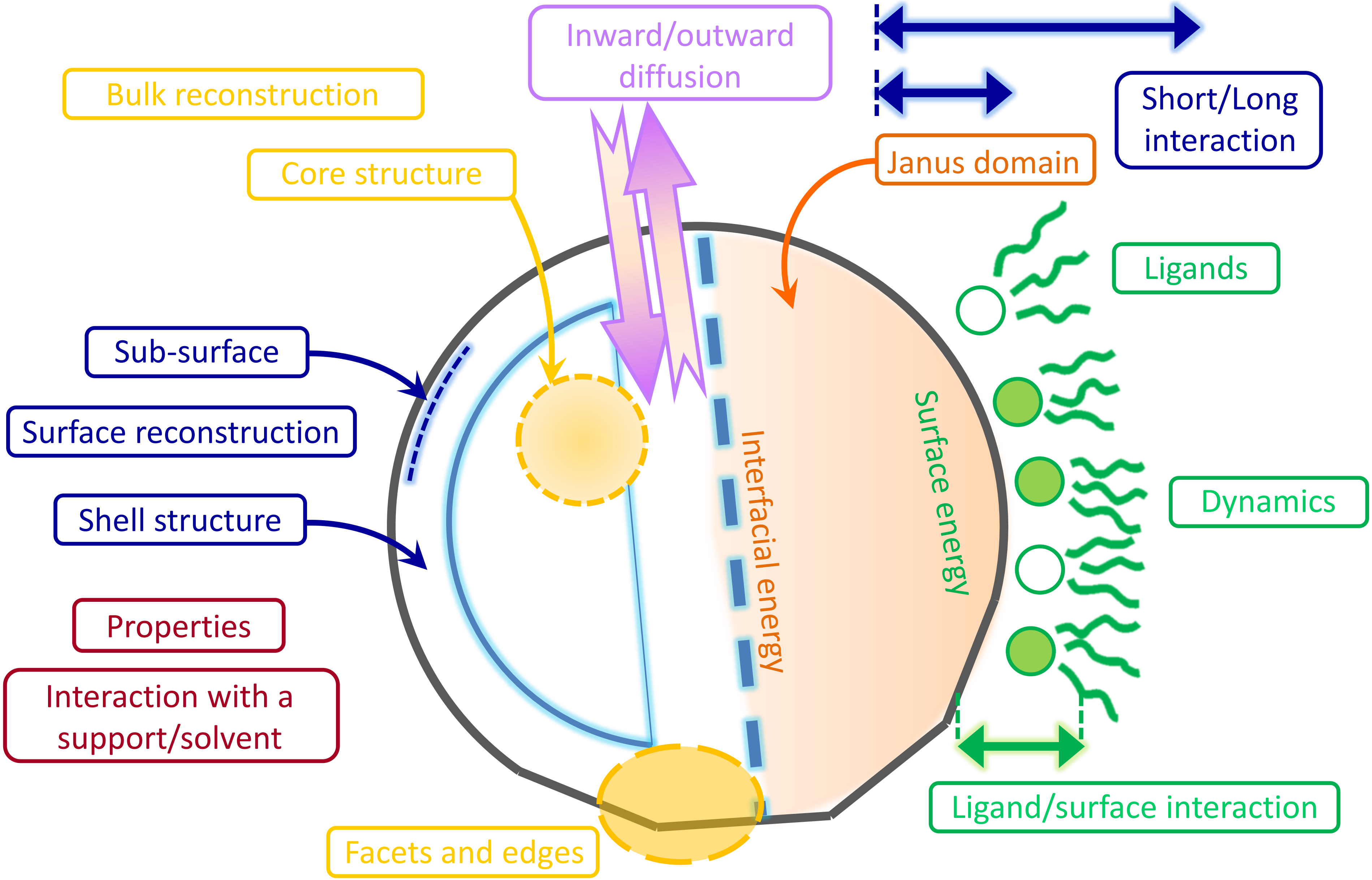
H_2, CO, CO_2, N_2 — *Abundant metals* → Alkanes, CH_4, NH_3…

Fischer-Tropsch Process, Sabatier Reaction, Haber-Bosch Process, etc.

Case study: Nickel-cobalt nanoparticles

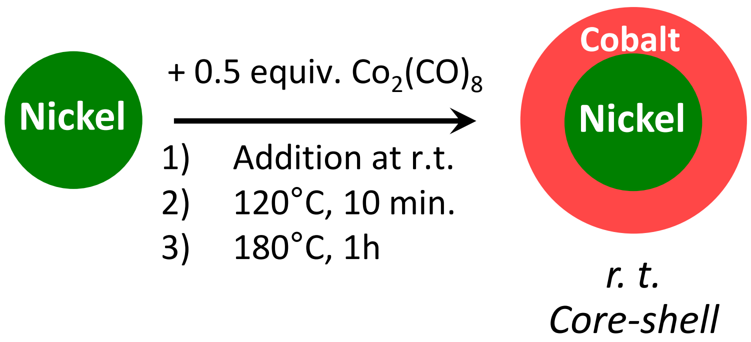


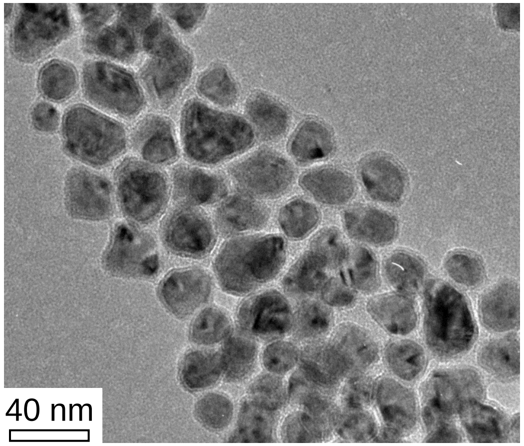
Nanochemistry: Concept Map

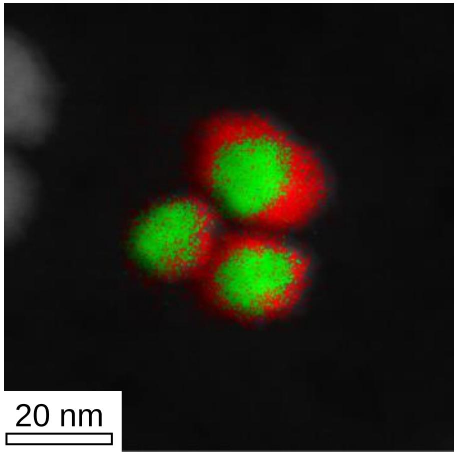


S. Carenco, D. Portehault, C. Boissière, N. Mézailles, C. Sanchez, *Adv. Mater.* **2014**, *26*, 371.

Nickel-Cobalt Nanoparticles for CO_2 reduction

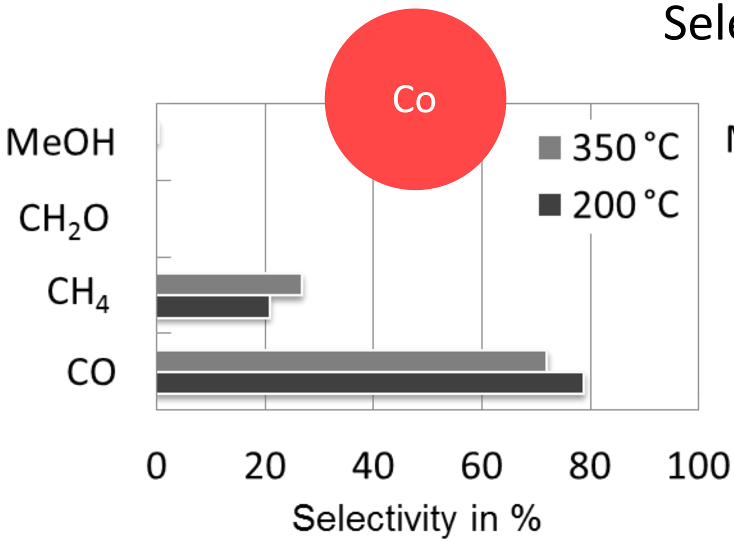


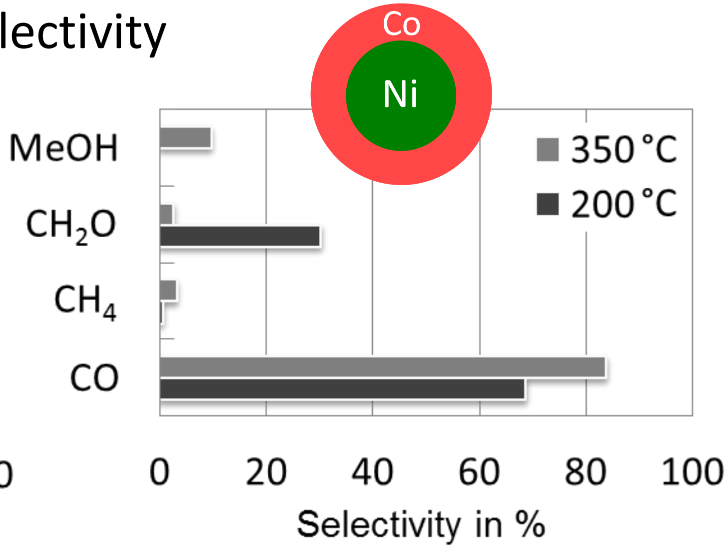




CO_2 hydrogenation by H_2 (1 bar total pressure)

Selectivity





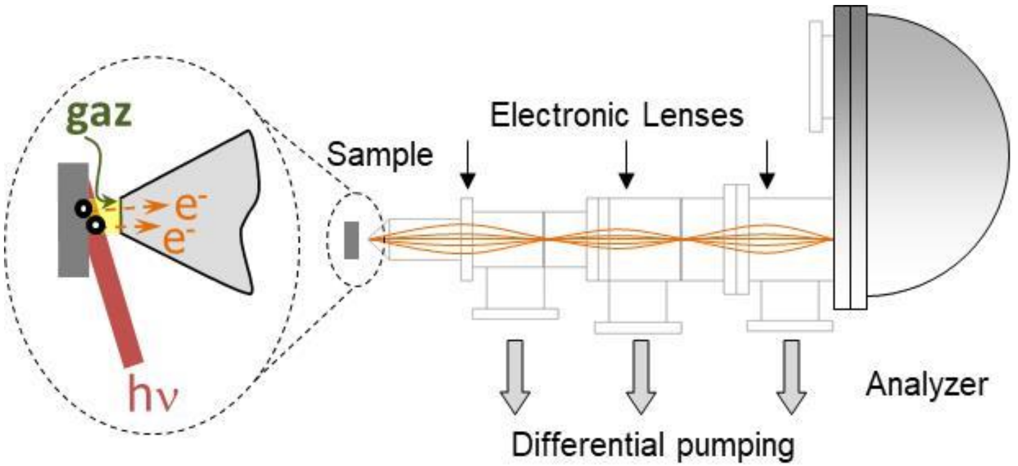
S. Carenco, C.-H. Wu, A. Shavorskiy, S. Alayoglu, G. A. Somorjai, H. Bluhm, M. Salmeron, *Small* **2015**, *11*, 3045–3053.

