Spring School on Nanoalloys, Cargese, France, 24-30 April 2022

NANOALLOYS
International Research Network

Introduction to catalysis by nanoalloys

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INSTITUT DE RECHERCHES
SUR LA CATALYSE
ET L'ENVIRONNEMENT

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Université de Lyon

Lyon 1

Outline

1. **Basics of nanocatalysis & alloying effects**

   Definitions, catalysis in practice, fundamental concepts

2. **Nanoalloy catalysts in their environment**

   Dynamical effects, operando approach, case study

3. **Promising alloy phases in catalysis**

   Single-atom alloys, intermetallics, and others

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1 **Basics of nanocatalysis & alloying effects**

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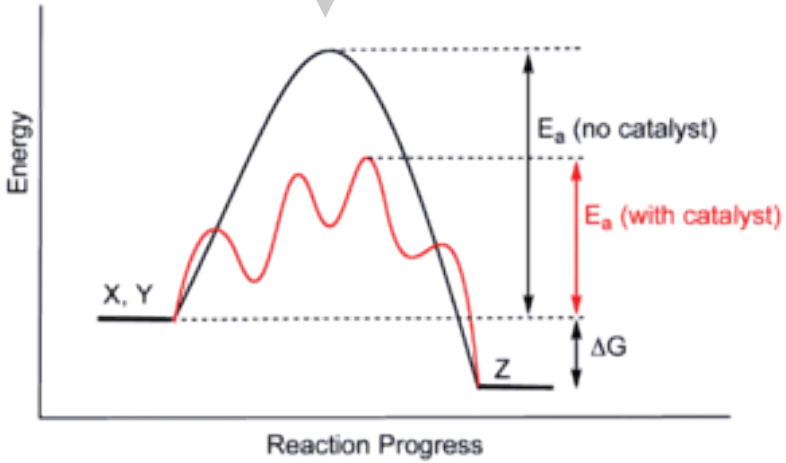
Single-atom alloys, intermetallics, and others

Definitions

Catalysis ⊃ (chemical) heterogeneous catalysis ⊃ (supported) metal nanocatalysis

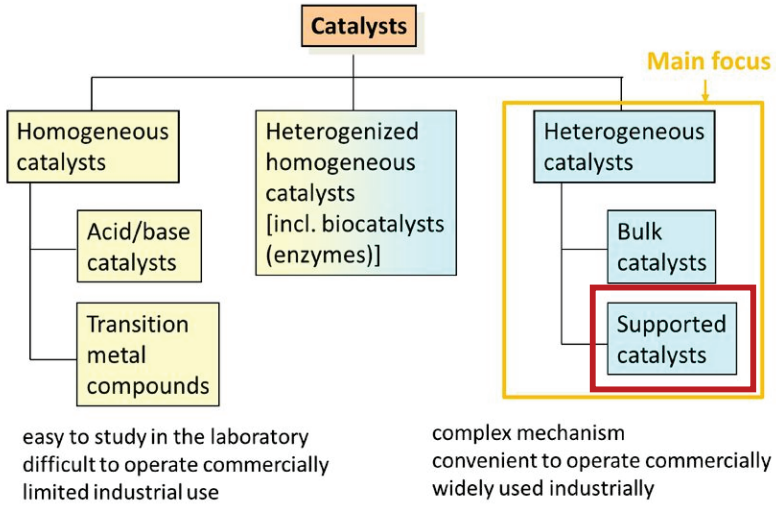


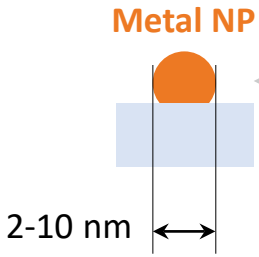
Gaseous or liquid reactants

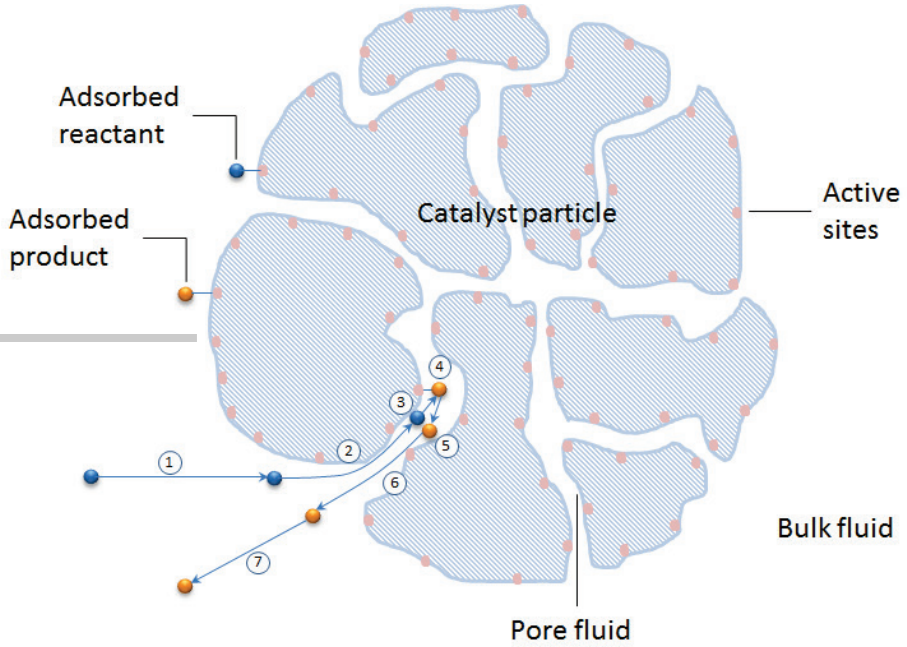
Interface

Solid catalyst

Porous support material 10-1000 m^2/g





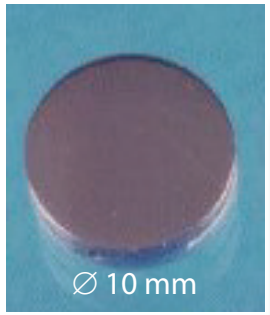


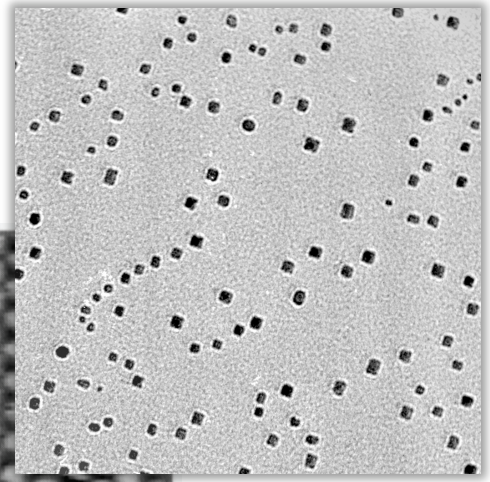
https://slideplayer.com/slide/13096241/

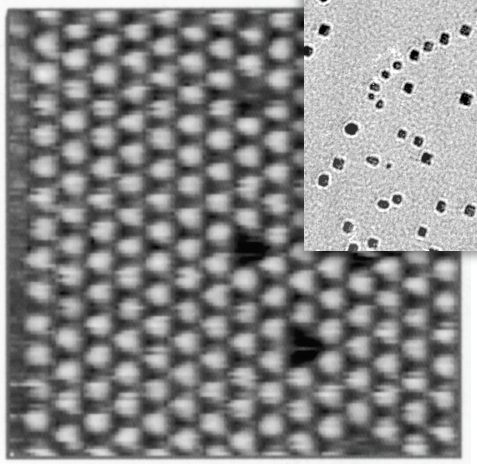
https://www.comsol.com/blogs/modeling-approaches-in-heterogeneous-catalysis/

Catalysis in practice I: materials

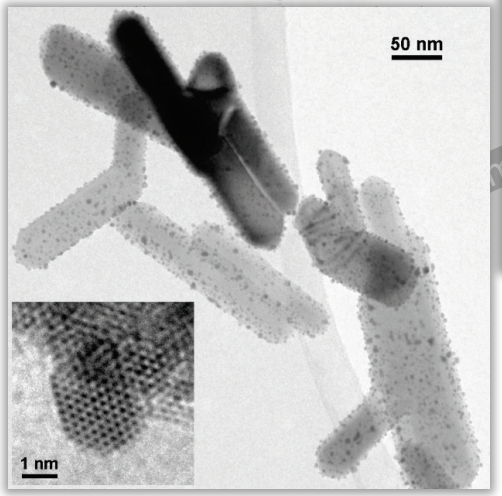
Model planar catalysts



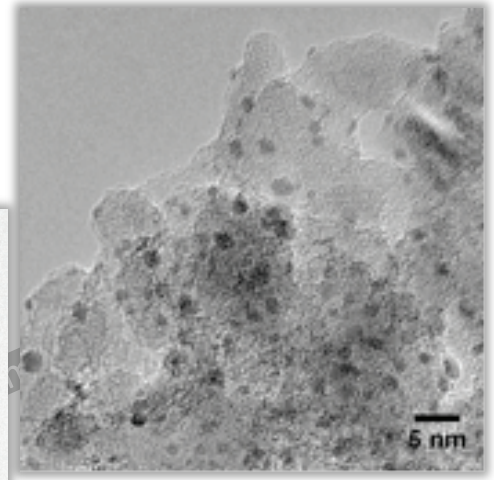




Powder supported catalysts



T.S. Nguyen *et al.*, *J. Catal.* **2016**, *344*, 136



https://nano.ku.dk/Events/a.boubnoy_master_thesis/

Industrial catalysts

https://www.medgadget.com/

- ❑ Active components
  - function: chemical activity
  - types: metals, metal oxides and sulfides, and nonmetallic oxide and sulfide
- ❑ Support
  - function: maximum active site & thermal/mechanical stability
    dual function activity modification of active component
  - types: high melting point oxides, clays, carbon
- ❑ Promoters
  - function: modification of catalytic properties (activity, selectivity, and stability)

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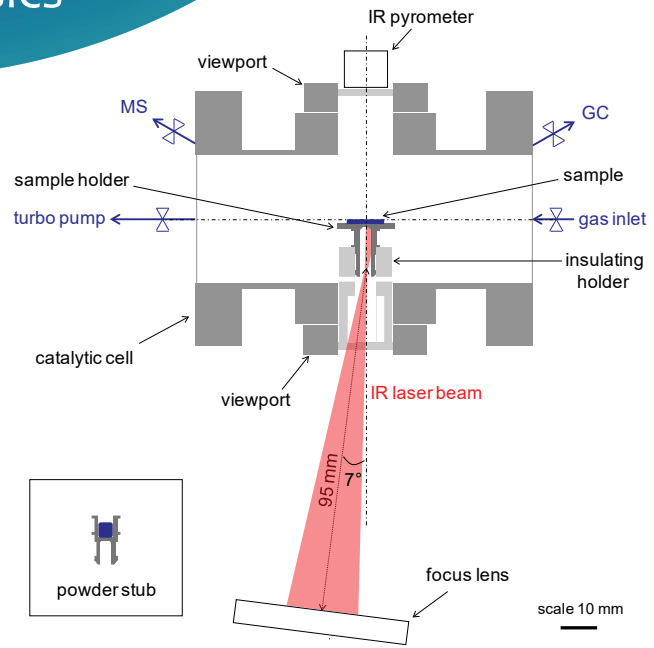
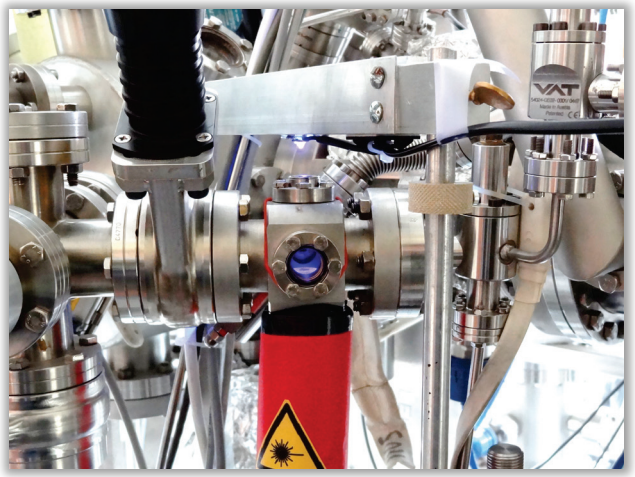
* *technology readiness level*

Catalysis in practice II: reactors

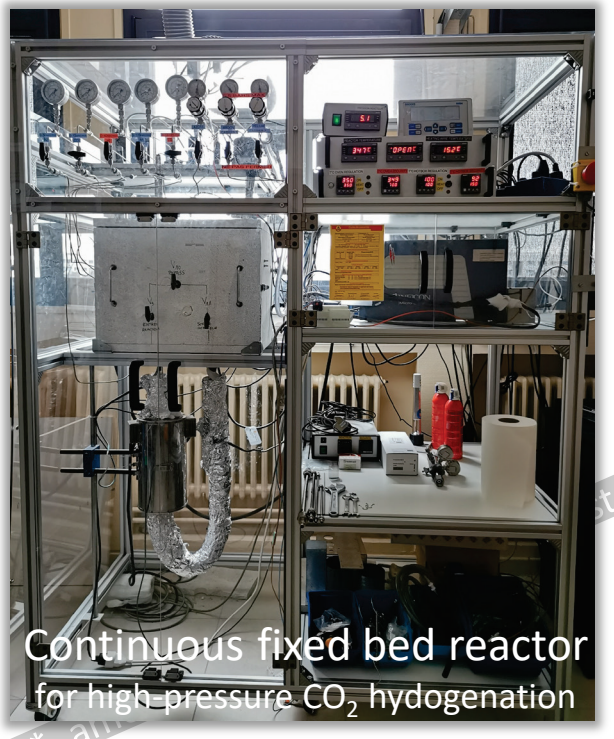


Surface-science reactor

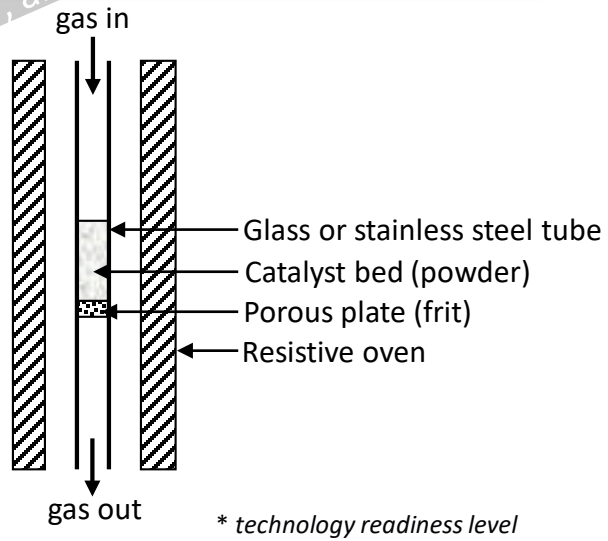


Laurent Piccolo
Nanoalloys 2022

F. Morfin & L. Piccolo,
Rev. Sci. Instrum. **2013**, *84*, 094101

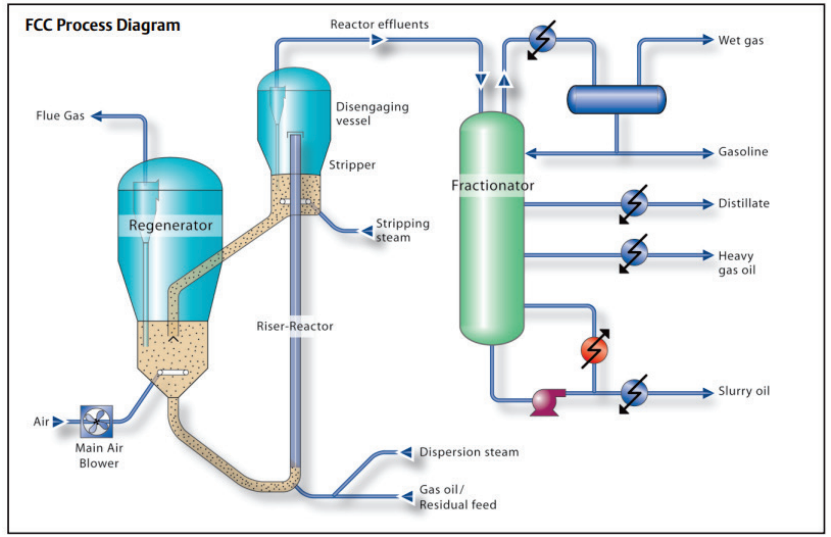


Continuous fixed bed reactor
for high-pressure CO_2 hydrogenation



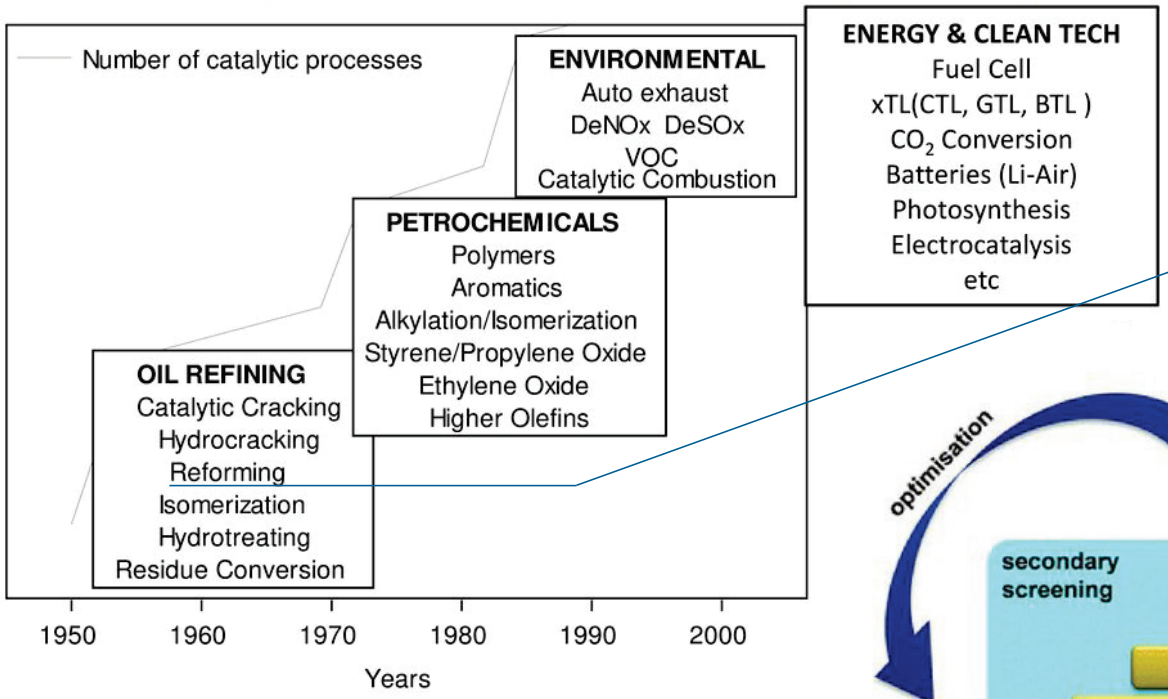
* *technology readiness level*

Fluid catalytic cracking unit in an oil refinery



www.emerson.com

Catalysis in practice III: applications



First industrial bimetallic catalysts

Pt-Re **1968** (Chevron)

Pt-Ir **1976** (Exxon)

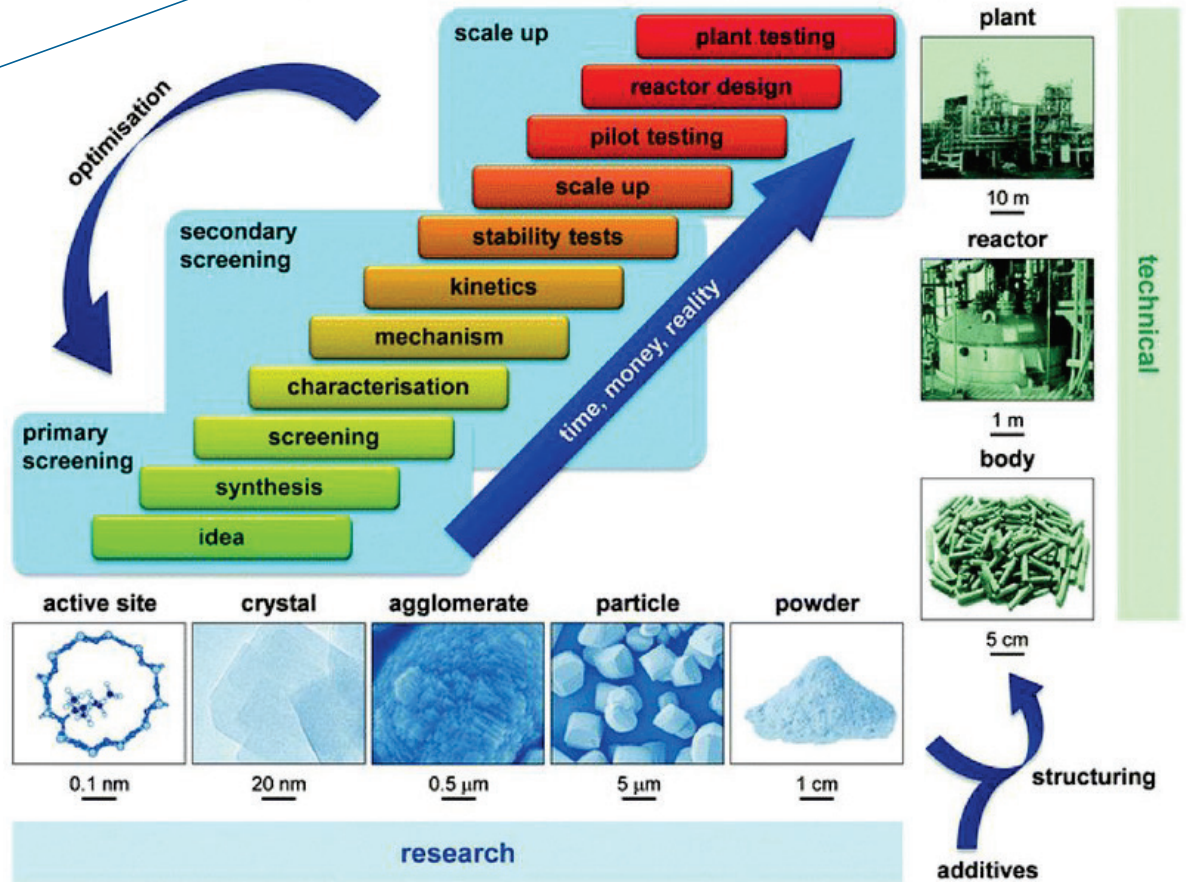
Naphta reforming to gasoline

Haber-Bosch process **1913** (BASF)

$N_2 + 3H_2 \xrightarrow{-Fe} 2NH_3$

~ 400 °C, ~200 bar

~170 Mt/year
⇒ fertilizers



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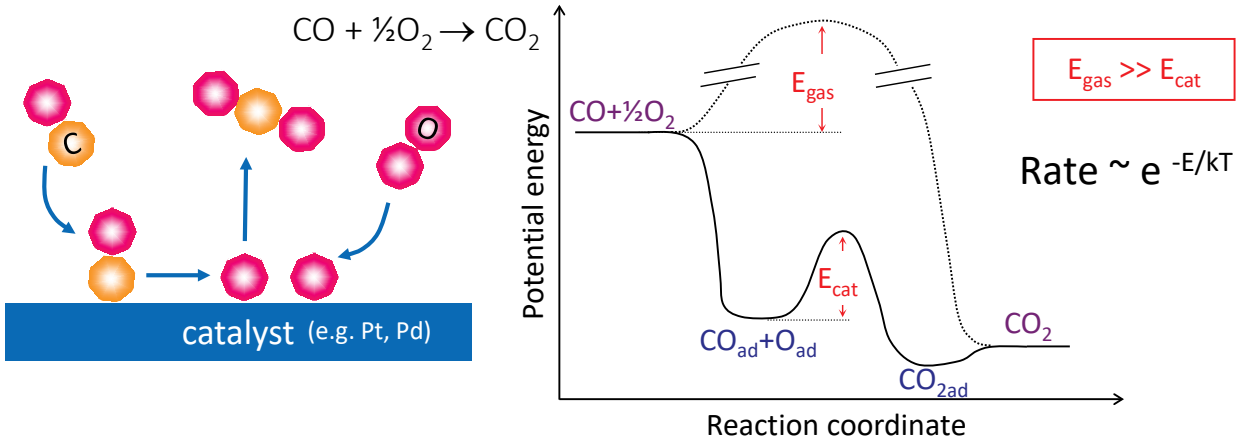
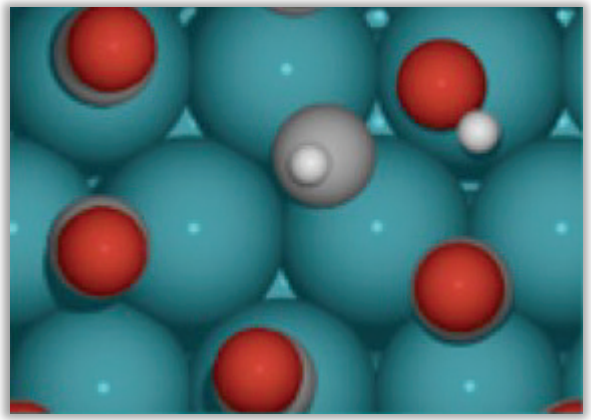
Basic concepts in catalysis by metals I: miscellaneous

Thermodynamics & kinetics

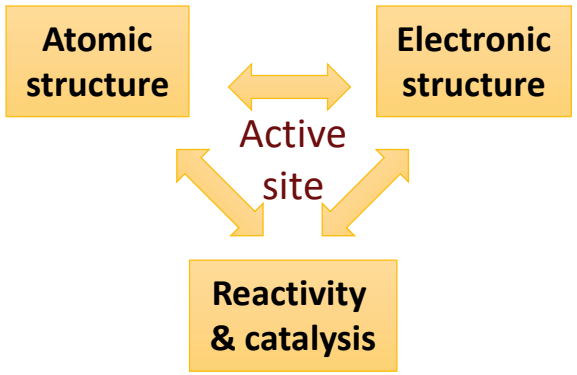
Example of CO oxidation on Pt-group metals



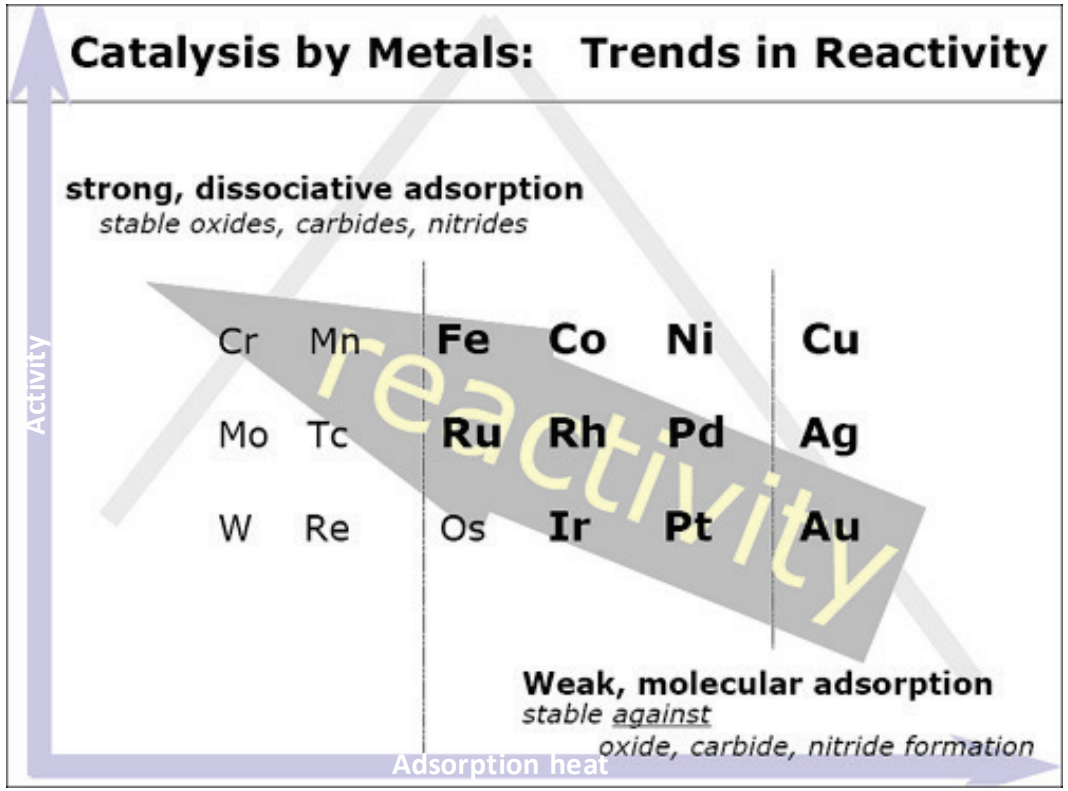
Chemisorption



https://www.nature.com/articles/ncomms14621



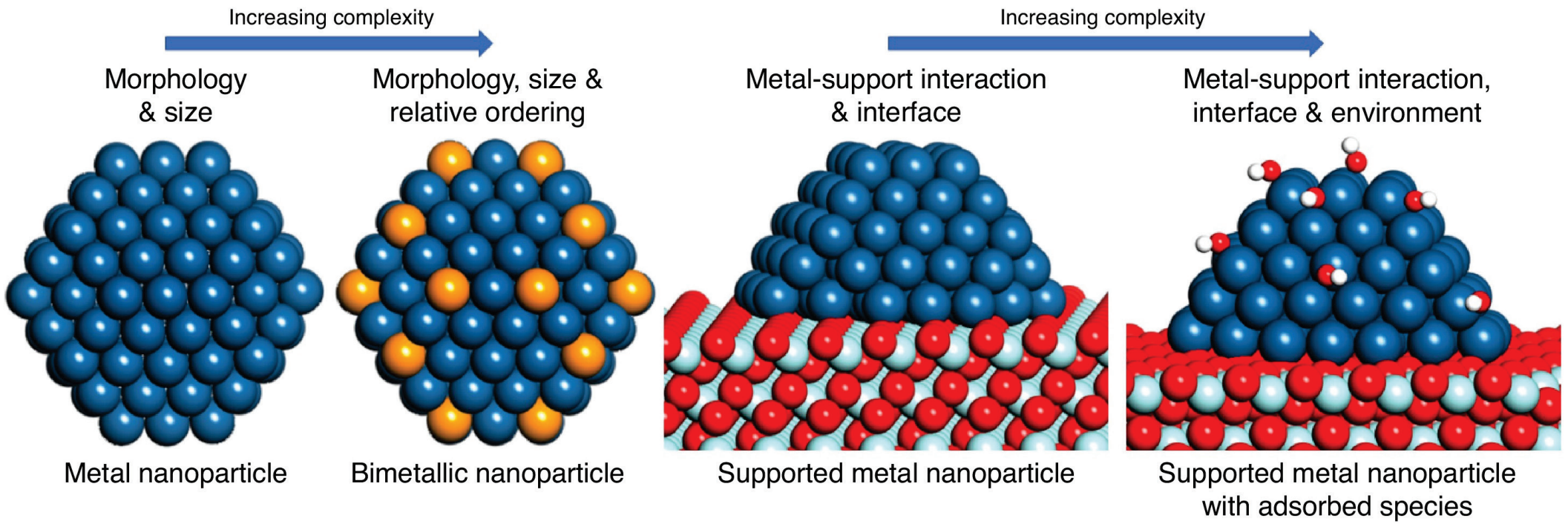
Sabatier's principle



reactivity ≠ activity (reactive ⊇ active)