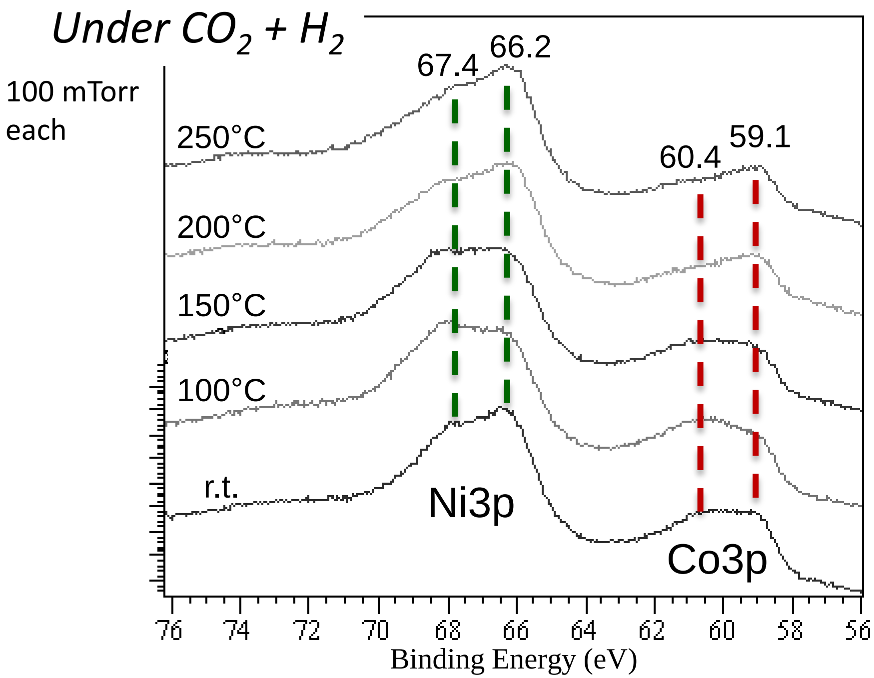
Near-Ambient Pressure XPS on Core-Shell Nanoparticles

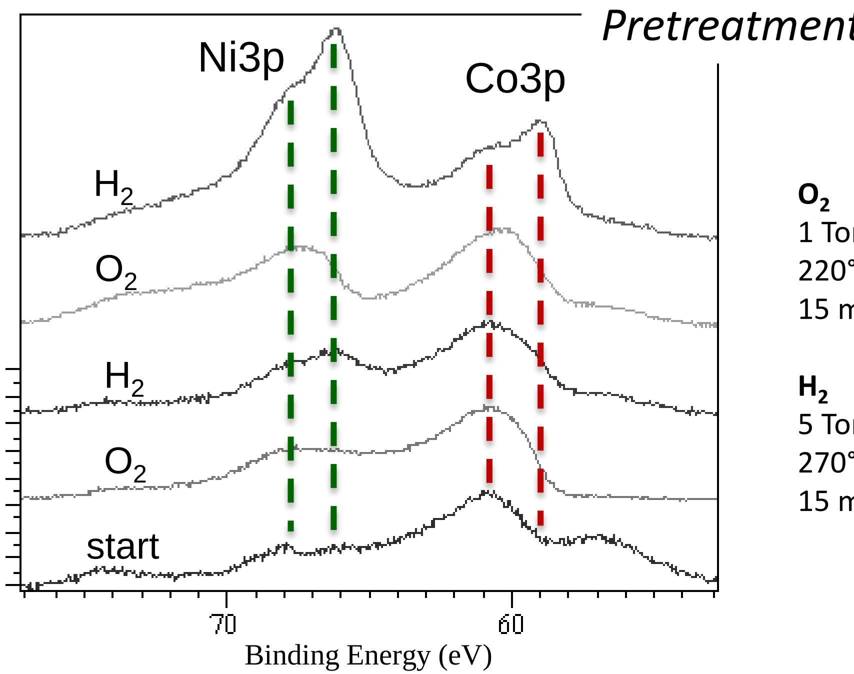
XPS collected under mbar of gas

- Nanoparticles on Au surface
- Ligands are burnt away
- Model reaction is performed

D. E. Starr, Z. Liu, M. Hävecker, A. Knop-Gericke, H. Bluhm, *Chem. Soc. Rev.* **2013**, *42*, 5833–5857.



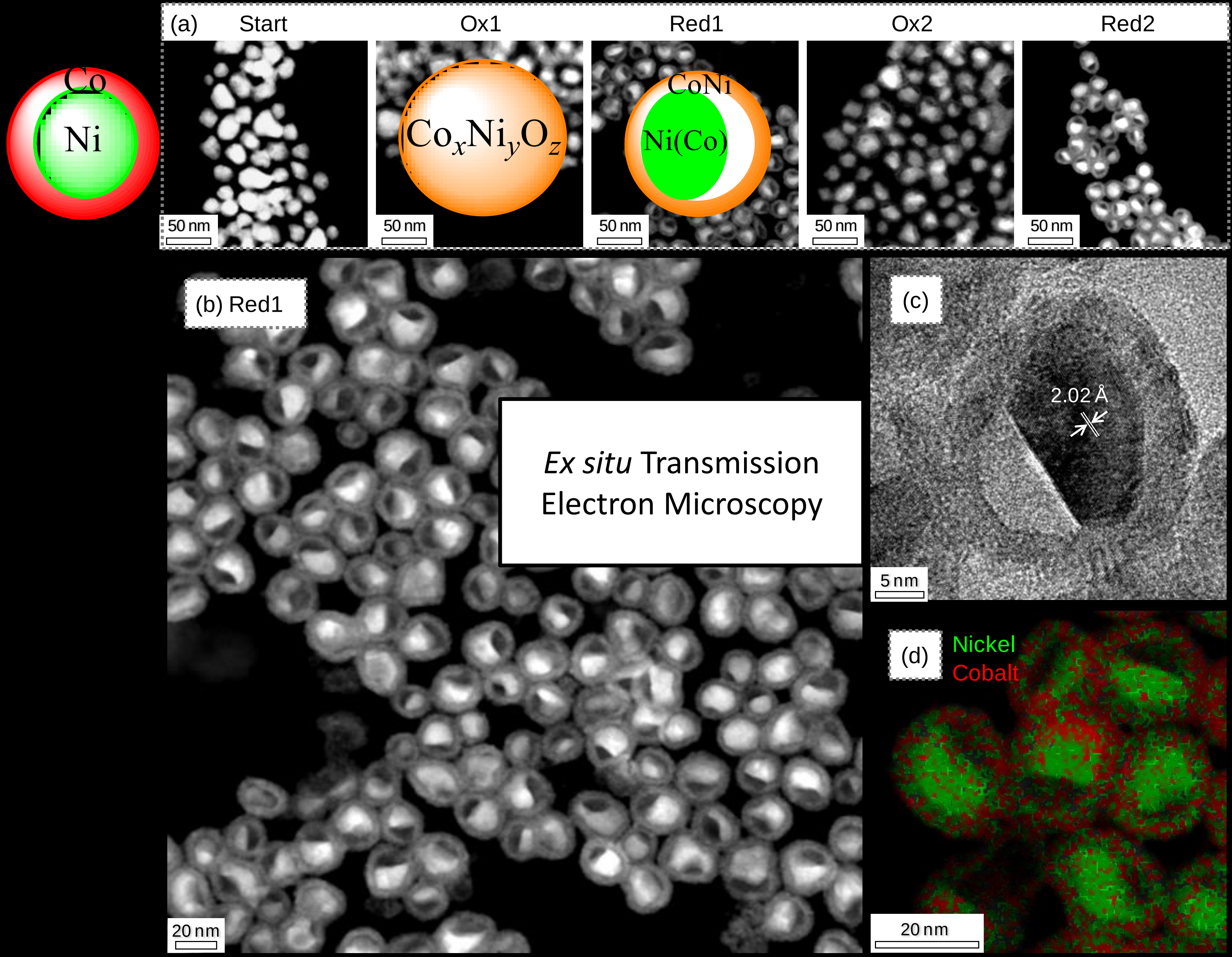




O_2
1 Torr
220°C
15 min

H_2
5 Torr
270°C
15 min

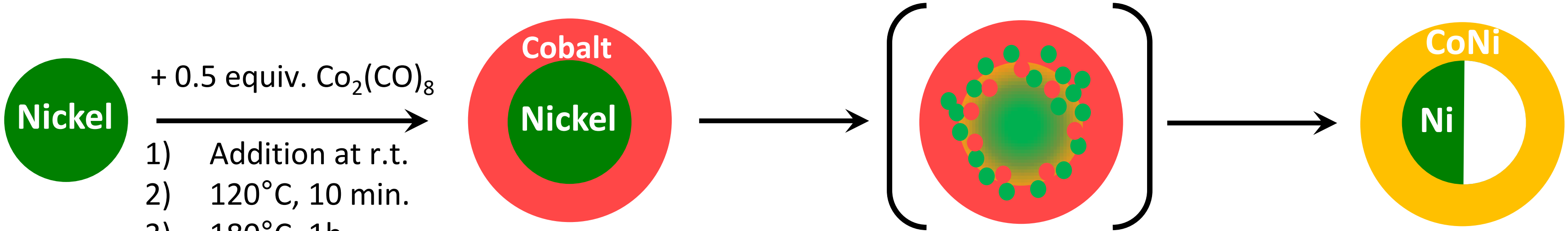
S. Carenco, C.-H. Wu, A. Shavorskiy, S. Alayoglu, G. A. Somorjai, H. Bluhm, M. Salmeron, *Small* **2015**, *11*, 3045–3053.



Co
Ni
(a)
Start
Ox1
Red1
Ox2
Red2
$Co_xNi_yO_z$
CoNi
Ni(Co)
50 nm
50 nm
50 nm
50 nm
50 nm
(b) Red1
Ex situ Transmission Electron Microscopy
20 nm
(c)
2.02 Å
5 nm
(d)
Nickel
Cobalt
20 nm

Core restructuring as a consequence of surface reaction

Cycles of oxidation and reduction, then exposure to CO_2 + H_2



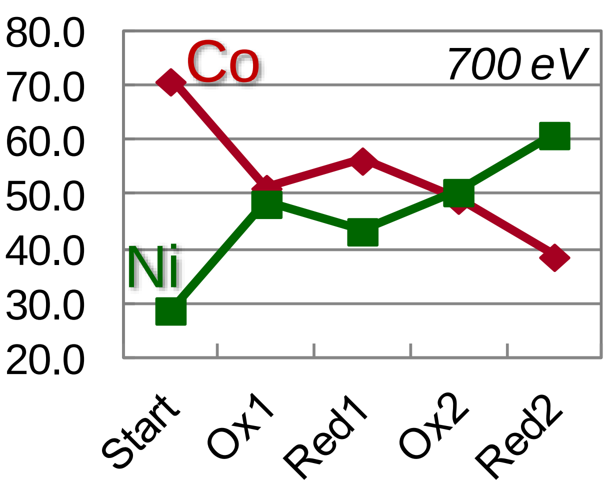
r. t.
Core-shell

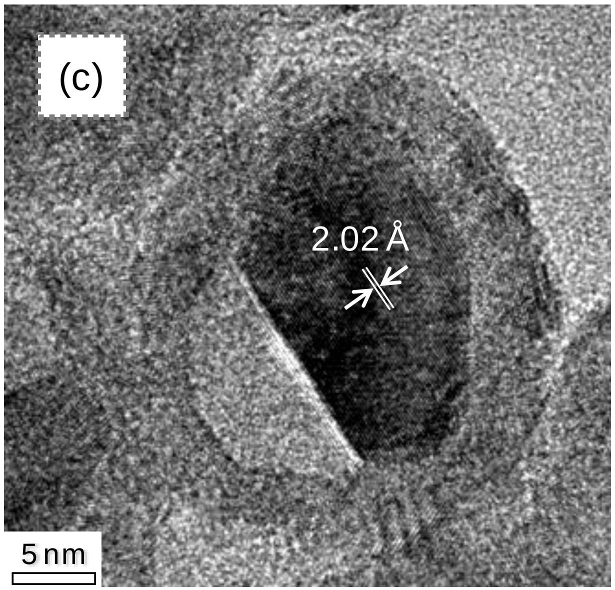
Gradient structure
200 – 250 °C

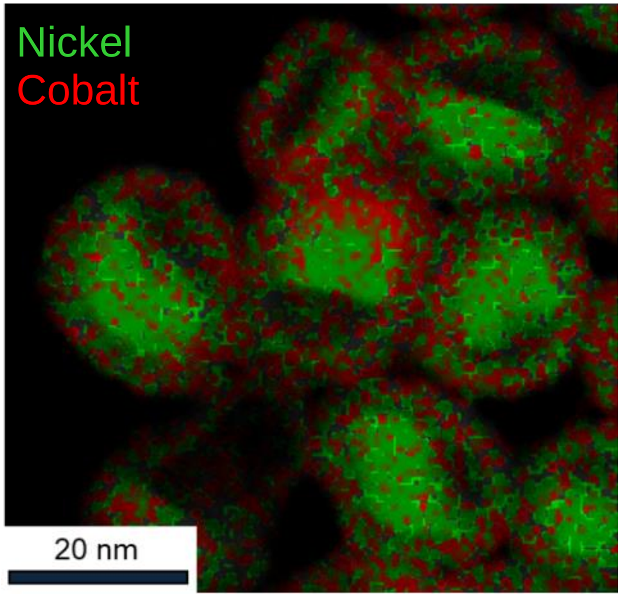
Semi-hollow Alloy

Reactivity at the surface is critical

Surface Ratio from NAP-XPS





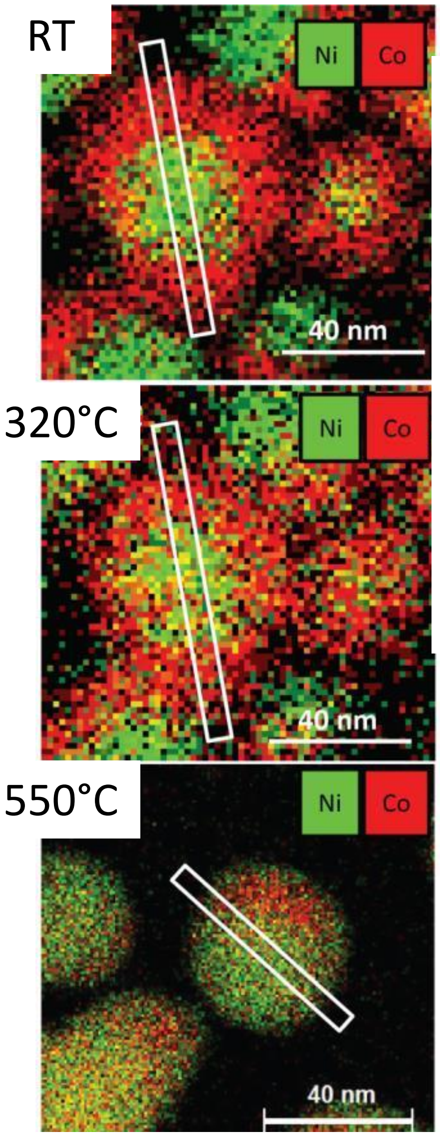


S. Carenco, C.-H. Wu, A. Shavorskiy, S. Alayoglu, G. A. Somorjai, H. Bluhm, M. Salmeron, *Small* **2015**, *11*, 3045–3053.

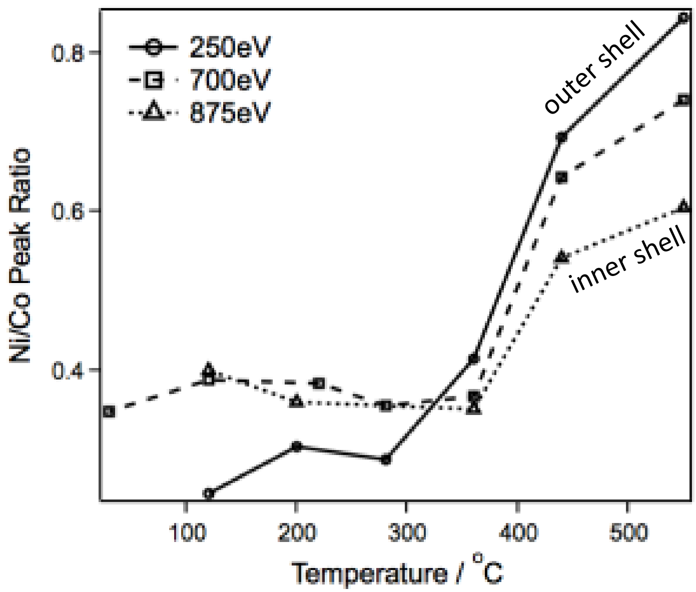
What happens without gases?