L. Piccolo in *Nanoalloys: Synthesis, structure and properties*, Springer (2012)

Basic concepts in catalysis by metals II: increasing complexity



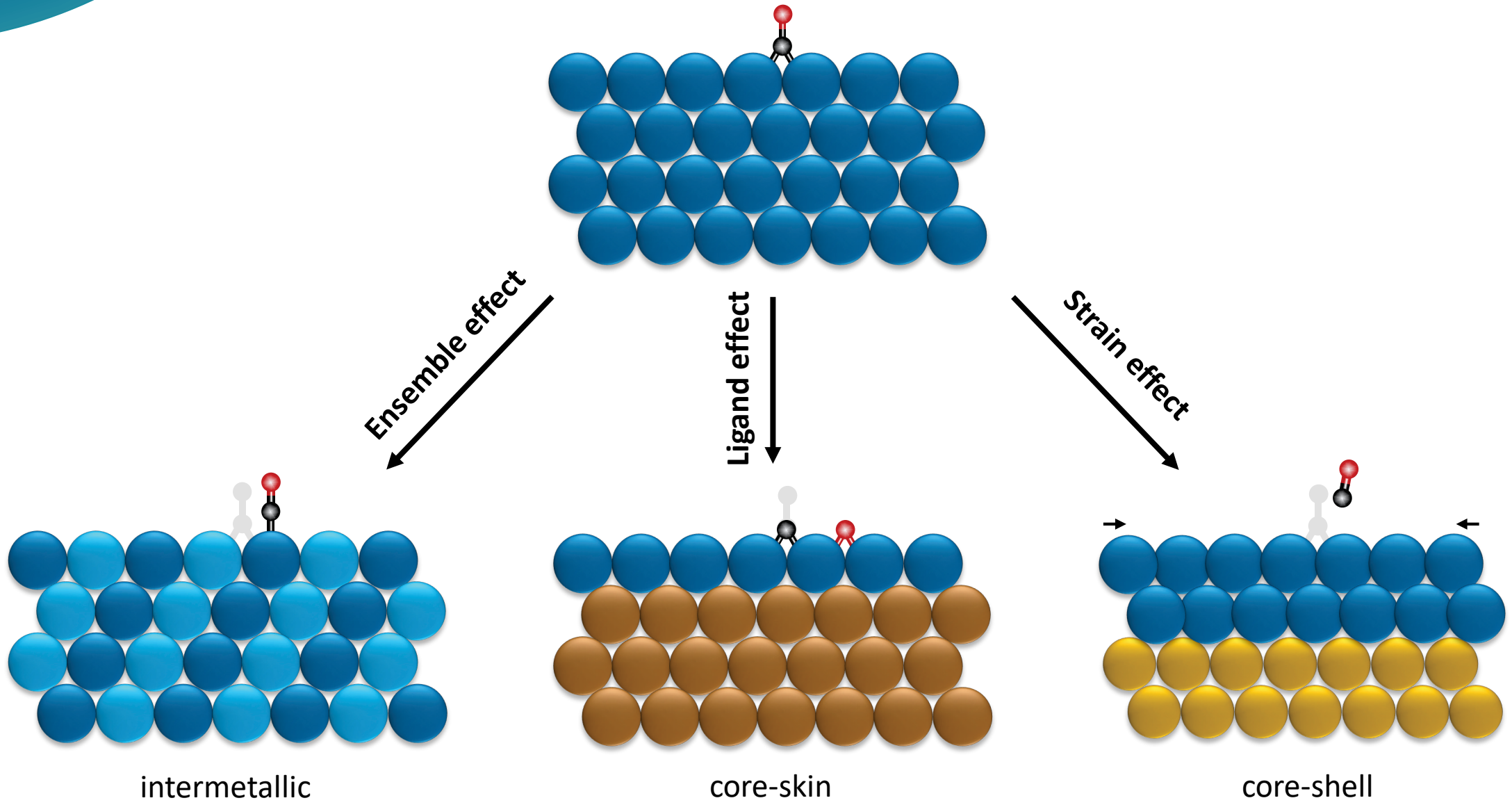
https://doi.org/10.1016/j.coche.2019.08.002

small NPs (low-coordination sites) not necessarily more active

multimetallic nanocatalyst ⊇ nanoalloy catalyst

L. Piccolo in *Nanoalloys: Synthesis, structure and properties*, Springer (2012)

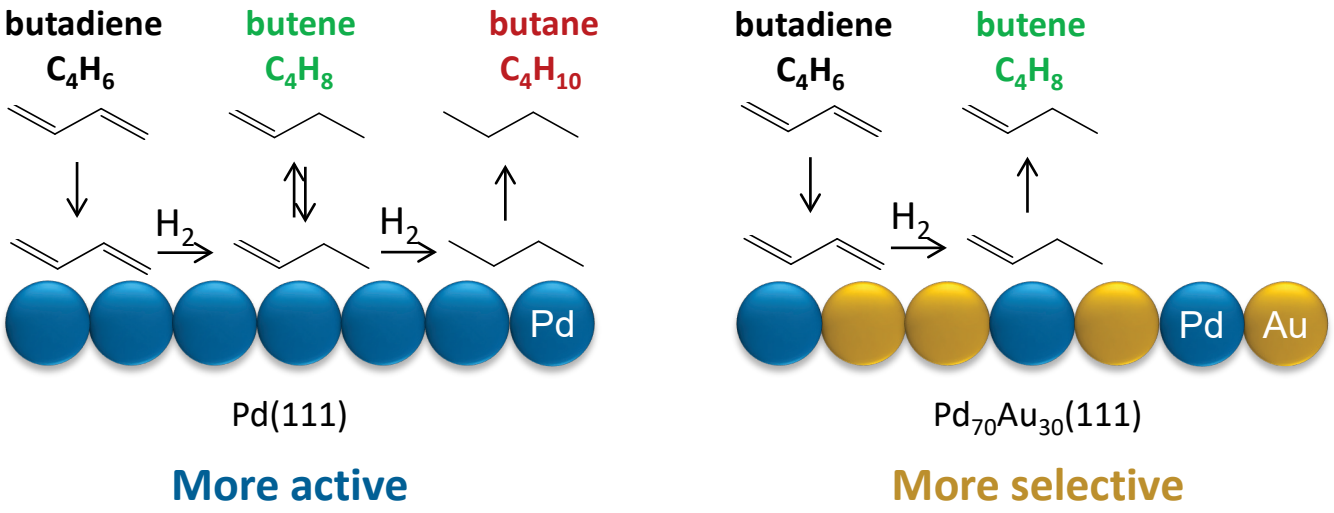
Basic concepts in catalysis by metals III: alloying effects



L. Piccolo in *Nanoalloys: Synthesis, structure and properties*, Springer (2012)

Synergistic alloying effects I: example of partial hydrogenation on Pd-Au

AB alloy more efficient (active, selective, stable) than A, B and A+B

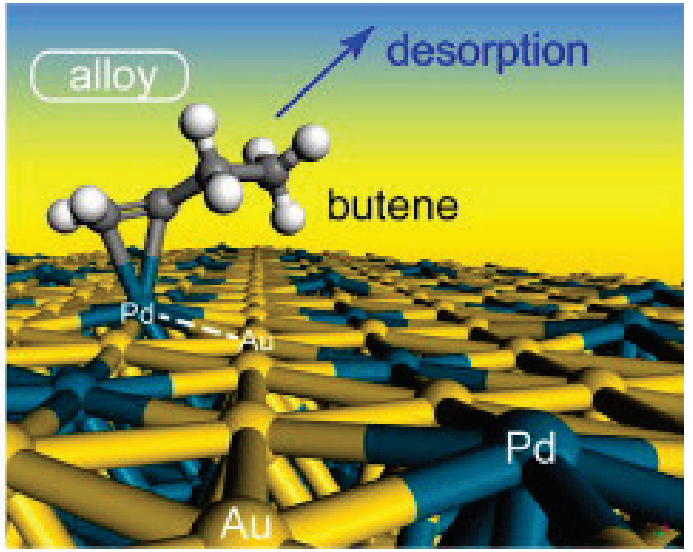


Pd(111)

More active

$Pd_{70}Au_{30}$(111)

More selective



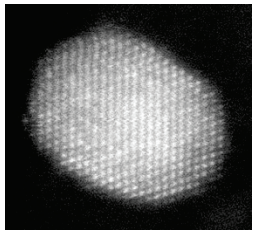
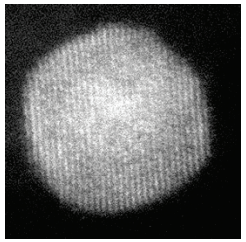
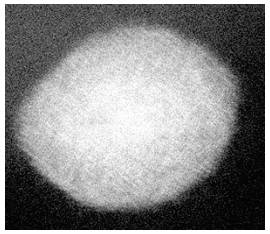
D. Loffreda *et al.*, *J. Catal.* **2013**, 308, 374

Smaller Pd **ensembles** or/and **ligand** effect of Au ⇒ softened HC bonding

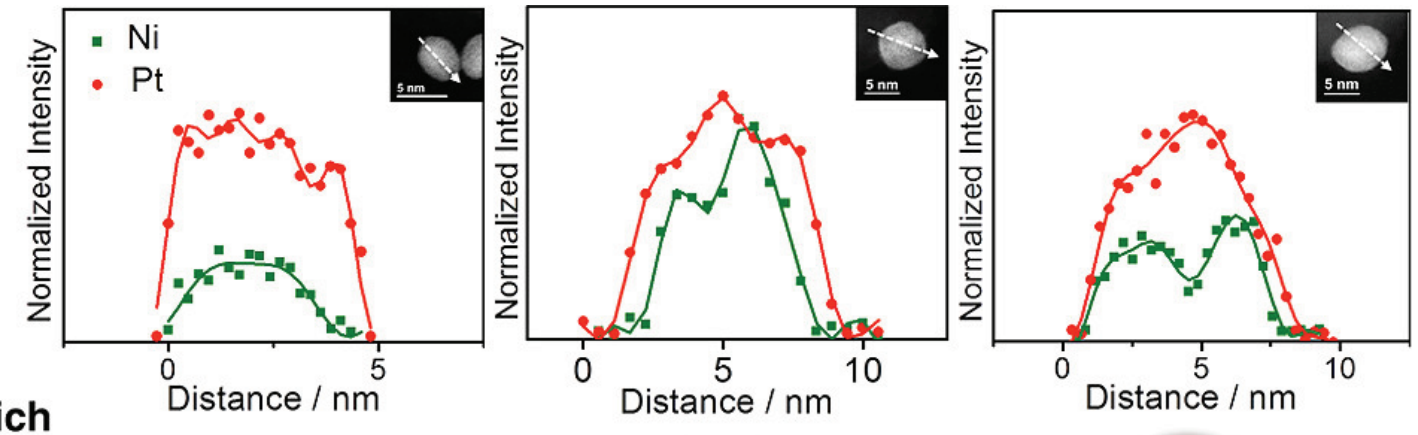
L. Piccolo *et al.*, *Surf. Sci.* **2005**, *592*, 169

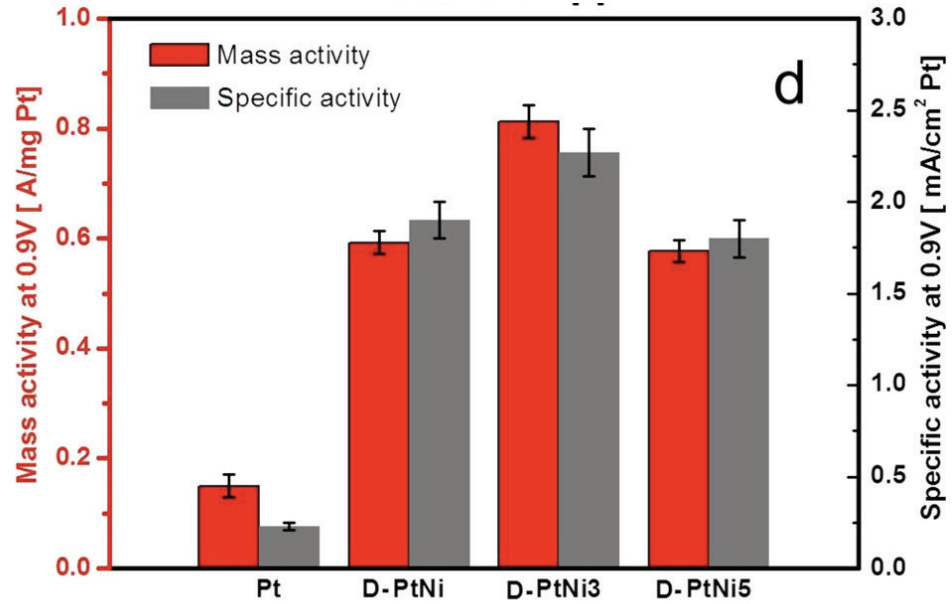
Synergistic alloying effects II: example of electrochemical ORR* on Pt-Ni

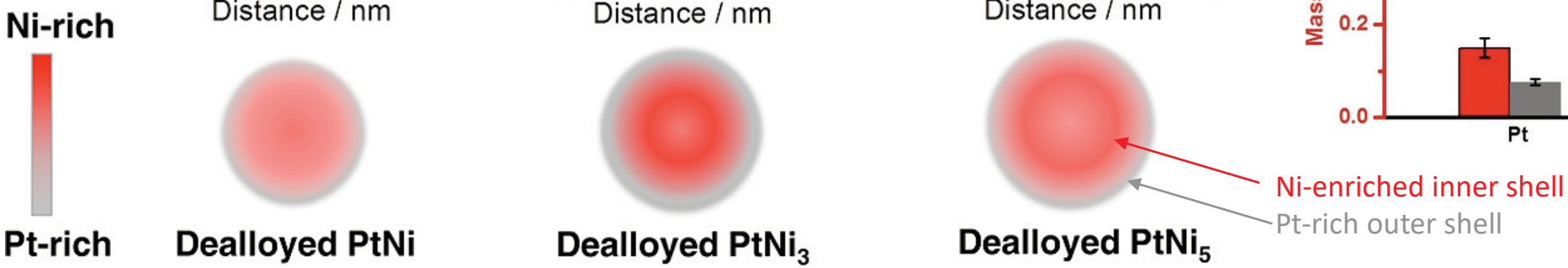
STEM-HAADF

EELS







Compressive **strain** in Pt shell ⇒ weaker binding of oxygenated intermediates ⇒ increased activity

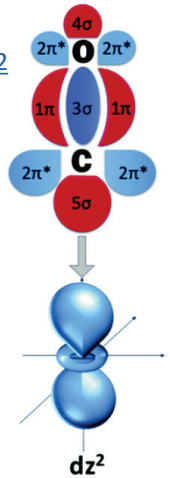
P. Strasser & coll., *Nano Lett.* **2012**, *12*, 5423

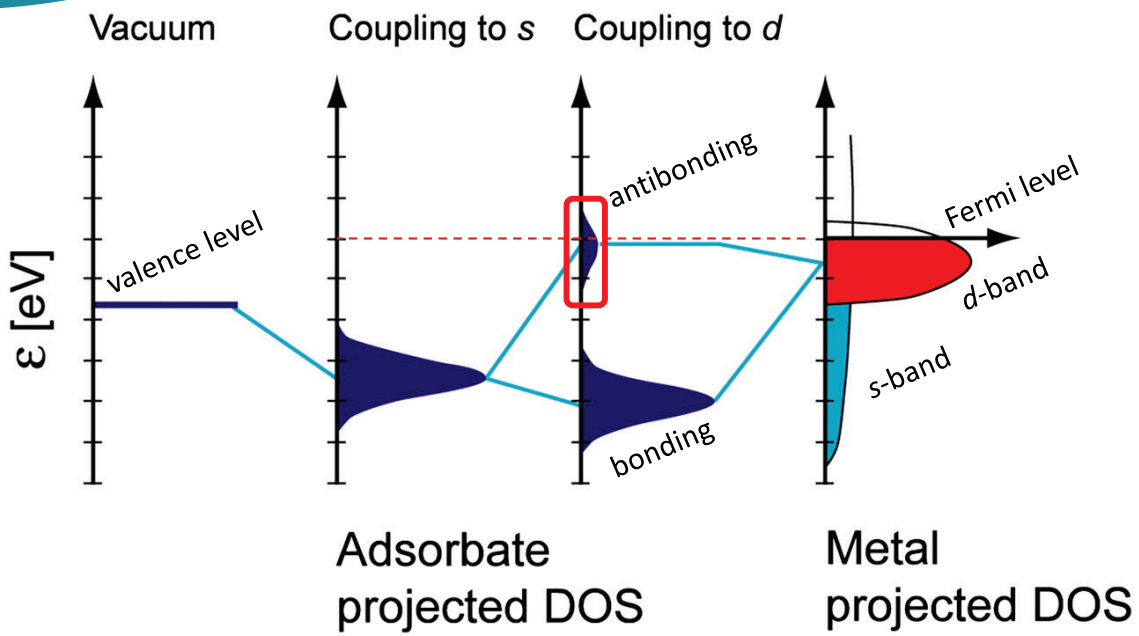
See also the review by L. Wang *et al.*, *ACS Catal.* **2018**, *8*, 9388