Alloy formation above 500 °C

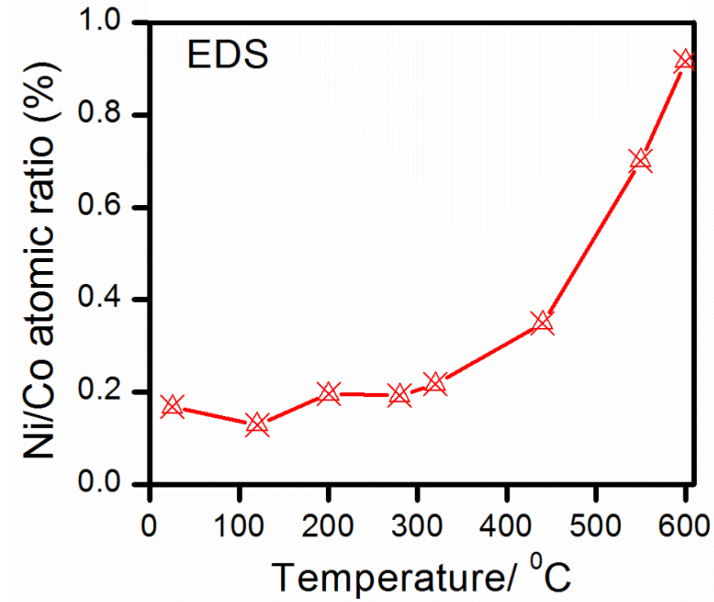
TEM with heating stage



XPS in UHV

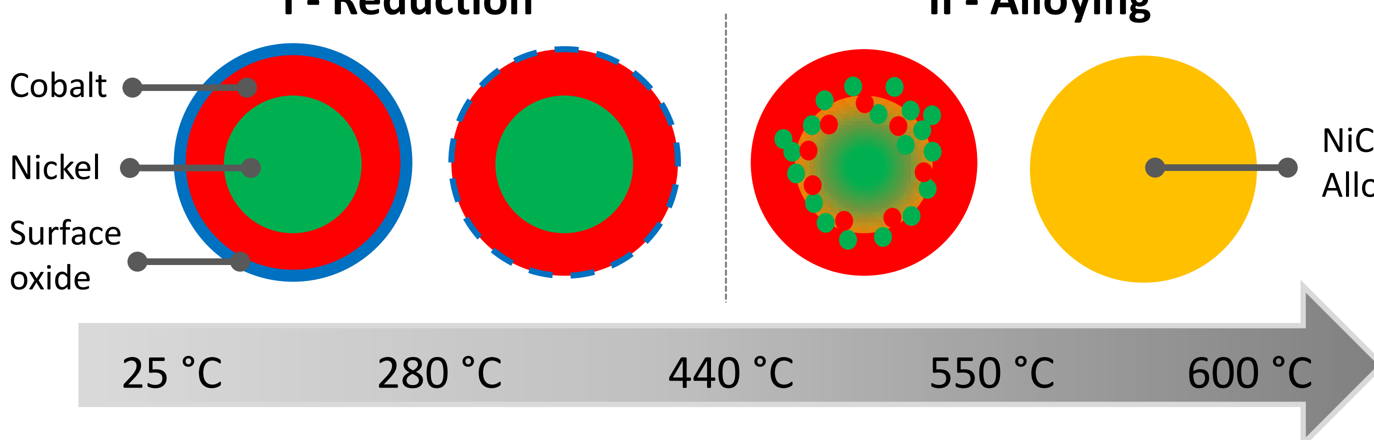


EDS of the shell



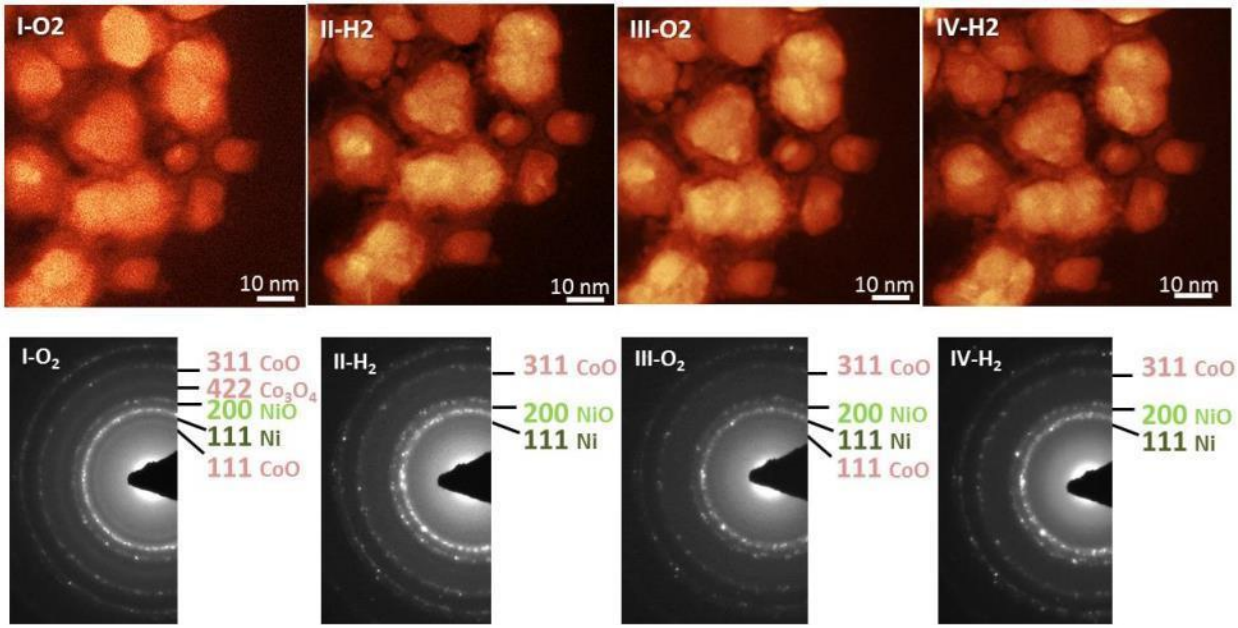
I - Reduction

II - Alloying



C. S. Bonifacio, S. Carenco, C. H. Wu, S. D. House, H. Bluhm, J. C. Yang, *Chem. Mater.* **2015**, *27*, 6960.

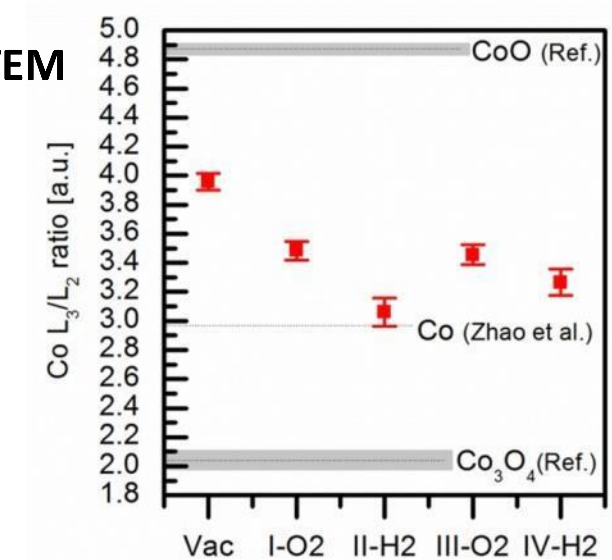
Reactivity: Combining ETEM and NAP-XPS



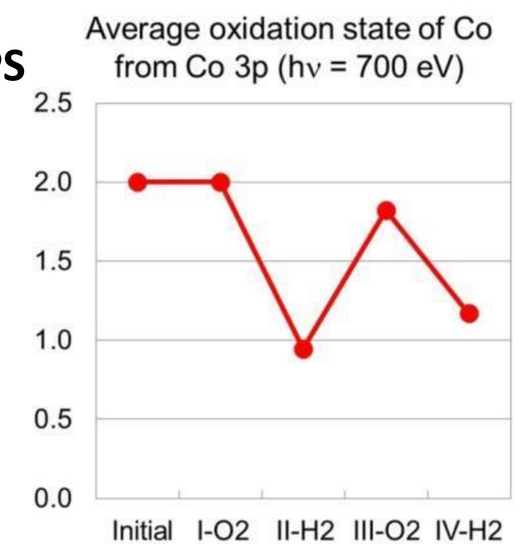
Environmental TEM
mbar Range

Pressure: 0.2 mbar
Oxidation at 220°C
Reduction at 260 °C

E-TEM



XPS

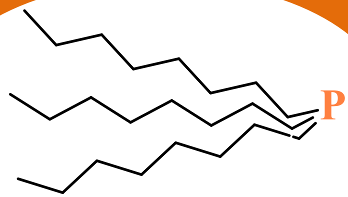


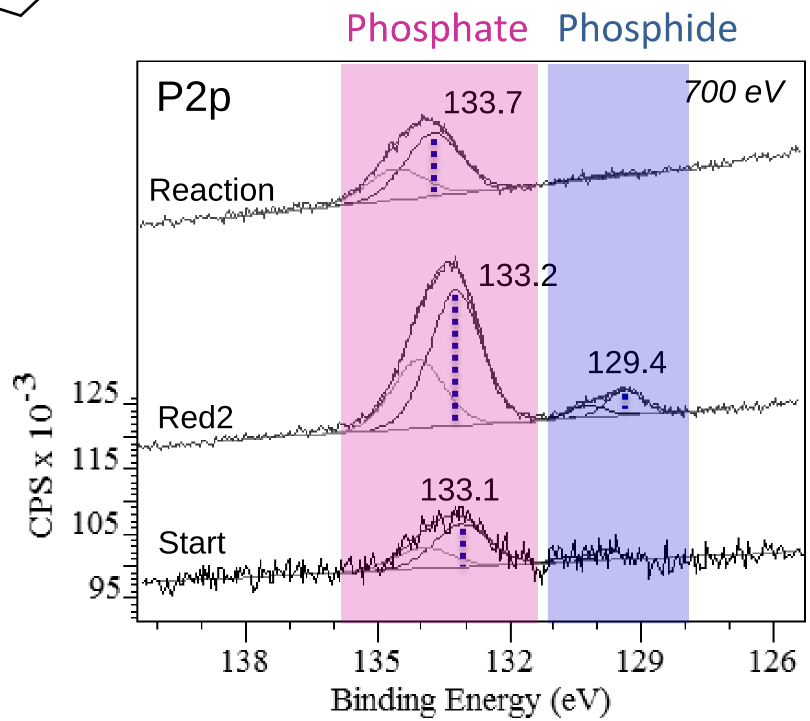
Mitigated result

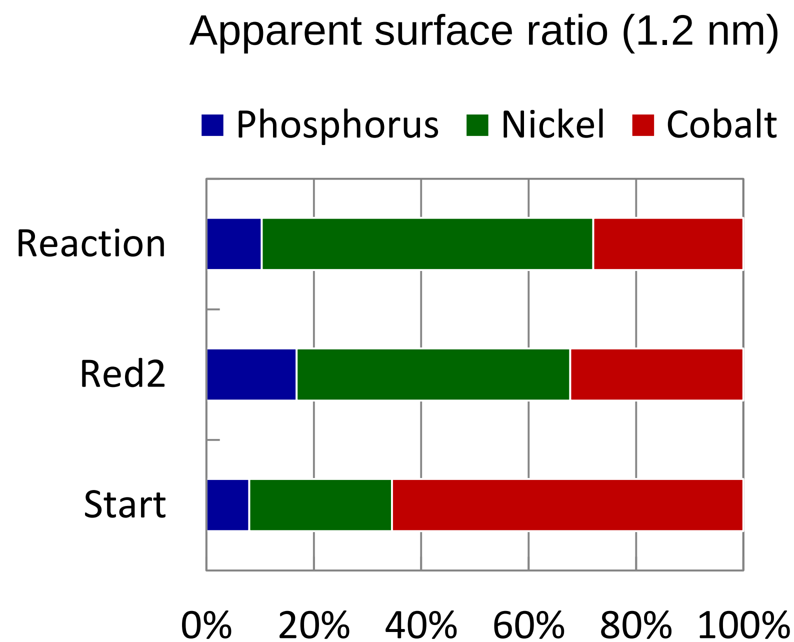
- Pressure gap?
- Mobility of atoms?

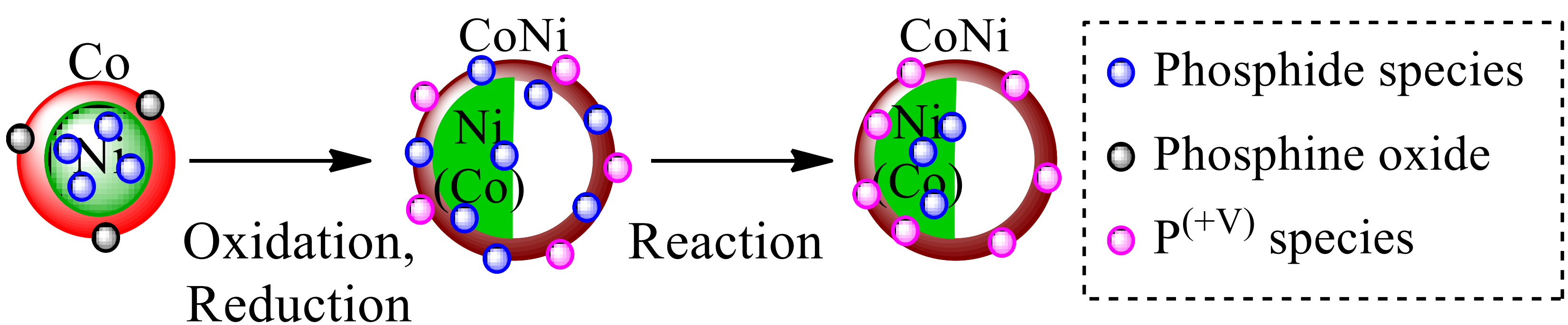
S. Carenco, C. S. Bonifacio,
J. C. Yang
Chem. Eur. J. **2018**, 24, 12037

What about surface ligands?





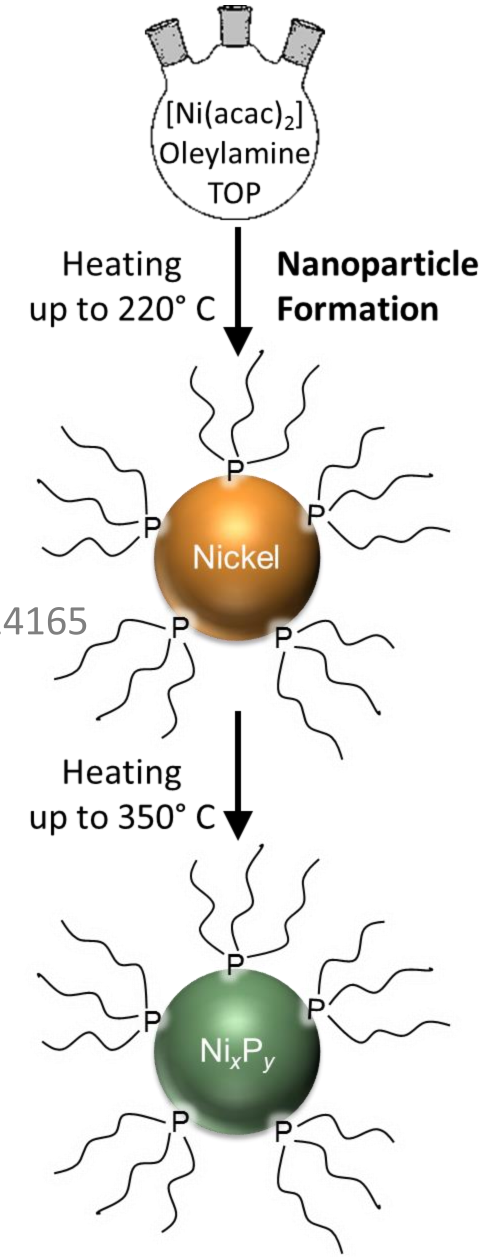




Carenco, Wu, Shavorskiy, Alayoglu, Somorjai, Bluhm, Salmeron, *Small* **2015**, *11*, 3045

Reactivity of phosphine ligands

Typical synthesis route

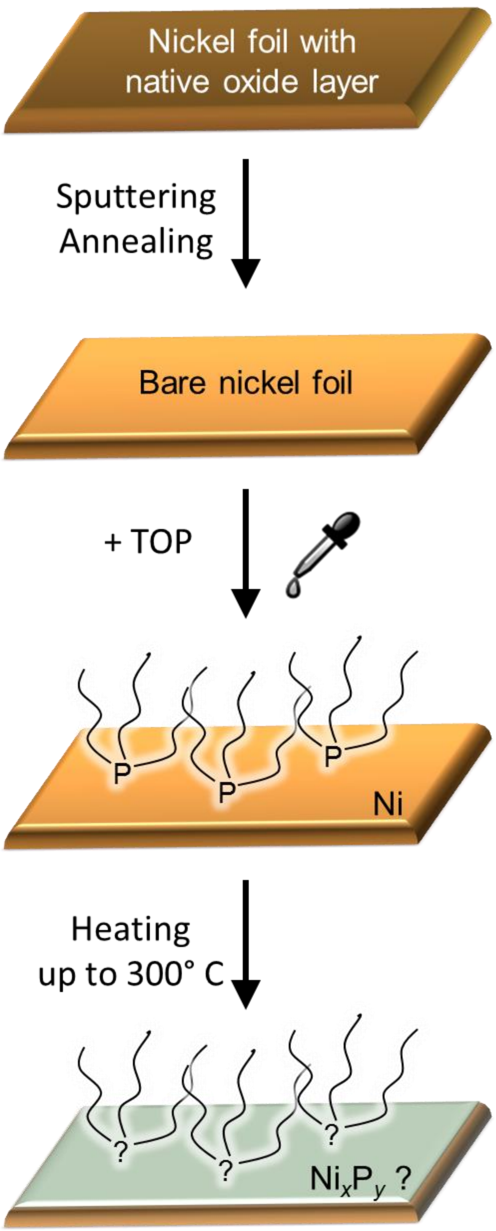


Reaction Intermediate

S. Carenco et al. *Chem. Eur. J.* **2012**, *18*, 14165

Ni_2P, $Ni_{12}P_5$

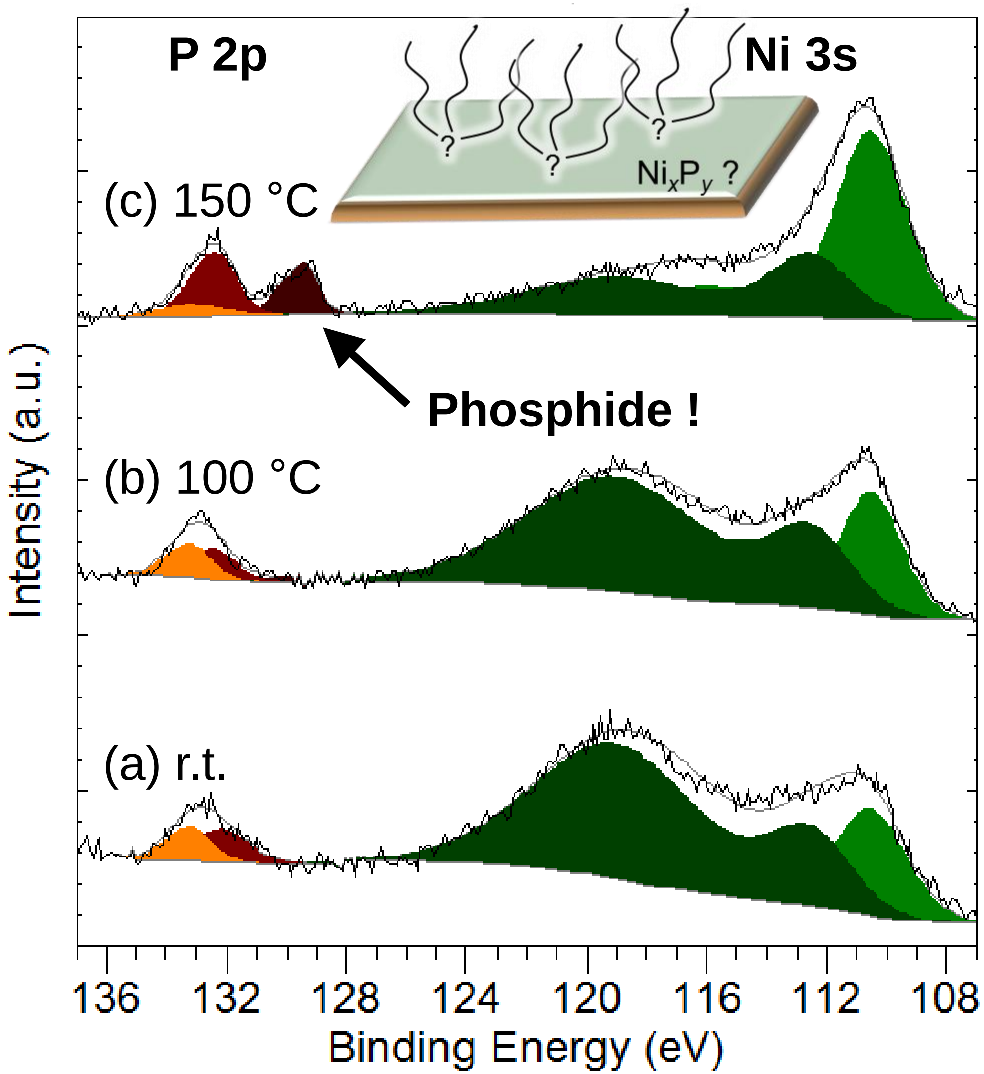
Our Model



Needs reducing atmosphere

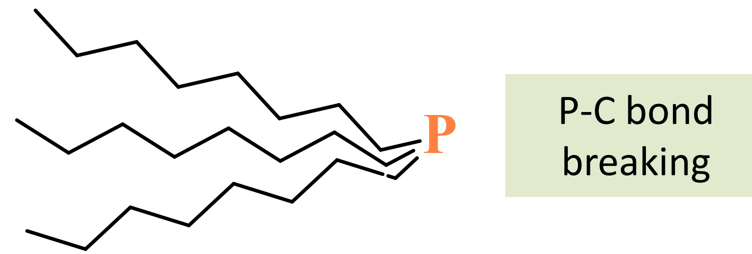
Phosphines as an easy source of phosphorus… and carbon

XPS while heating under H_2 (0.13 mbar)

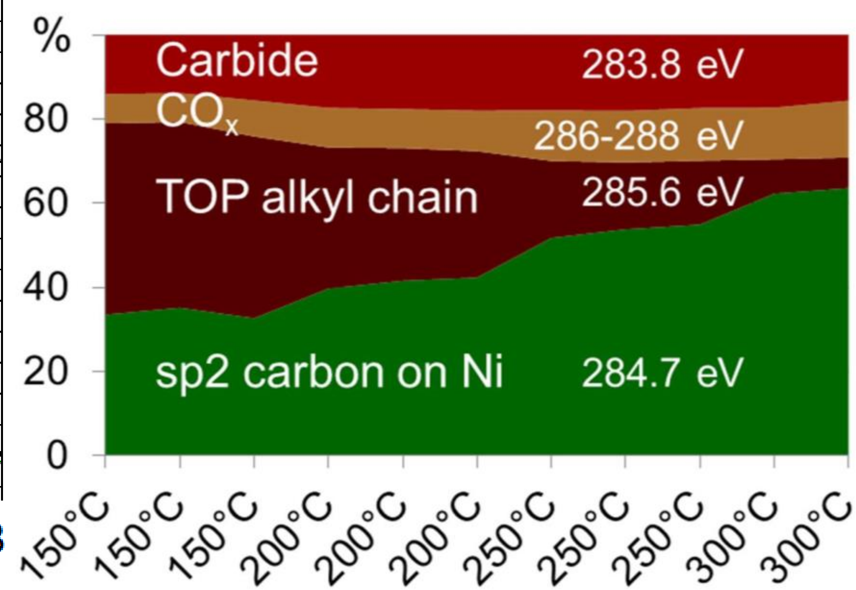


S. Carenco, Z. Liu, M. Salmeron, *ChemCatChem* **2017**, *9*, 2318

Tri-*n*-octylphosphine
"P-donor at **250-350°C**" (litt.)