* *Oxygen reduction reaction*

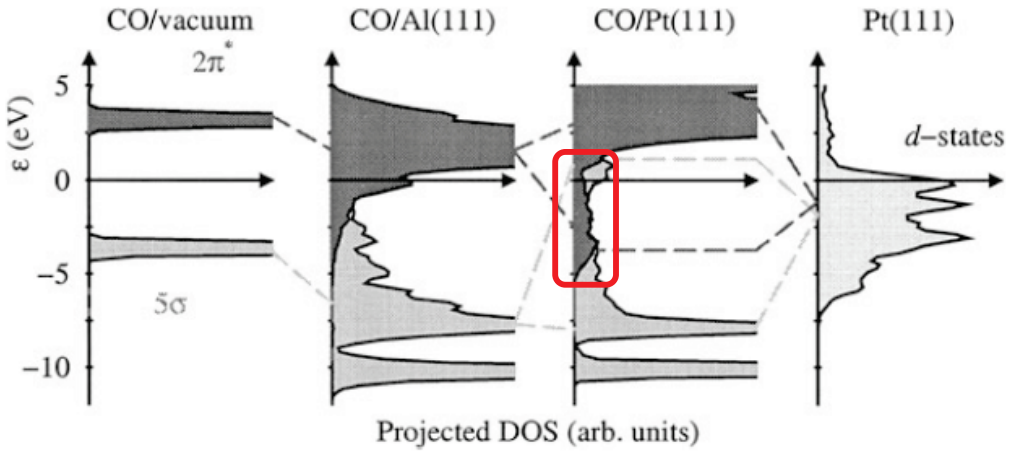
Rationalizing alloying effects I: Nørskov's *d*-band model

K.M. Gameel *et al.*, *PCCP* **2018**, *20*, 25892





Adapted from J.K. Norskov *et al. PNAS* **2011**, *108*, 937



Hybridization energy: $\Delta E_{d\text{-}hyb} \approx 2f\,\beta_{2\pi}{}^2\,(\gamma_{2\pi} - 1/(\varepsilon_{2\pi}-\varepsilon_d))$

Filling of the *d*-band — Orbital overlap — *d*-band center

Higher metal *d*-band ⇒ adsorbate-metal orbital antibonding more filled ⇒ softer adsorbate-metal bonding

Explains most effects of metal nature, alloying, strain, coordination…

L. Piccolo in *Nanoalloys: Synthesis, structure and properties*, Springer (2012)

Rationalizing alloying effects II: *d*-band model application to alloy surfaces

J.R. Kitchin *et al.*, *J. Chem. Phys.* **2004**, 120, 10240

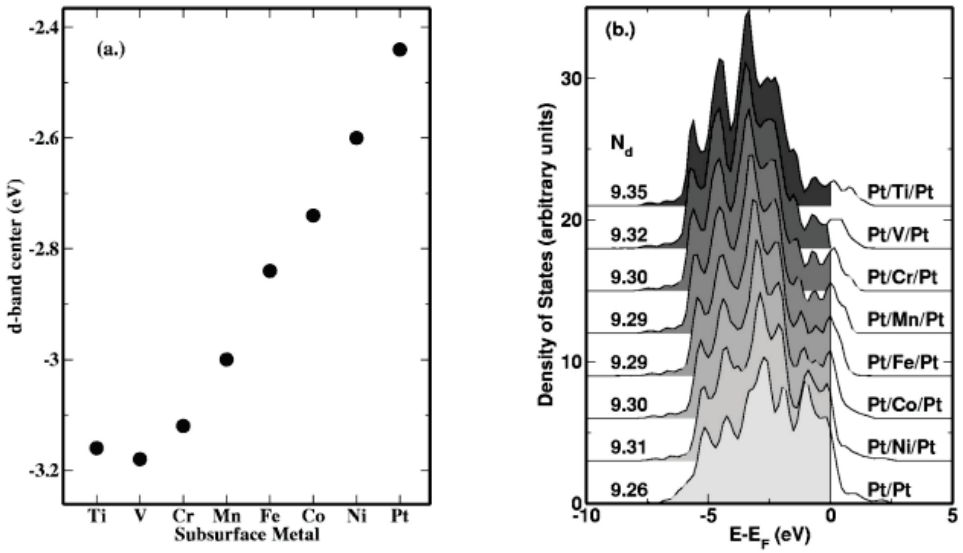


FIG. 1. (a) Variations in the surface *d*-band center of Pt(111) slabs containing subsurface 3*d* metals. (b) Calculated surface *d*-band DOS for subsurface-3*d*-metal-containing Pt slabs. The number of *d*-electrons/surface atom is shown for each band.

Adapted from J.R. Kitchin *et al.*, *PRL* **2004**, *93*, 156801

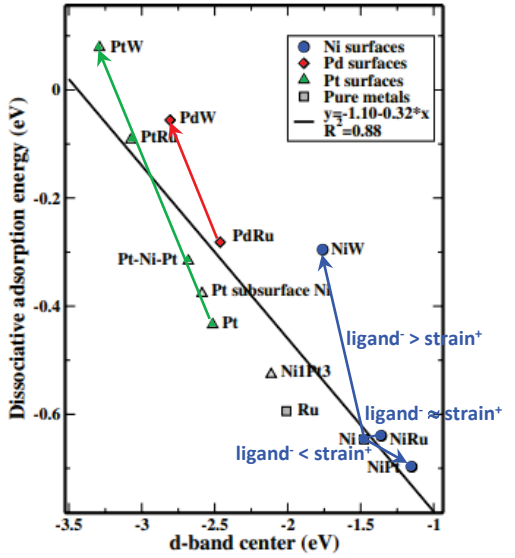


FIG. 3. Correlation between the dissociative adsorption energy of H_2 on bimetallic surfaces and the *d*-band center of those surfaces.

V.R. Stamenkovic *et al.*, *Nat. Mater.* **2007**, *6*, 241

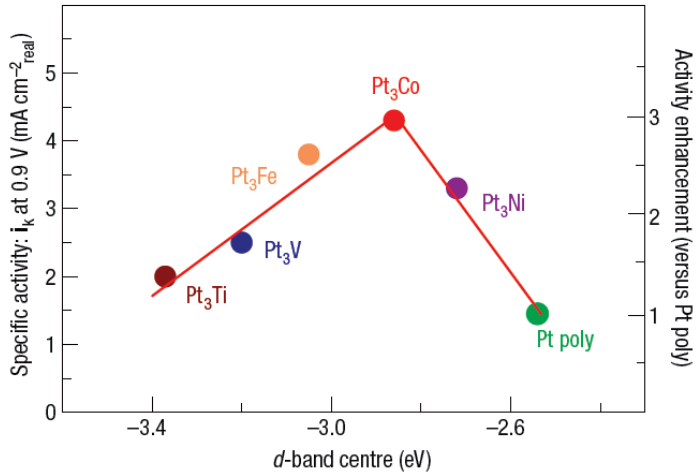


Figure 4 Relationships between the catalytic properties and electronic structure of Pt_3M alloys. a,b, Relationships between experimentally measured specific activity for the ORR on Pt_3M surfaces in 0.1 M $HClO_4$ at 333 K versus the *d*-band centre position for the Pt-skin (**a**) and Pt-skeleton (**b**) surfaces.

Pure ligand effect:
Downshift of the *d*-band (+ broadening to keep its filling constant) as the subsurface element moves to the left in the periodic table

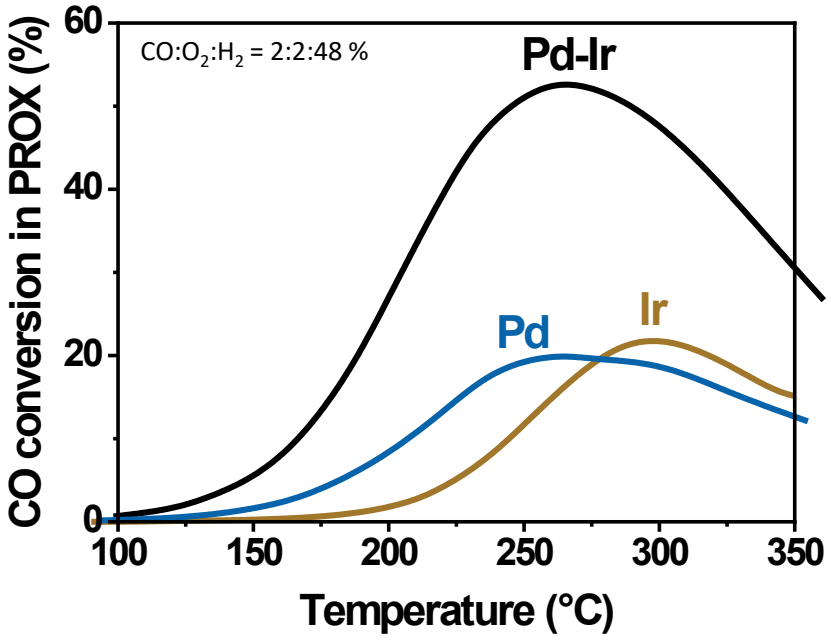
Mixed ligand and strain effects:
Adsorption strength correlated to *d*-band position through *d*-*d* orbital overlap

The *d*-band model is consistent with experimental volcano curves

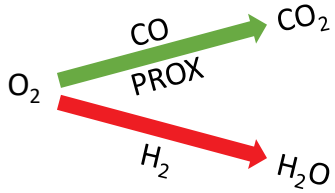
L. Piccolo in *Nanoalloys: Synthesis, structure and properties*, Springer (2012)

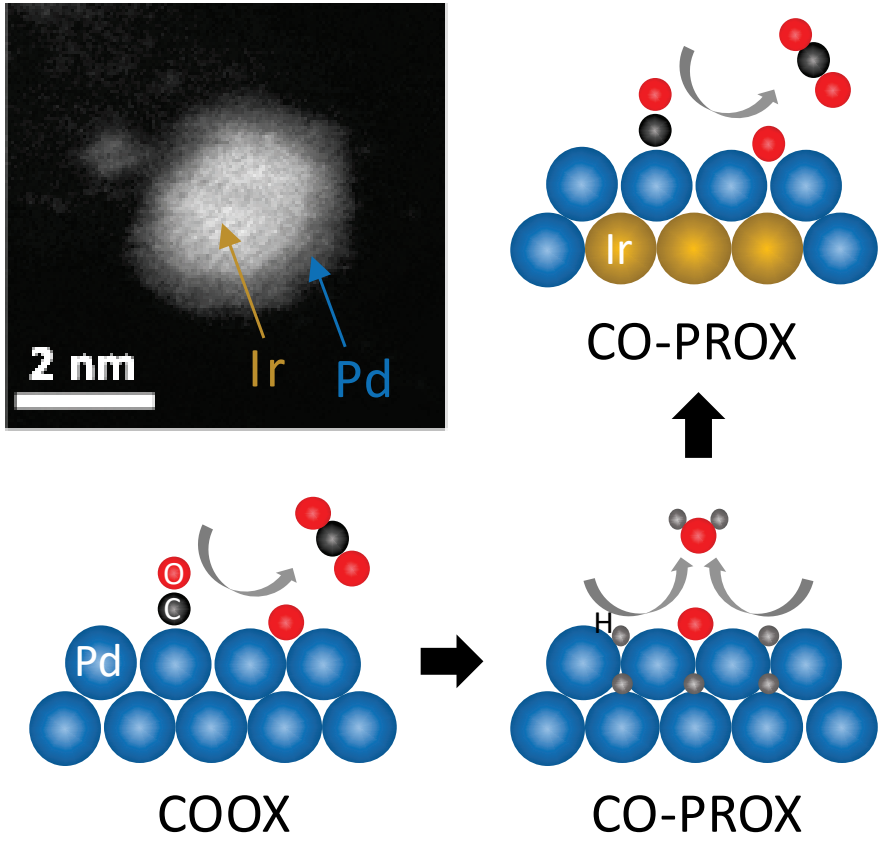
Alloying to prevent an environment effect: example of CO-PROX on Pd-Ir

NPs supported on alumina or amorphous silica-alumina



Preferential CO oxidation in hydrogen





Interplay between structure, hydrogen sorption and catalysis

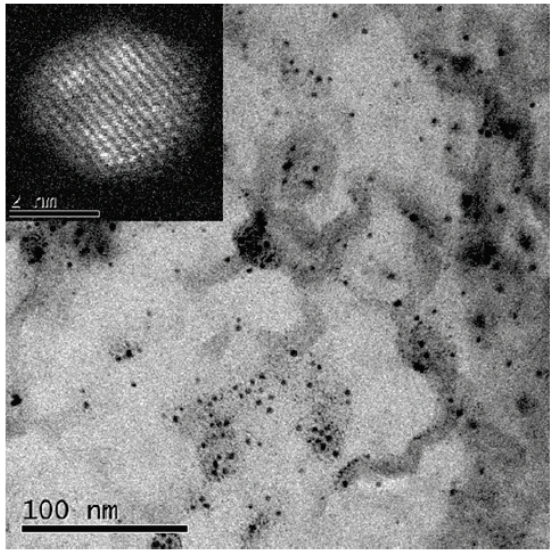
S. Nassreddine thesis
Dr. F. Morfin

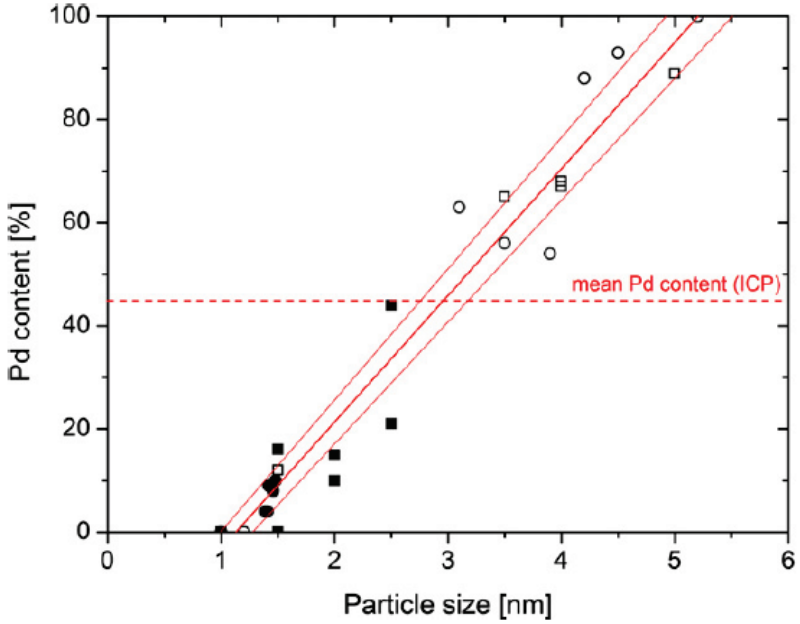
Experiments (catalysis, H_2 sorption, TEM, STEM, XAS): L. Piccolo & coll., *J. Catal.* **2012**, *292*, 173; *ACS Catal.* **2012**, *2*, 2161; *Nanoscale* **2014**, *6*, 9955

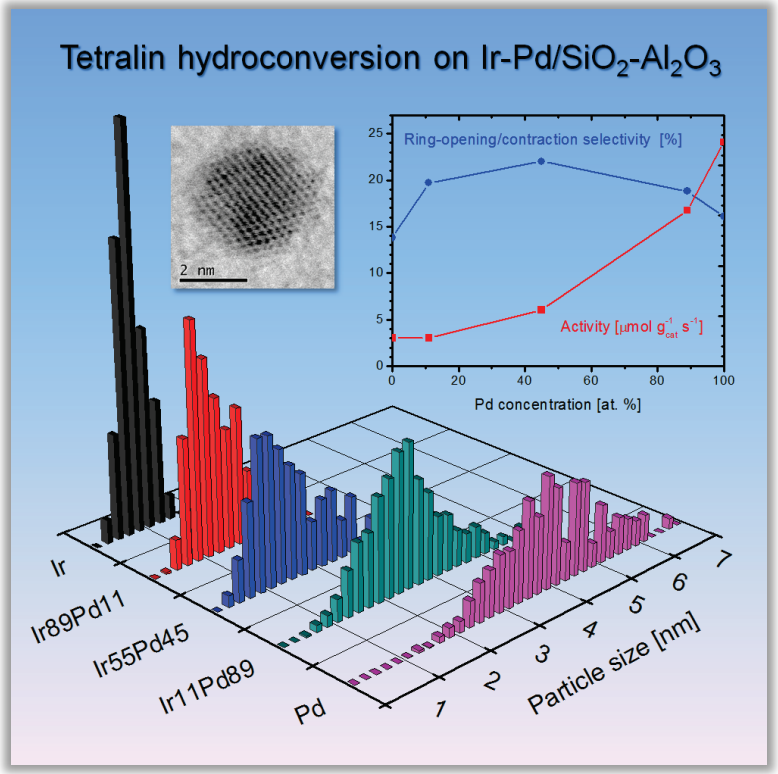
Calculations (MC, DFT): C.Goyhenex & coll., *J. Nanopart. Res.* **2015**, *17*, 217; *PCCP* **2017**, *19*, 32451

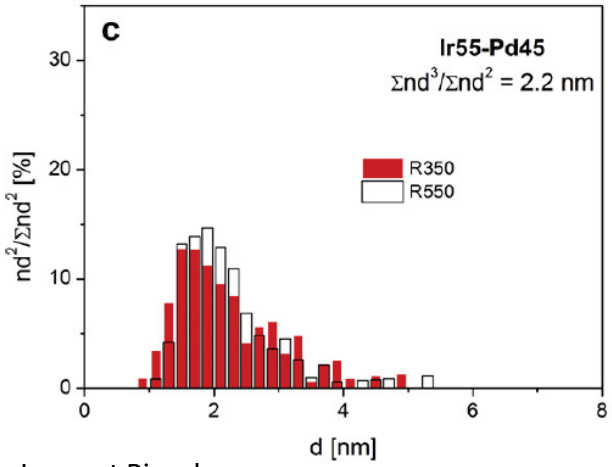
Consequences of Ostwald ripening on nanoalloy catalysts prepared by impregnation

Preparation by incipient wetness co-impregnation of silica-alumina support (500 m^2/g) with Ir and Pd acetylacetonates + thermal treatment in H_2 flow up to 550 °C









NP size dispersion

NP size-composition correlation

Thermal treatment ⇒ preferential enrichment of the bigger NPs with the “less interacting” element (Pd)

See Damien Alloyeau et al.