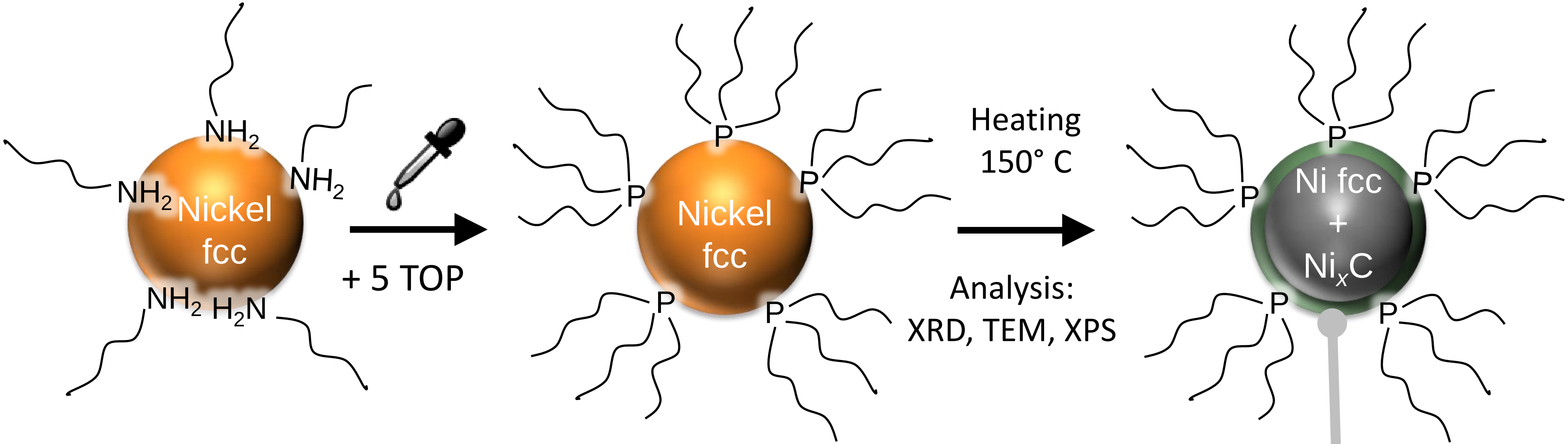


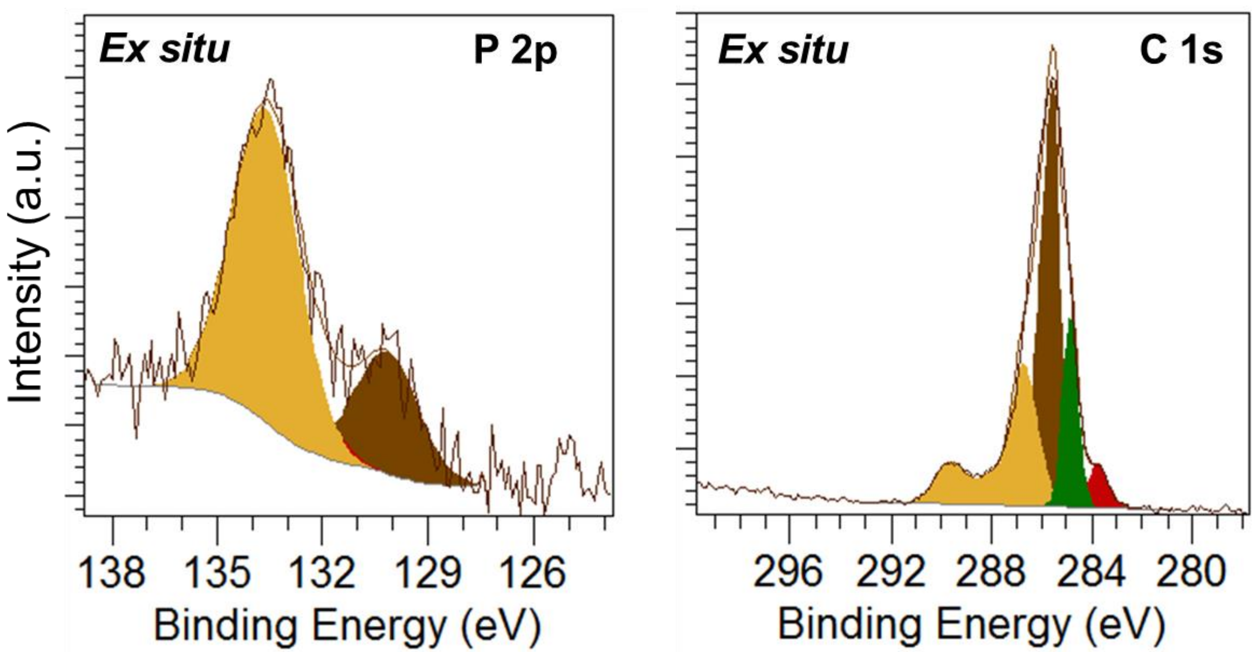
Phosphide forms **at 150 °C**!*
sp2 carbon also form!



***Confirmed by DFT:** R. García-Muelas, Q. Li, N. López, *J. Phys. Chem. B* **2018**, *122*, 672–678.

Control Experiment in colloidal suspension at 150 °C





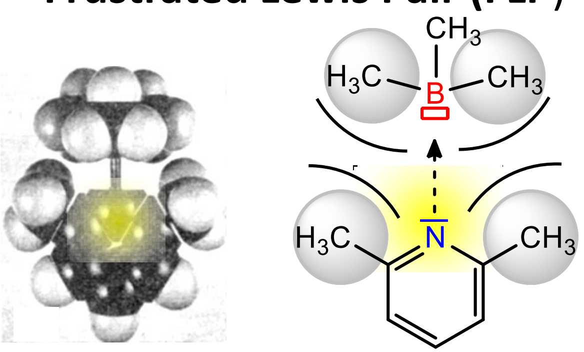
Surface Layer: Phosphide and carbon sp2

S. Carenco, Z. Liu, M. Salmeron, *ChemCatChem* **2017**, FCCat Special Issue, DOI 10.1002/cctc.201601526.

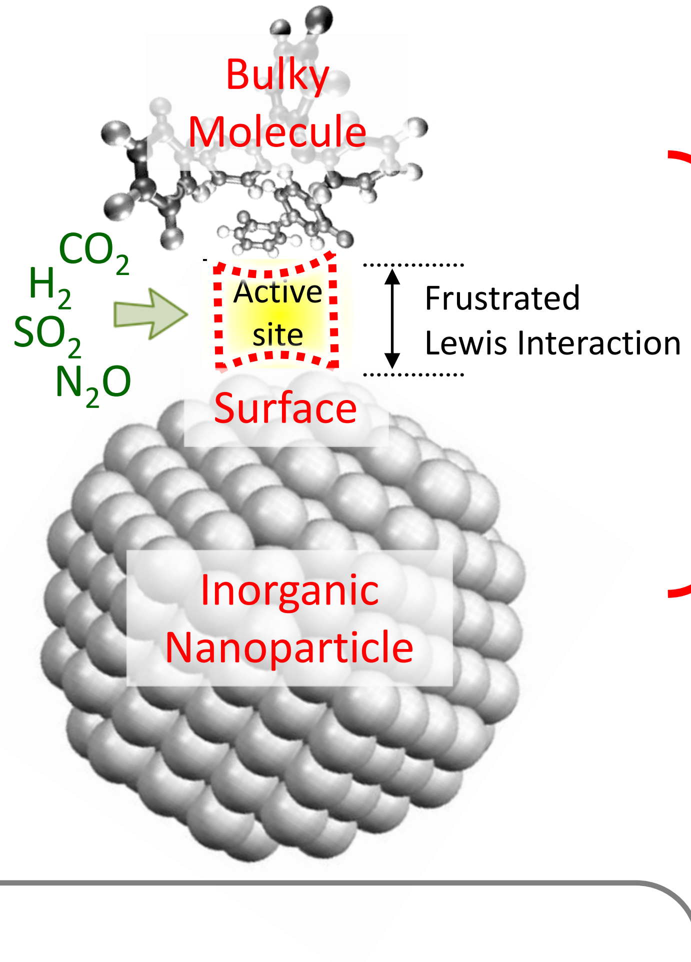
Ligands as an asset to enhance surface reactivity?

ERC NanoFLP

Molecular Frustrated Lewis Pair (FLP)



H. Brown et al., *JACS* **1942** *64*, 325–329

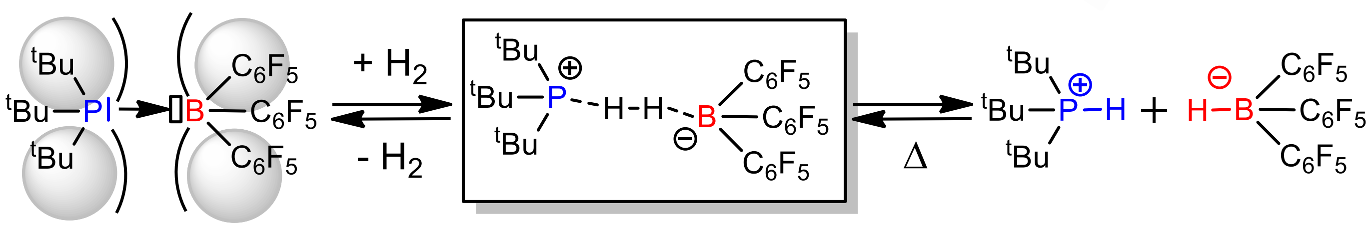


Strong Lewis Acid (resp. Base)

NanoFLP

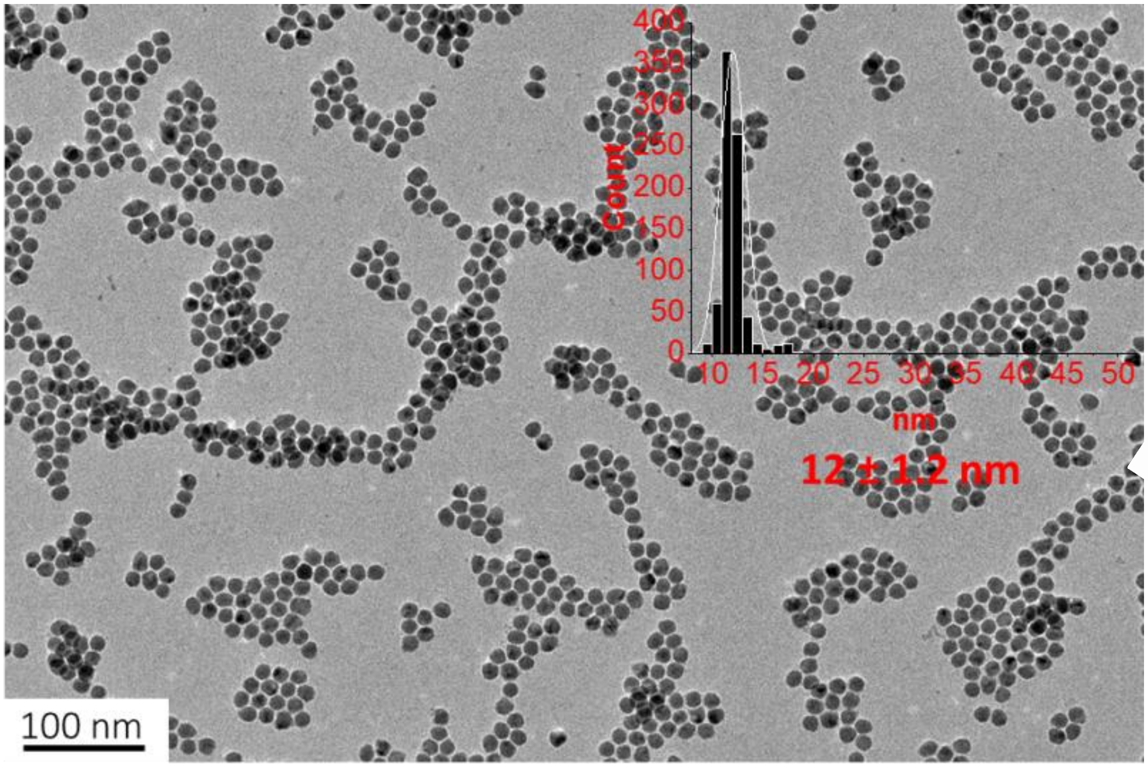
Strong Lewis Base (resp. Acid)

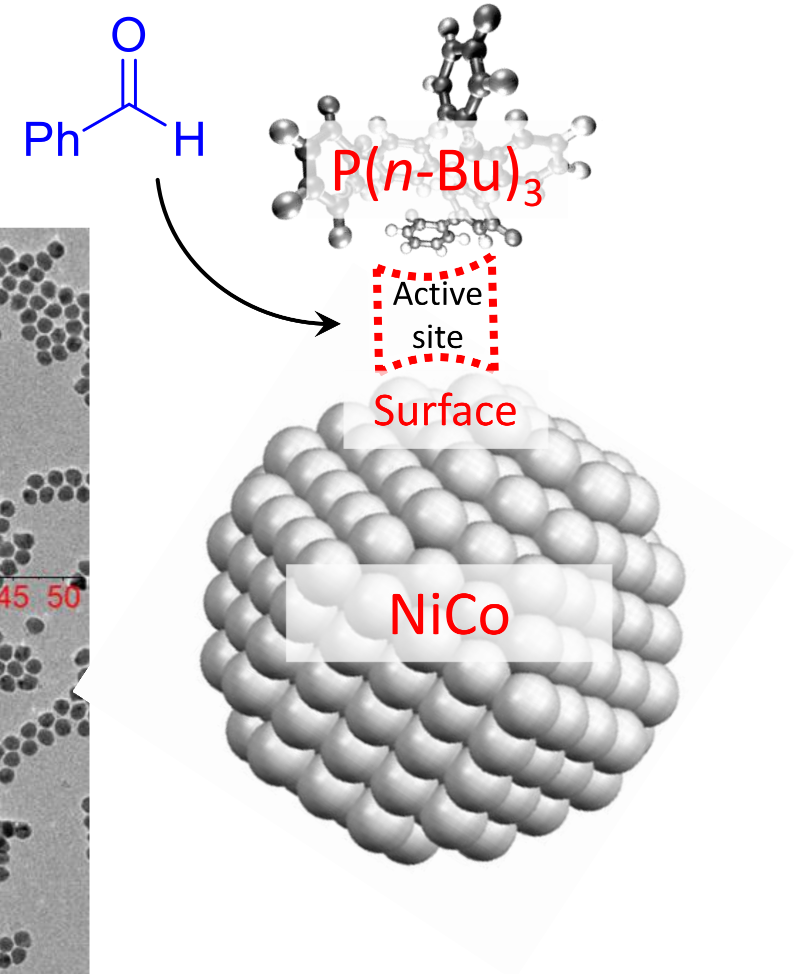
H_2 cleavage at 1 bar and 25°C



G. C. Welch, D. W. Stephan, *JACS* **2007**, *129*, 1880–1881.

Nickel-Cobalt NanoFLP in colloidal suspension?

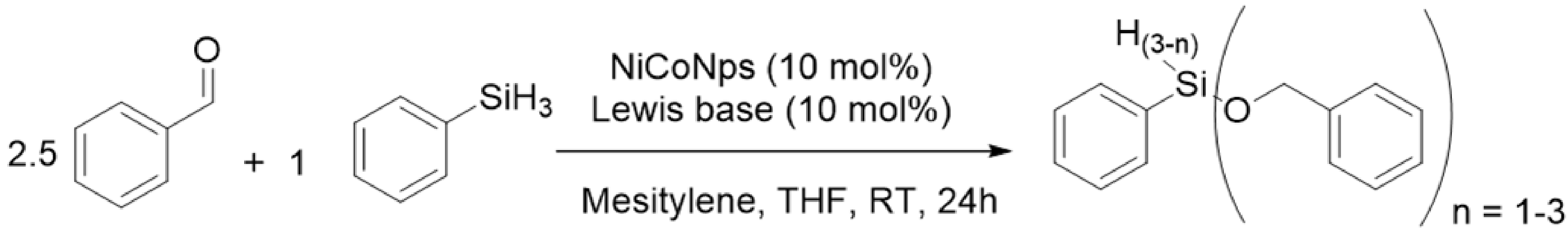




About the synthesis:
A. Palazzolo et al., *Nanoscale* **2022**, *14*, 7547

+ Silane as H source

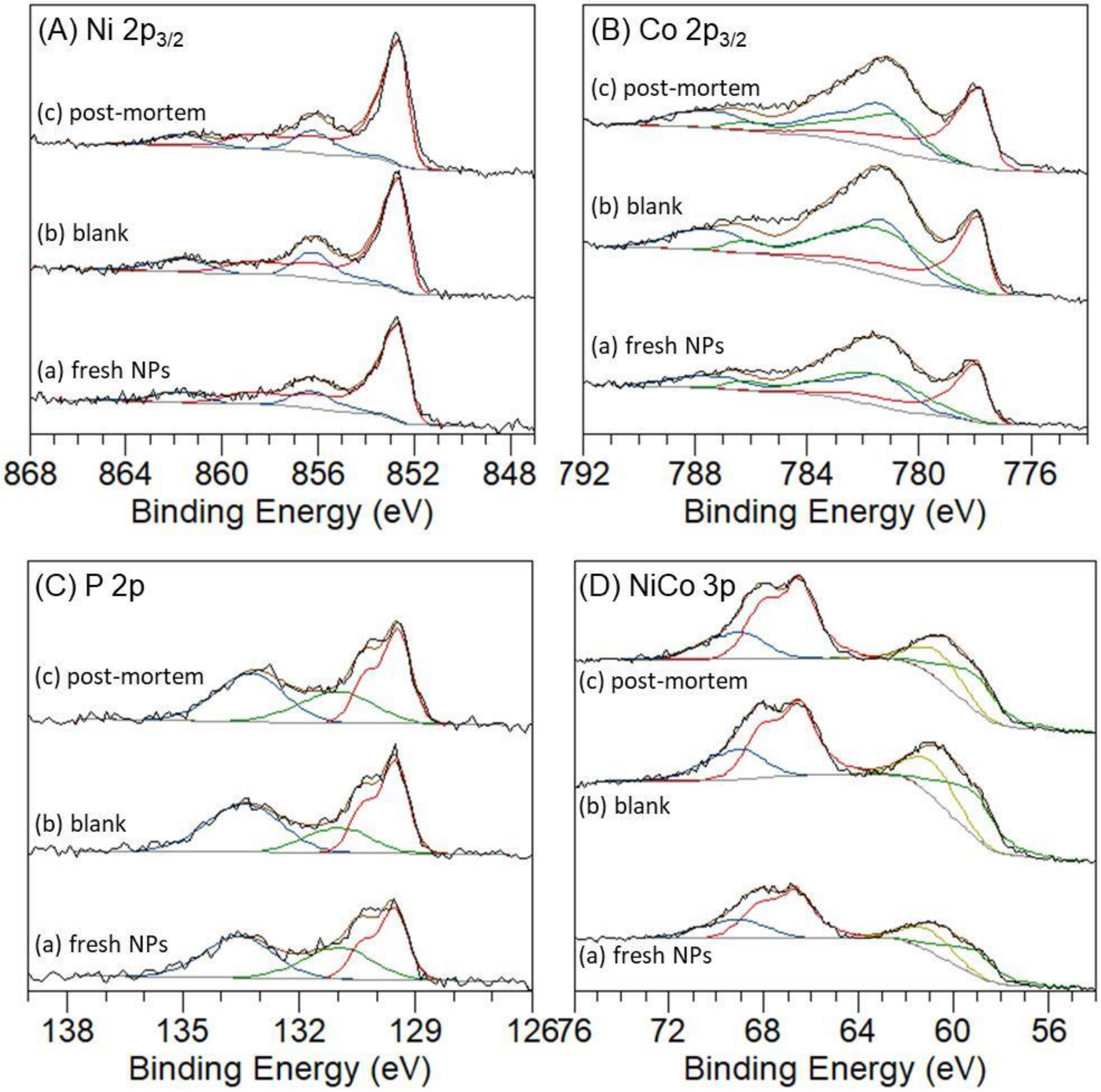
First catalytic results



	Entry	Lewis acid	Lewis base	Silane consumption[a]
	1	-	-	0%
	2	NiCoNps	-	0%
	3	-	P*n*Bu$_3$	0%
	4	NiCoNps	P*n*Bu$_3$	77%
5 mol %	5[b]	NiCoNps	P*n*Bu$_3$	22%
20 mol %	6[c]	NiCoNps	P*n*Bu$_3$	100%
	7	NiCoNps	P*n*Oct$_3$	55%
	8	NiCoNps	PCy$_3$	7%
	9	NiCoNps	PMe$_3$	20%
	10	NiCoNps	PPh$_3$	100%

A. Palazzolo, S. Carenco, *Chem. Mater.* **2021**, *33*, 7914-7922

Is the nanoparticle surface affected by the reaction?