L. Piccolo *et al.*, *J. Catal.* **2012**, *292*, 173

Outline

1 **Basics of nanocatalysis & alloying effects**

Definitions, catalysis in practice, fundamental concepts

2 **Nanoalloy catalysts in their environment**

Dynamical effects, operando approach, case study

3 **Promising alloy phases in catalysis**

Single-atom alloys, intermetallics, and others

Prelude: CO on Au surfaces

Au NPs: see H. Guesmi, J. Nelayah et al.

"Why gold is the noblest of all the metals"

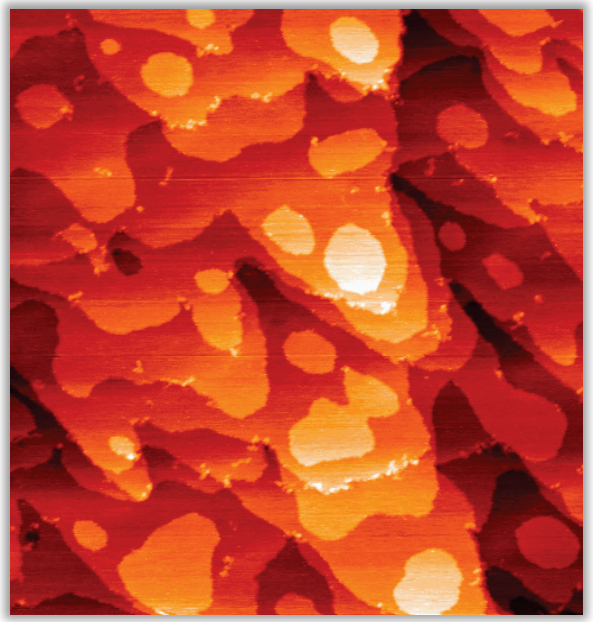
Hammer & Norskov, *Nature* **1995**, *376*, 238

Au(111) in UHV (10^{-9} Torr)

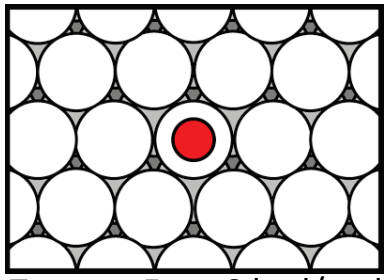
STM, RT, 350 × 350 nm

Au(111) under CO (100 Torr)

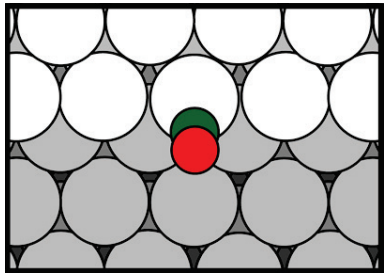
Au(110) under CO (20 Torr)



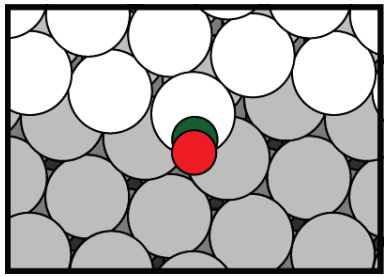
CO/Au(111) DFT



Terrace: E_{ads} = 8 kcal/mol



Step: E_{ads} = 16 kcal/mol



Kink: E_{ads} = 18 kcal/mol

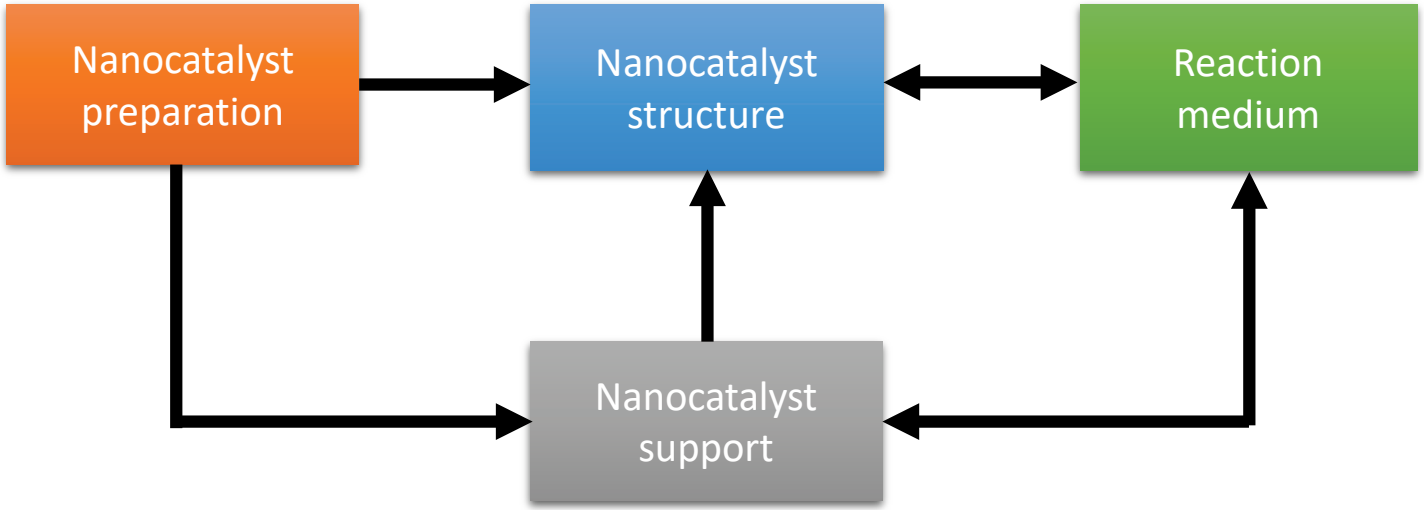
Experiments (STM, IRAS):

Y. Jugnet *et al.*, *Surf. Sci.* **2002**, *521*, L639; L. Piccolo *et al.*, *Surf. Sci.* **2004**, *566*, 995

Calculations (DFT):

D. Loffreda *et al.*, *Phys. Rev. B* **2005**, *71*, 113414

Environment effects in nanocatalysis



- **Phase, nature and concentration of the reactants/products, solvant/carrier gas**
- **Temperature, pressure**
- Thermodynamics and kinetics of the reaction (exothermicity…)
- Contact time (flow rate, stirring rate…)
- Light (photocatalysis)
- Voltage (electrocatalysis)

Nanoparticle environment = Reaction medium + Support

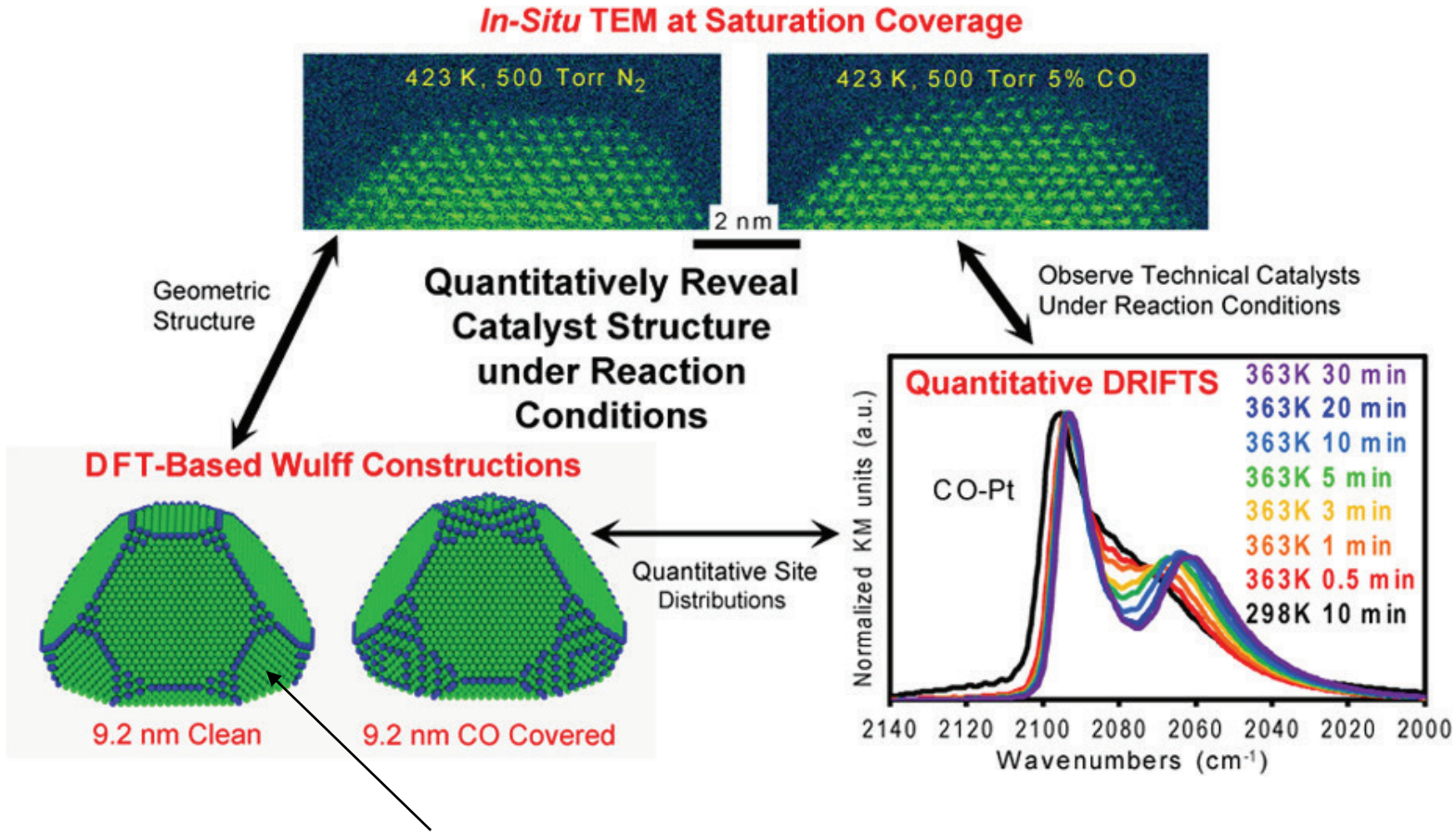
L. Piccolo, *Catal. Today* **2021**, *373*, 80

Adsorption-induced restructuring I: typology

Nanocatalyst structure		Reaction medium effects
Size		Coalescence
Atomic & electronic structure		Phase transition, surface relaxation/reconstruction
Shape		Reshaping, surface facetting/roughening
Chemical composition		Oxidation, hydriding…
Chemical distribution		Segregation, ordering

L. Piccolo, *Catal. Today* **2021**, *373*, 80

Adsorption-induced restructuring II: example of CO on Pt nanoparticles



"facet-selective surface reconstruction"

P. Christopher & coll., *JACS* **2017**, *139*, 4551

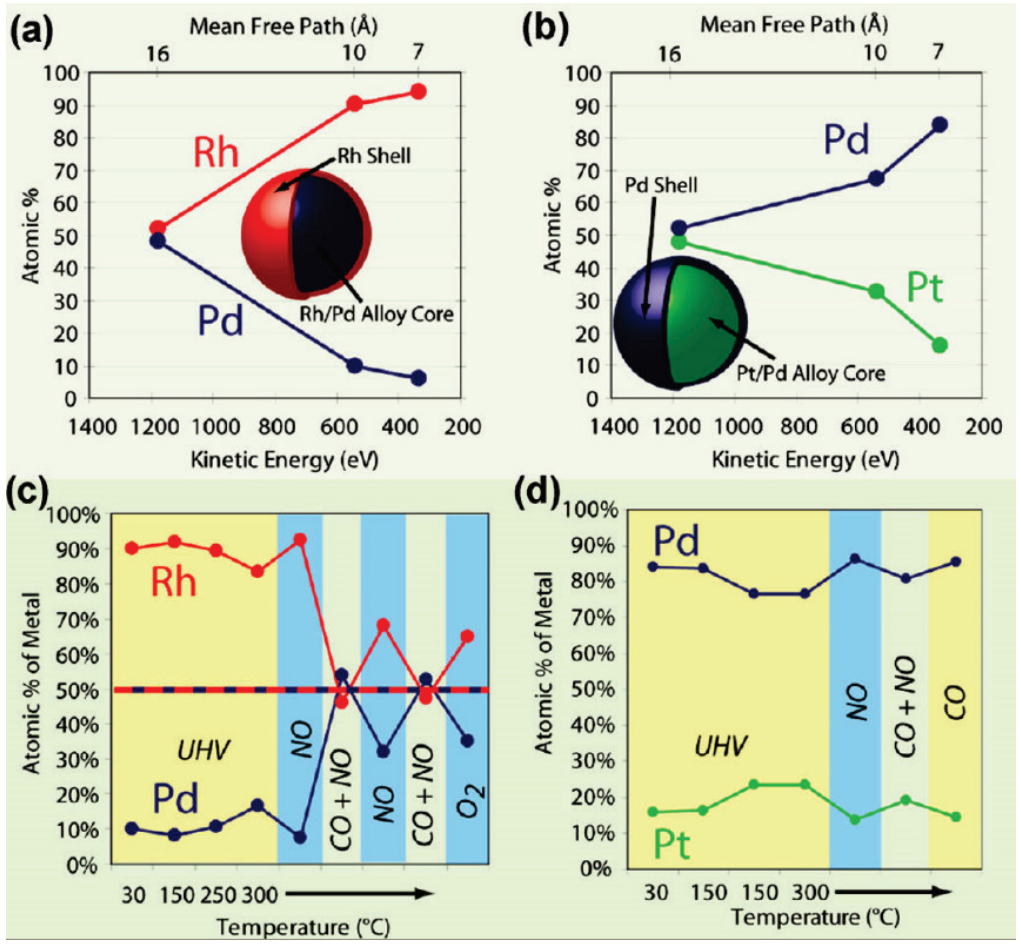
Adsorption-induced restructuring III: example of CO and/or NO on nanoalloys

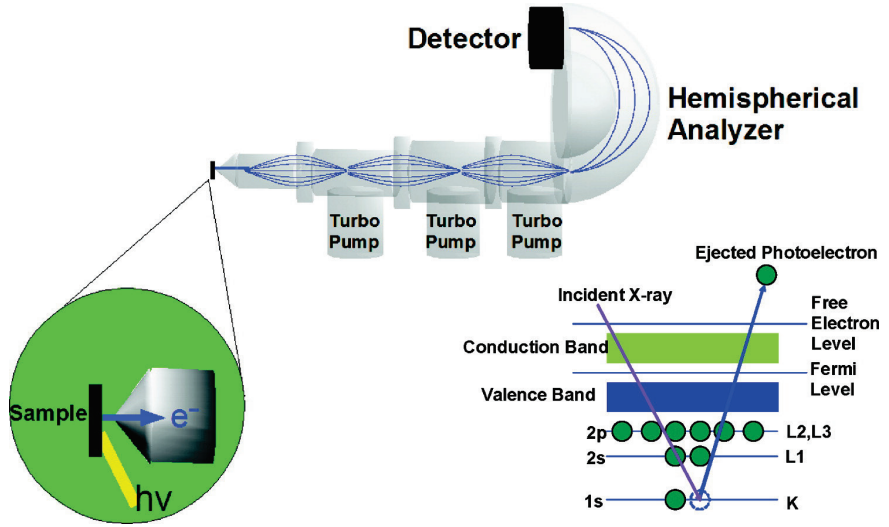
~15 nm-sized colloidal NPs on SiO_x/Si wafer
NAP-XPS, Berkeley Synchrotron Facility + lab (UHV)

CO and/or NO on: **$Pd_{0.5}Rh_{0.5}$** **$Pd_{0.5}Pt_{0.5}$**

UHV

NO, CO, O_2 (0.1 Torr)





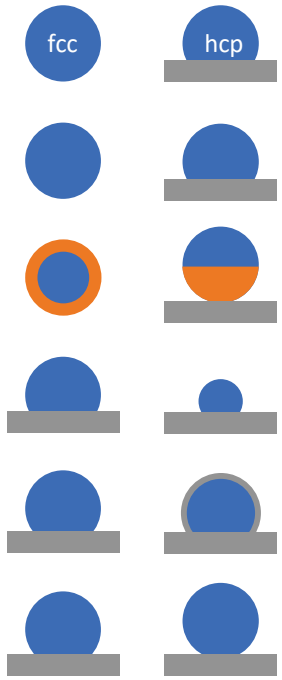
Caution: oxidized metals

G.A. Somorjai & coll., *Science* **2008**, *322*, 932; *JACS* **2009**, *131*, 16589

Adsorption and support-induced restructuring I: typology

Nanocatalyst structure

Support effects



Atomic & electronic structure	Phase transition, strain, charge transfer
Shape	Reshaping, truncation
Chemical distribution	Segregation
Size	Sintering/redispersion
Chemical composition	Encapsulation (“SMSI”)
NP/support adhesion	Wetting/dewetting

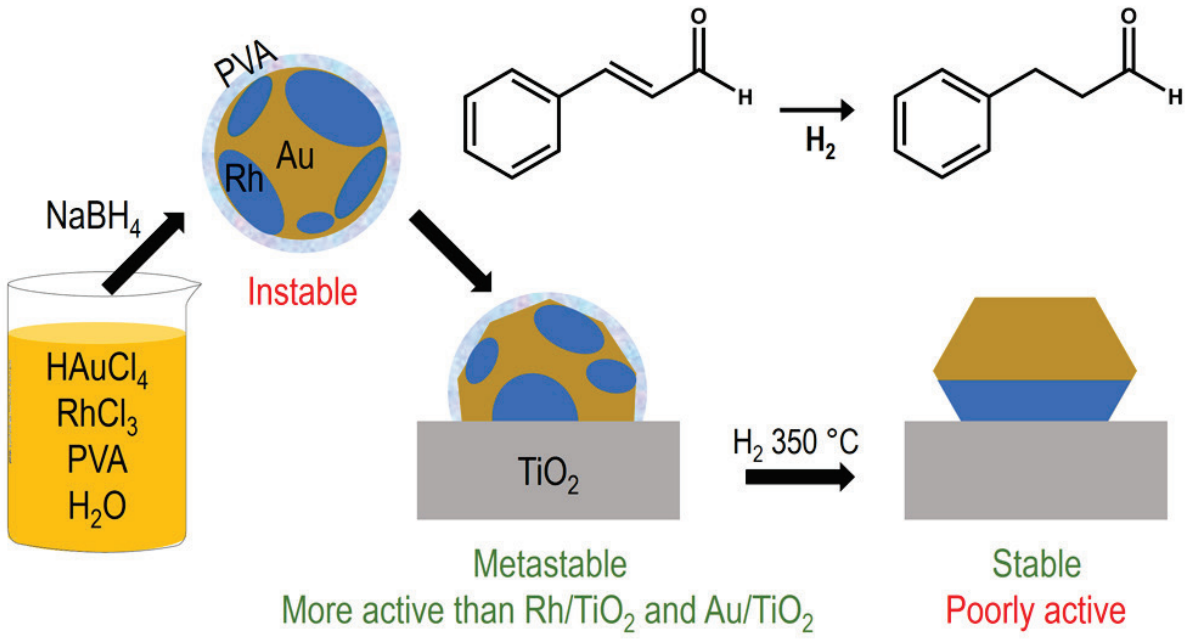
Reaction medium effects

L. Piccolo, *Catal. Today* **2021**, *373*, 80

Adsorption and support-induced restructuring II: example of $AuRh/TiO_2$

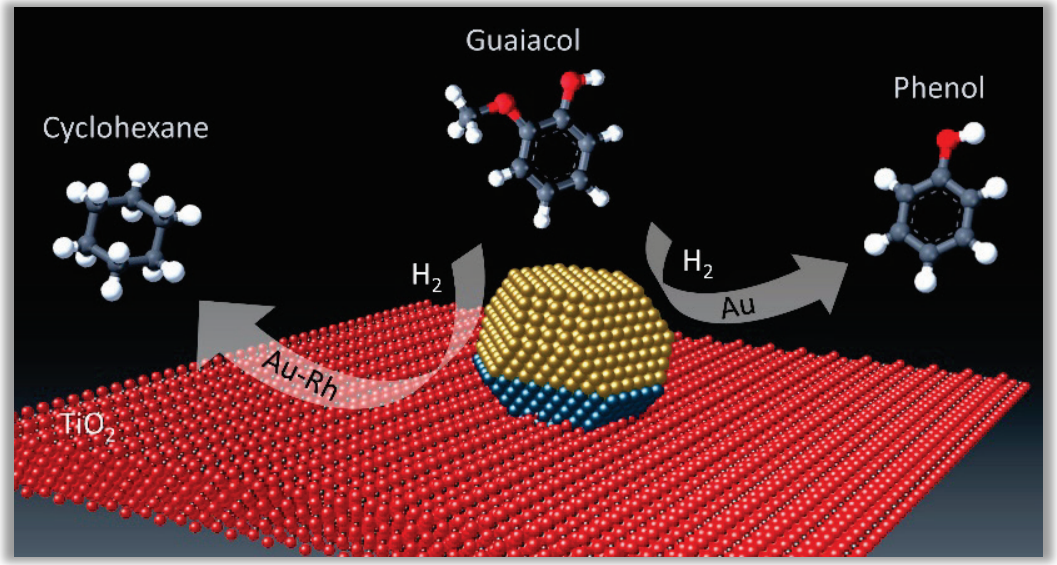
a/ Synthesis, restructuring and catalysis

Cinnamaldehyde hydrogenation



Ligand effect?

Guaiacol hydrodeoxygenation



Cooperative effect?

Z. Konuspayeva *et al.*, *J. Mater. Chem. A* **2017**, *5*, 17360

T.S. Nguyen *et al.*, *J. Catal.* **2016**, *344*, 136

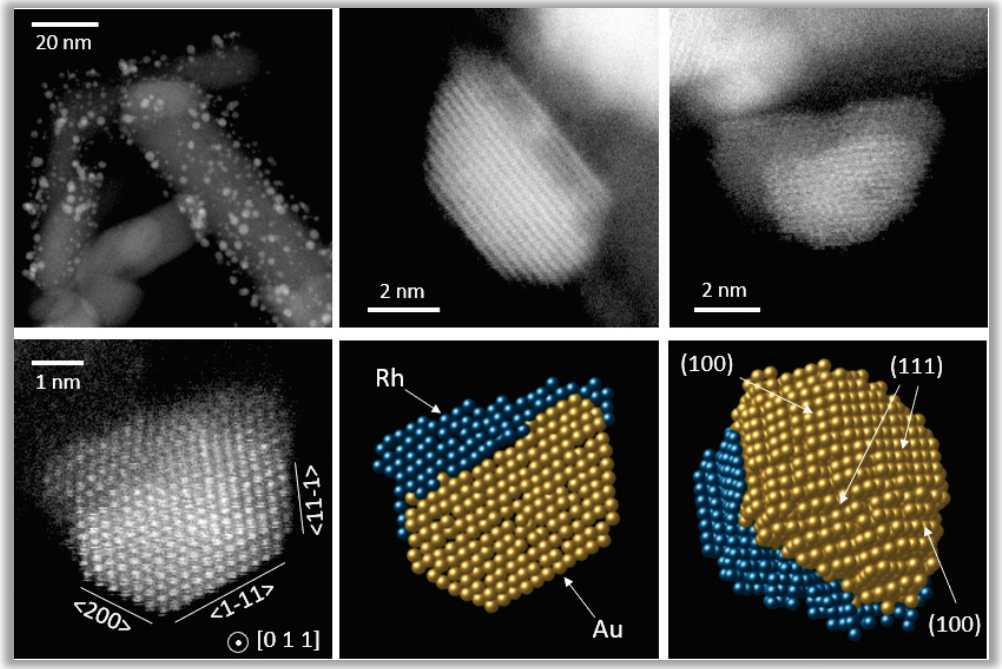
Adsorption and support-induced restructuring II: example of $AuRh/TiO_2$

b/ Rationalizing support-directed segregation

STEM-HAADF characterization

Dr. Ziyou Li

UNIVERSITY OF BIRMINGHAM



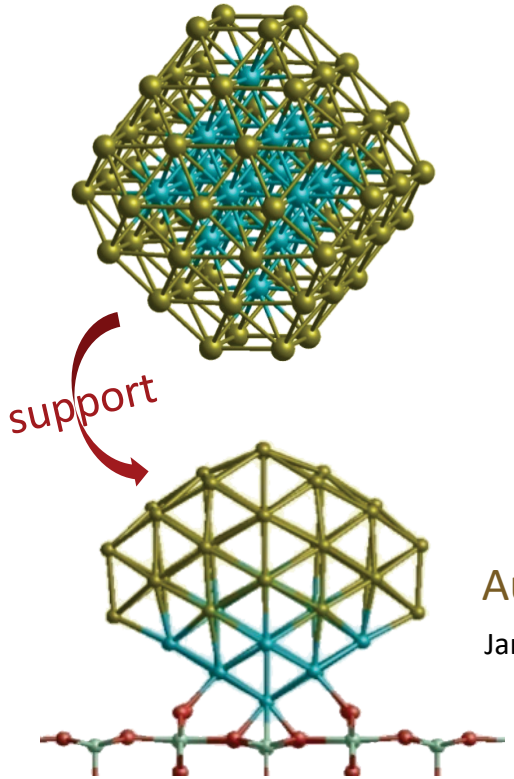
Atom counting

Dr. W. Lefebvre

GPM

DFT modeling

Prof. R.L. Johnston



$Au_{50}Rh_{29}/TiO_2(110)$

Rh@Au

Core-shell

Au/Rh/TiO_2

Janus or cup-ball

Similar behavior

Ir@Pd

Core-shell

Pd/Ir/TiO_2

Janus or cup-ball

Lower cohesion/ surface energy

Positive mixing enthalpy

Higher reactivity

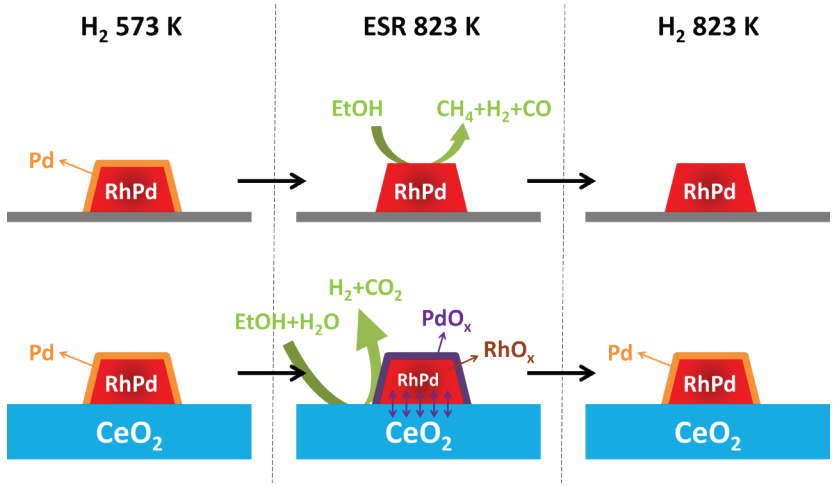
L. Piccolo *et al., Sci. Rep.* **2016**, *6*, 35226

I. Demiroglu *et al., Faraday Discuss.* **2018**, *208*, 53

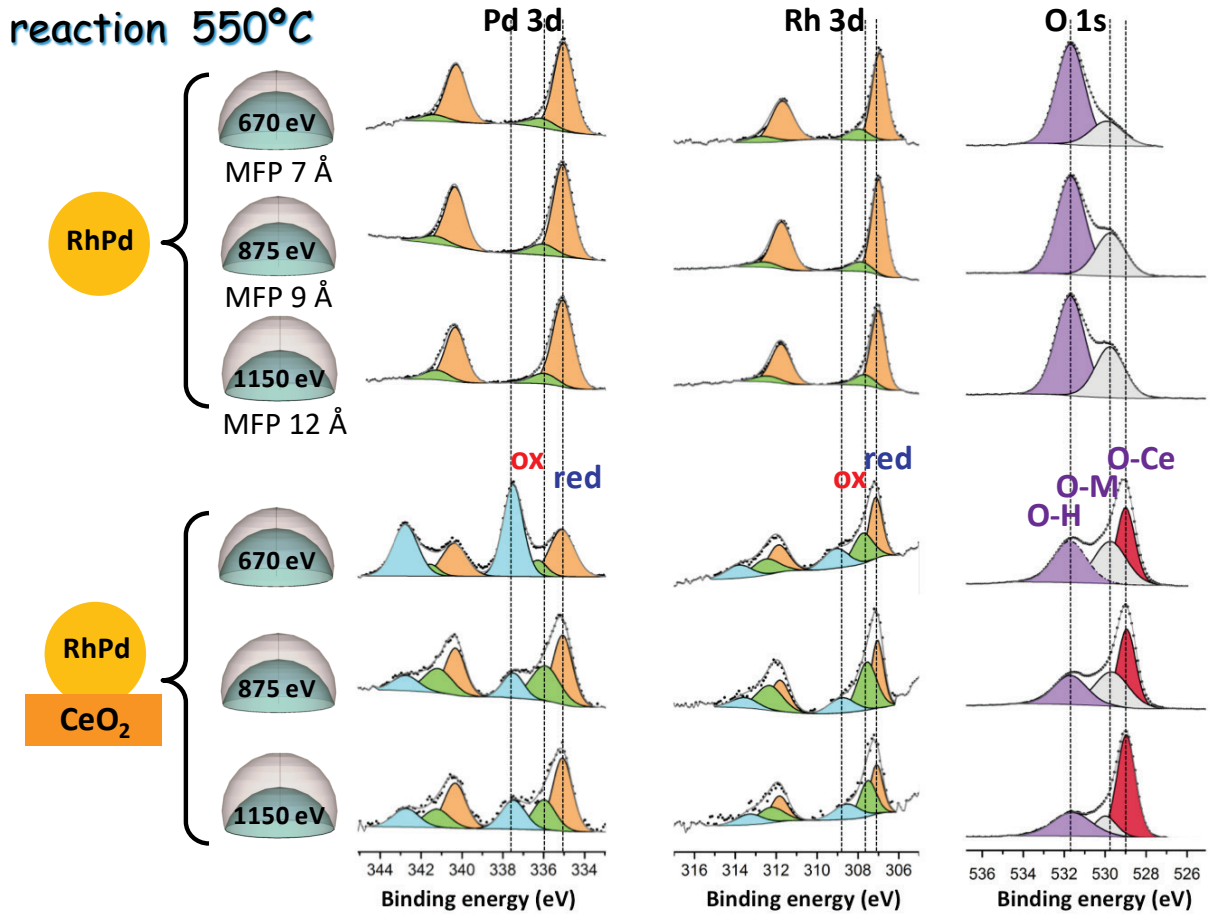
Adsorption and support-induced restructuring III: ethanol steam reforming on PdRh/CeO_2

NAP-XPS, ALBA synchrotron, CIRCE beamline, pressure 0.05 mbar, 6-nm NPs

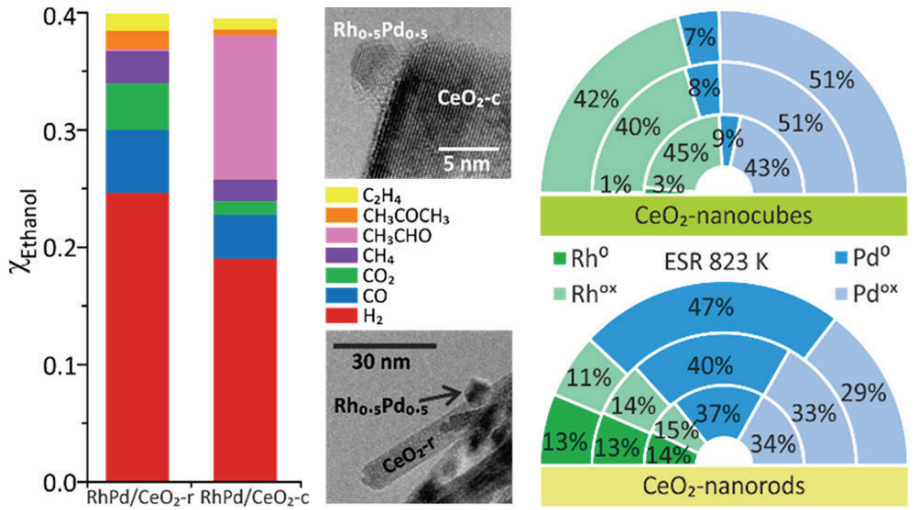
Ceria favors active Rh@Pd oxidized structure