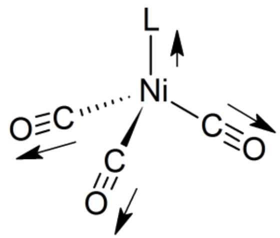


A. Palazzolo, S. Carenco, *Chem. Mater.* **2021**, *33*, 7914-7922

How can we rationalize the silane consumption?

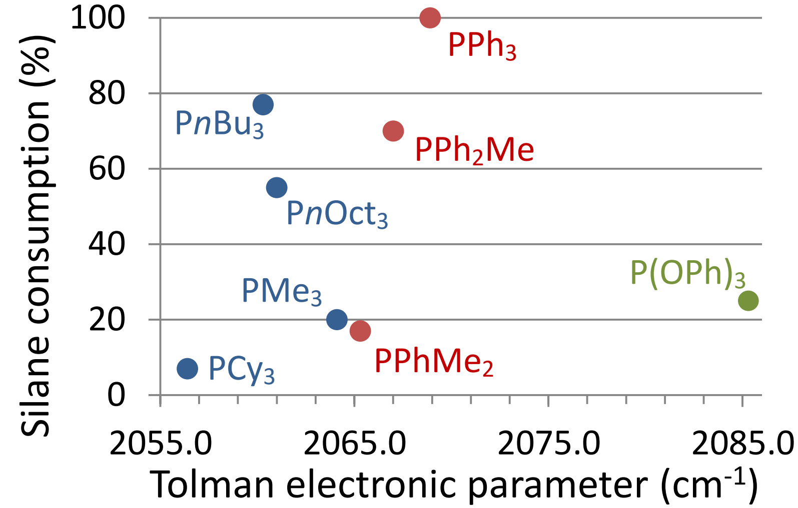
Tolman electronic parameter

electron donating /withdrawing ability of a ligand



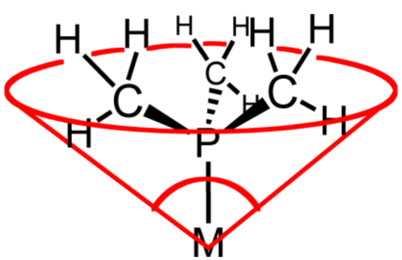
C. A. Tolman, *Chem. Rev.* **1977,** *3*, 313–348

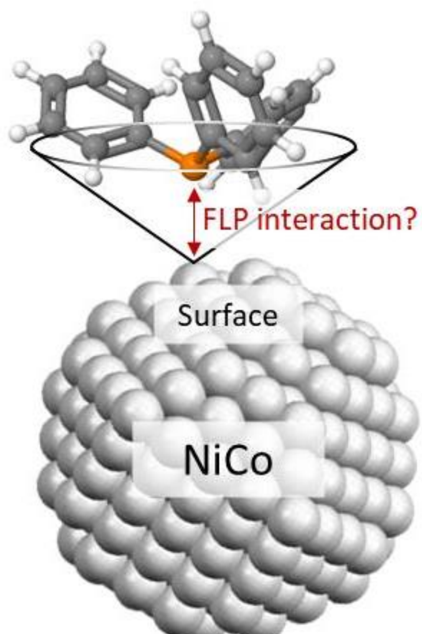
Si-H activation vs. TEP

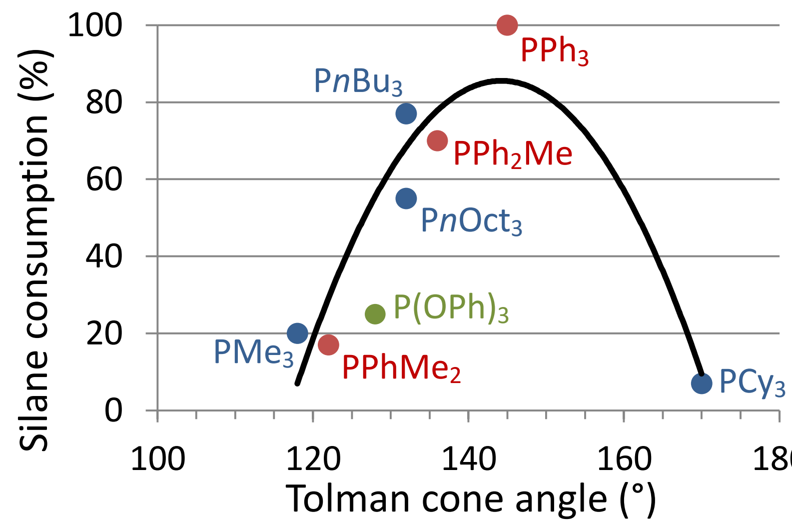


Tolman cone angle

Steric hindrance at the coordination site







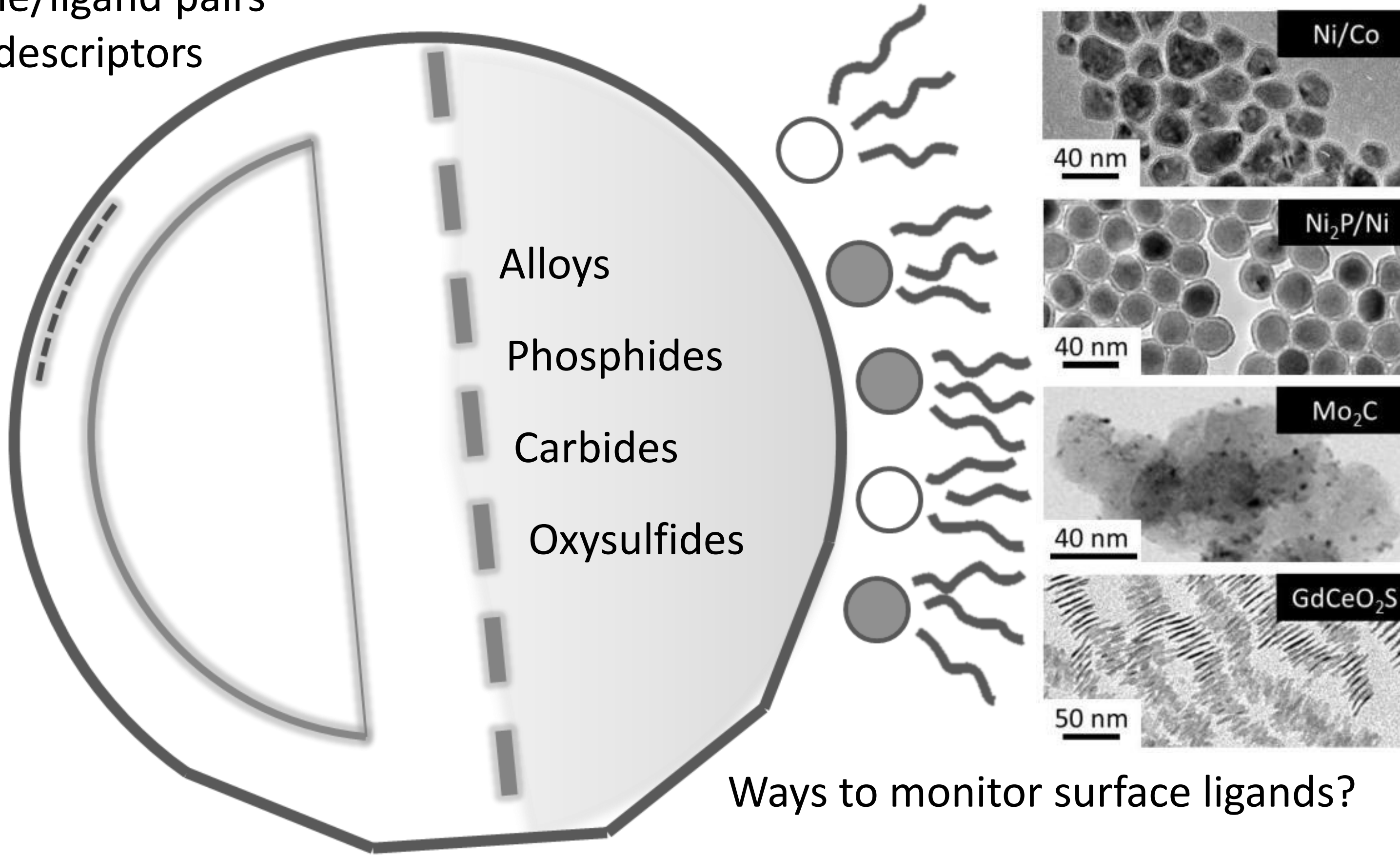
Opportunities and bottlenecks

Perspectives
- Reactions with gases (H_2, CO_2…)
- Other nanoparticle/ligand pairs
- Identify relevant descriptors

Surface design and reconstruction

Dynamics and chemical evolution

Catalysis
Homogeneous
Heterogeneous
Electro/photo
Colloidal
…



Ways to monitor surface ligands?

WANTED!
Same *in situ* cell for (HR)(S)TEM and X-Rays (XAS…)

Challenges:
- Loading of air-sensitive samples
- Non-aqueous solvents

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Team members

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Université Toulouse III Paul Sabatier: Nicolas Mézailles, Sébastien Dreyfuss

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IRCP Institut de Recherche de Chimie Paris: Dimitri Mercier

IPCM Chimie Moléculaire: Louis Fensterbank, Denis Lesage

cea: David Carrière

ETH Zürich: Hansjörg Grützmacher, Erik Schrader

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iemn: Djamila Hourlier

UCL: Damien Debecker

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