Effect of the support presence on radial composition



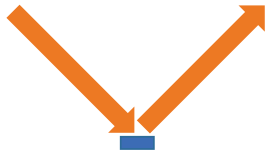
Effect of the support morphology on radial composition

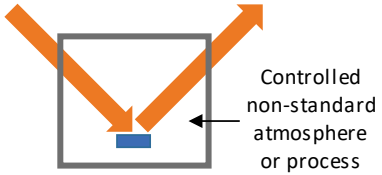


J. Llorca & coll., *Science* **2014**, *346*, 620; *ACS Catal.* **2019**, *9*, 3641

Operando spectroscopies

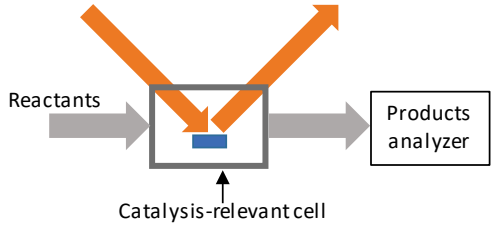
From *ex situ*…



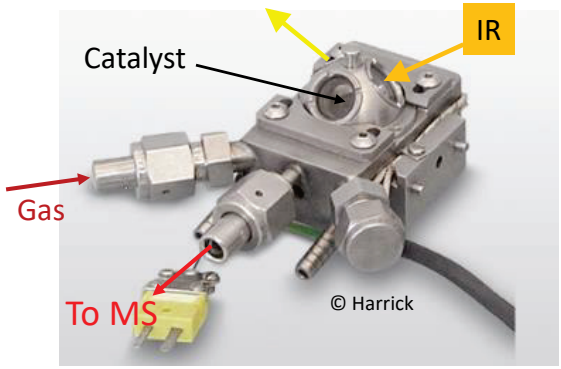


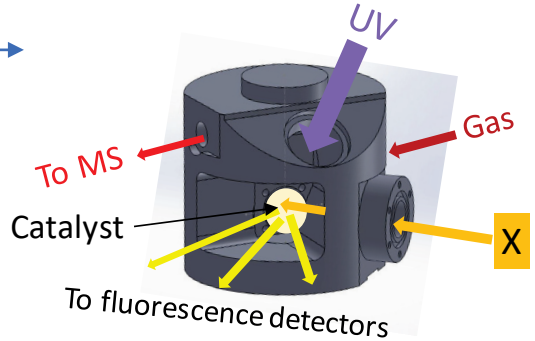
e.g. NAP-XPS, ETEM…

…to *operando* catalyst characterization



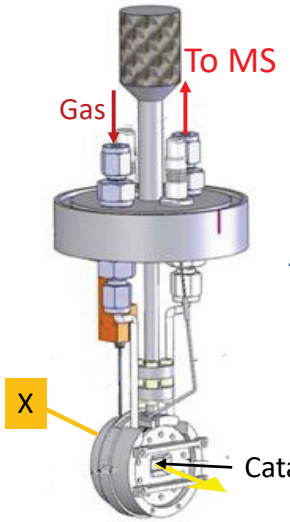
Photonic technique	Information
IR spectroscopy (FTIR/DRIFTS/ATR/IRAS)	Adsorbate nature and amount, adsorption site
Raman spectroscopy (SERS/TERS)	Nanoscale structure
XAS (EXAFS/XANES/QXAS)	Local atomic structure, oxidation state
SAXS (GISAXS)	Nanoparticle size and morphology
WAXS - XRD (PXRD/SXRD/HEXRD)	Crystal phase and size, atomic order





L. Piccolo *et al.*, *ACS Catal.* **2020**, *10*, 12696

Examples of gas flow cells



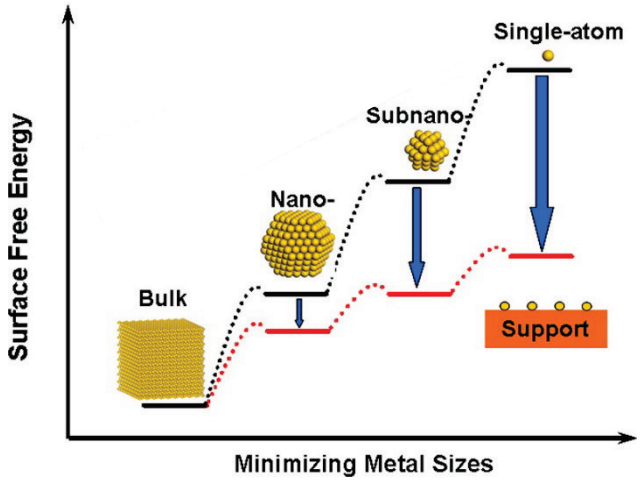
Details on SAXS and WAXS: see Pascal Andreazza
In situ electron microscopy: see S. Giorgio, C. Ricolleau et al.

L. Piccolo, *Catal. Today* **2021**, *373*, 80

Case *operando* study I: the $Pt_1/\gamma\text{-}Al_2O_3$ system

C. Dessal thesis
Dr. P. Afanasiev
Dr. F. Morfin

La Région Auvergne-Rhône-Alpes
LABEX IMUST UNIVERSITÉ DE LYON

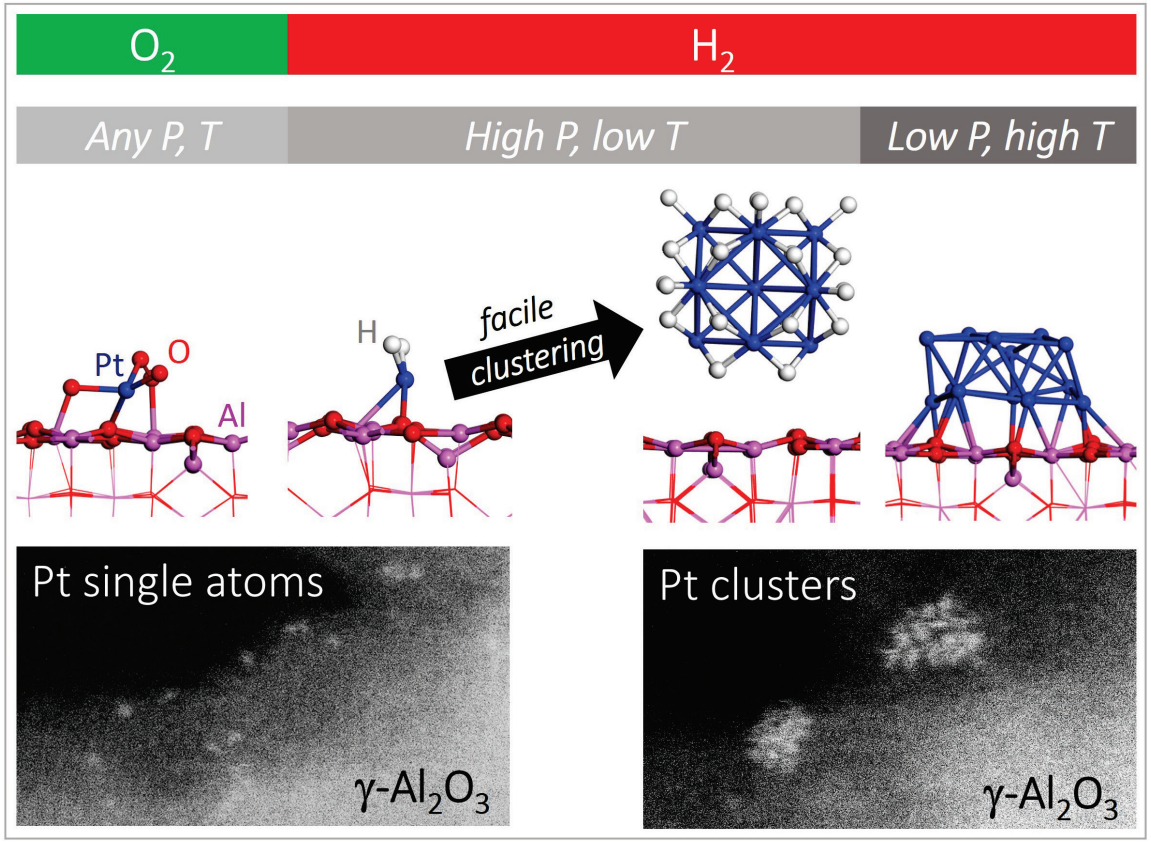


Adapted from X.F. Yang. *et al.*, *Acc. Chem. Res.* **2013**, *46*, 1740

- Catalysts prepared by incipient wetness impregnation + calcination at 300 °C-450 °C in air flow
- Support $\gamma\text{-}Al_2O_3$, 157 m^2/g ; Metal precursor $Pt(NH_3)_4(NO_3)_2$; Pt loading < 1 wt%

DFT
Dr. C. Chizallet

E-STEM
Dr. M. Aouine

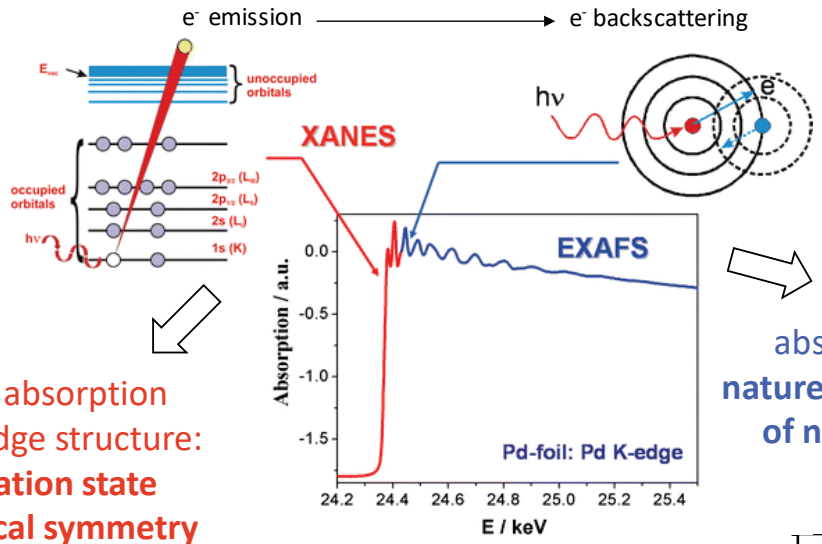


C. Dessal *et al.*, *Nanoscale* **2019**, *11*, 6897

Case *operando* study II: experimental

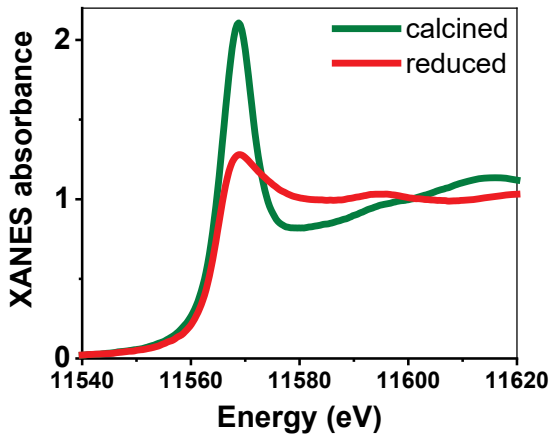
X-ray absorption spectroscopy

Adapted from J.D. Grunwaldt & A. Baiker, *PCCP* **2005**, *7*, 3526

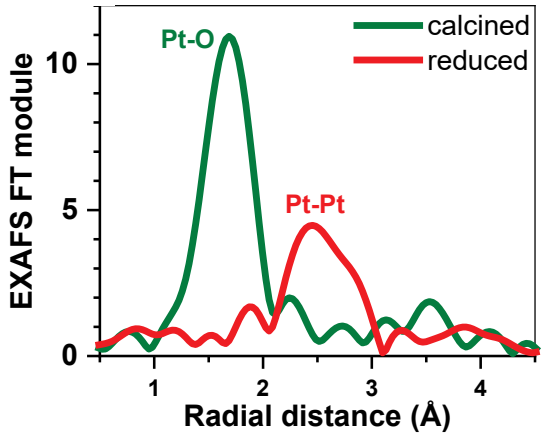


X-ray absorption near-edge structure: **oxidation state and local symmetry**

Extended X-ray absorption fine structure: **natures, distances and numbers of nearest-neighbor atoms**



XAS monitoring of Pt L3 edge

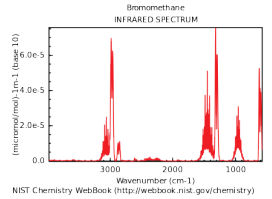


Diffuse reflectance infrared spectroscopy

Adapted from https://en.wikipedia.org/wiki/Infrared_spectroscopy

"Vibrational spectroscopy":
light absorption at resonant frequencies
⇒ **probe molecules in the gas-phase or adsorbed on catalysts**

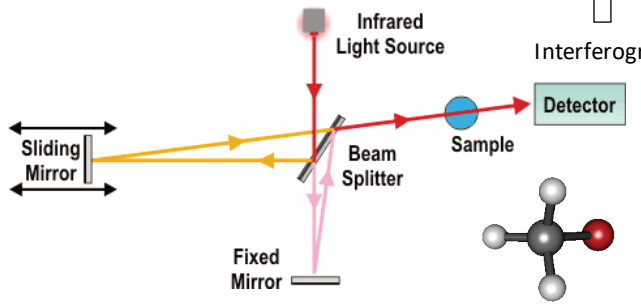
"molecular fingerprint"



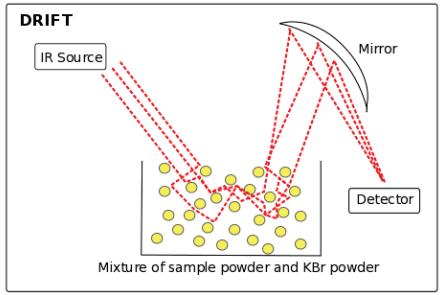
Single spectrum

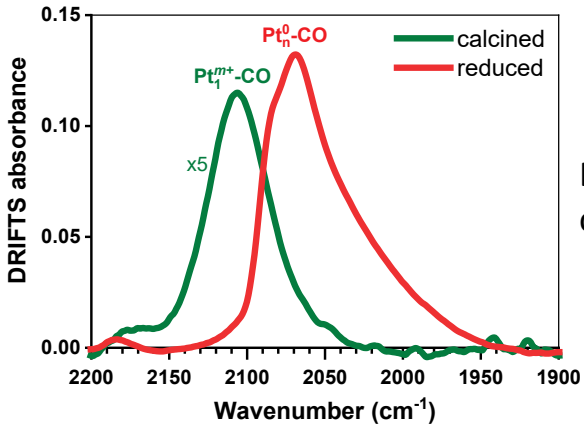
FT

Interferogram



Interferometer

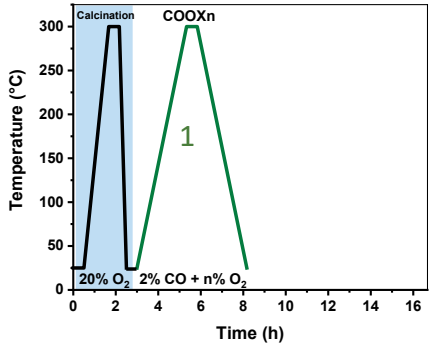


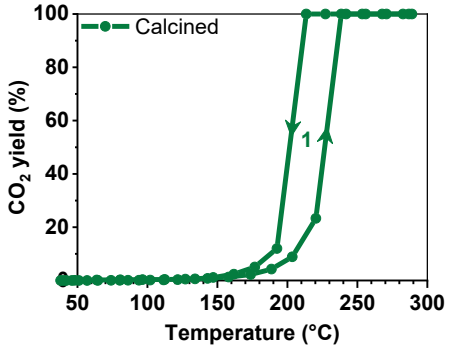


DRIFTS monitoring of νC-O vibration

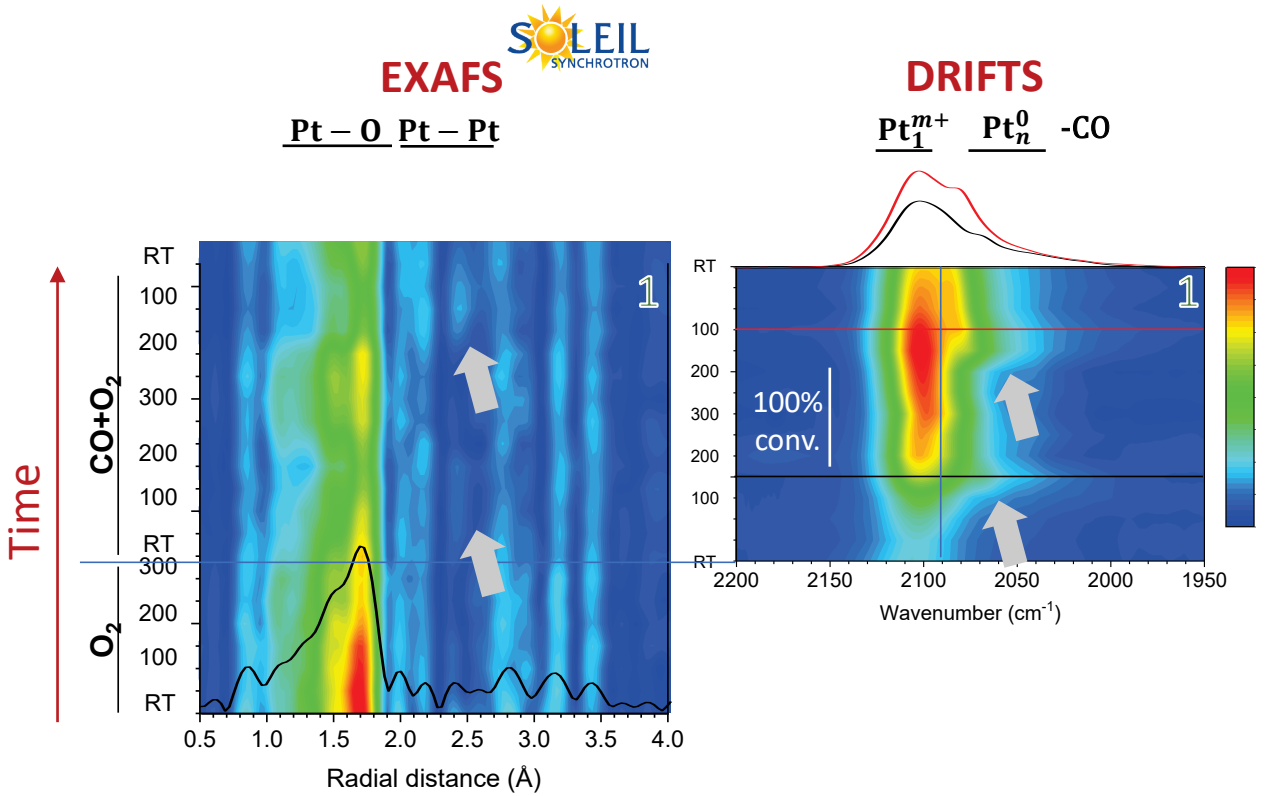
C. Dessal *et al.*, *ACS Catal.* **2019**, *9*, 5752

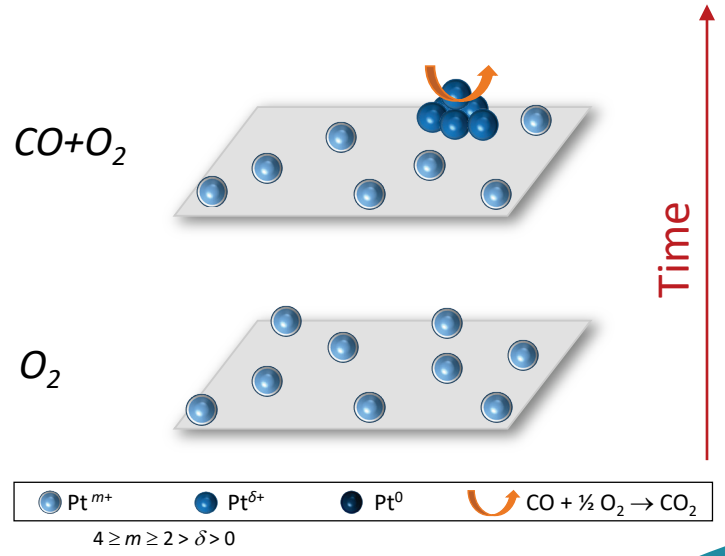
Case *operando* study III: monitoring $CO+O_2$ reaction on Pt_1/Al_2O_3





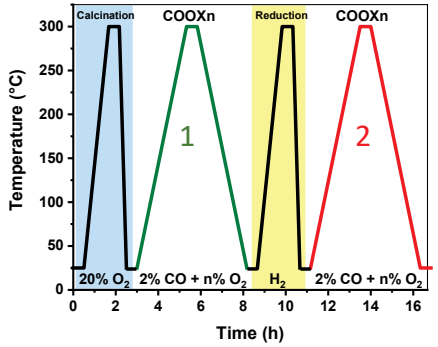
0.3 wt% $Pt/\gamma\text{-}Al_2O_3$
2% CO + 10% O_2 (+ He)

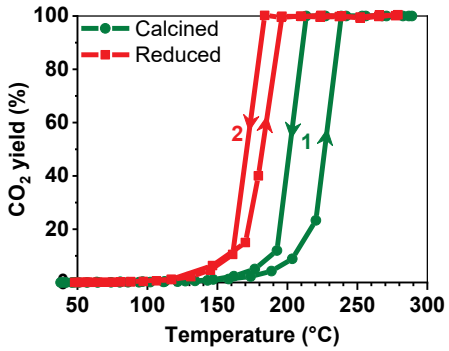




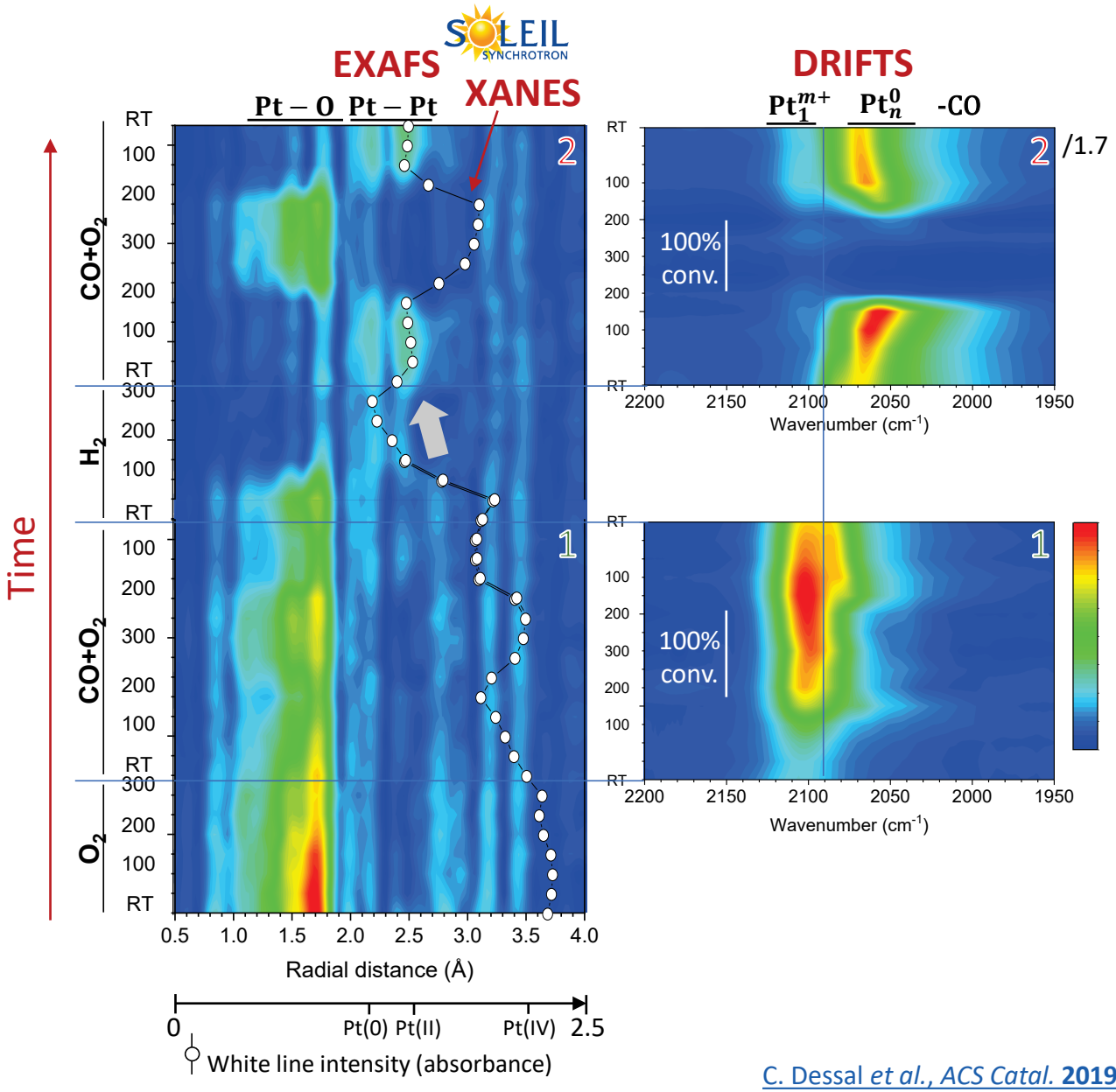
C. Dessal *et al.*, *ACS Catal.* **2019**, *9*, 5752

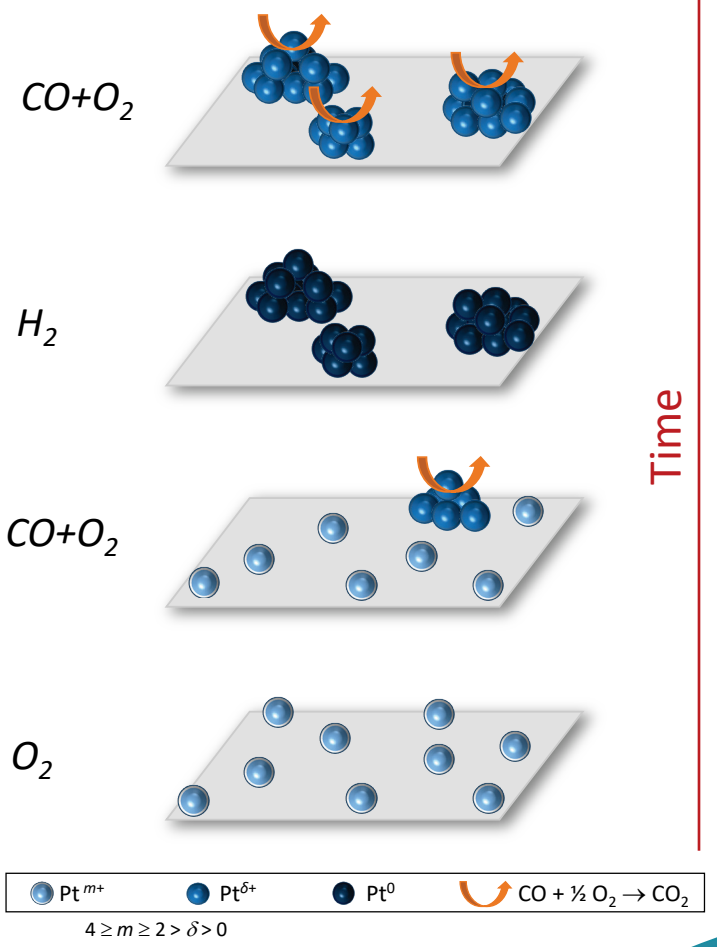
Case *operando* study III: monitoring $CO+O_2$ reaction on Pt_1/Al_2O_3





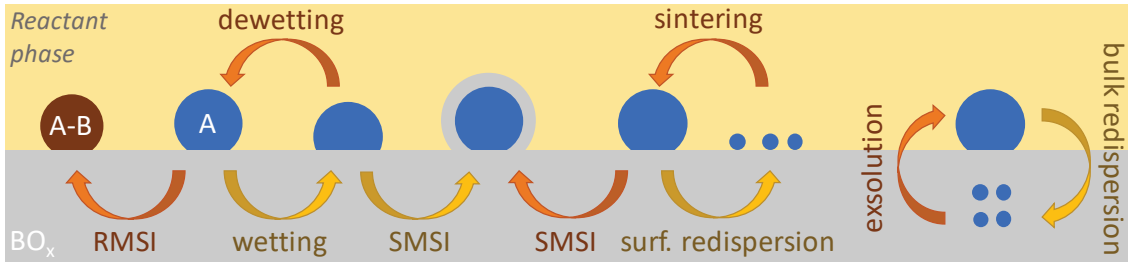
0.3 wt% $Pt/\gamma\text{-}Al_2O_3$
2% CO + 10% O_2 (+ He)

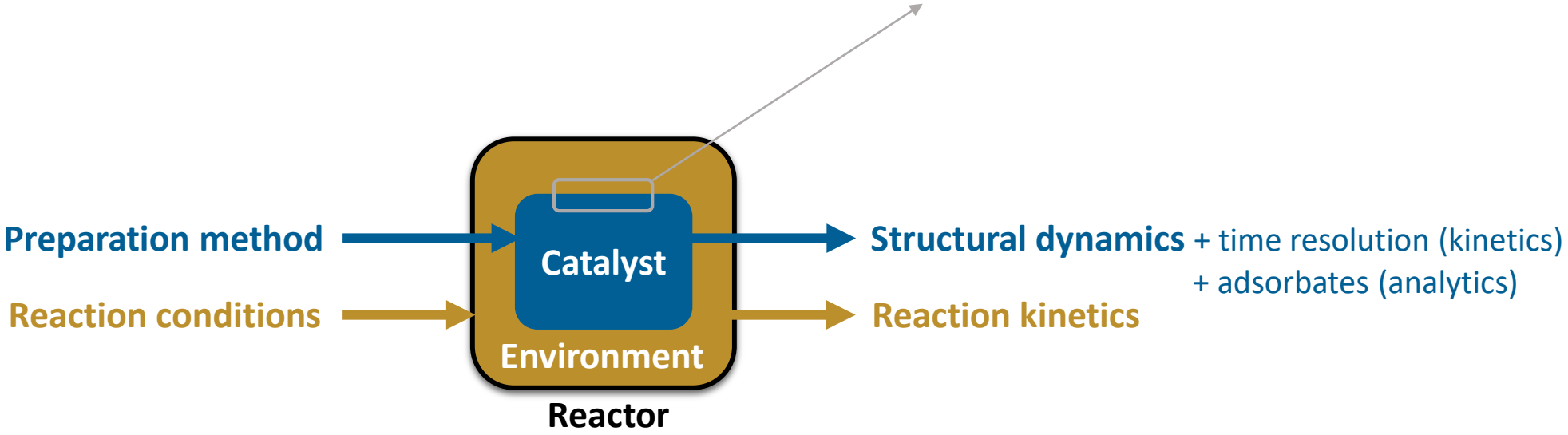




C. Dessal *et al.*, *ACS Catal.* **2019**, *9*, 5752

Summary: *operando* approach of nanocatalysis





L. Piccolo, *Catal. Today* **2021**, *373*, 80

A. Fortunelli & coll. in *Nanoalloys: from fundamentals to emergent applications*, Elsevier (2020)

Outline

1 **Basics of nanocatalysis & alloying effects**

Definitions, catalysis in practice, fundamental concepts

2 **Nanoalloy catalysts in their environment**

Dynamical effects, operando approach, case study

3 **Promising alloy phases in catalysis**

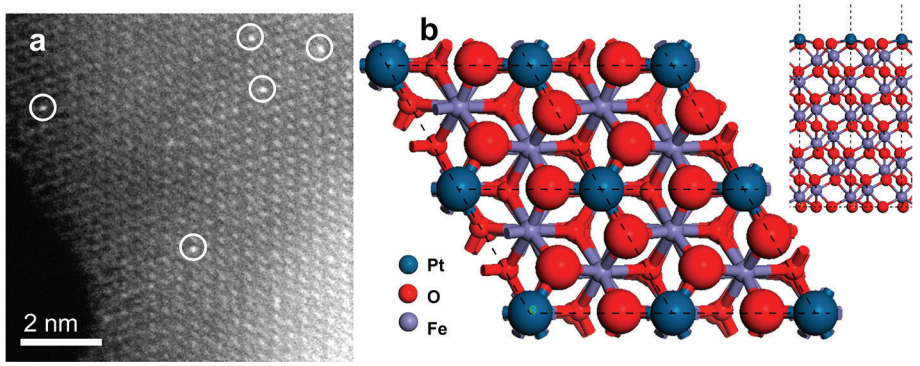
Single-atom alloys, intermetallics, and others

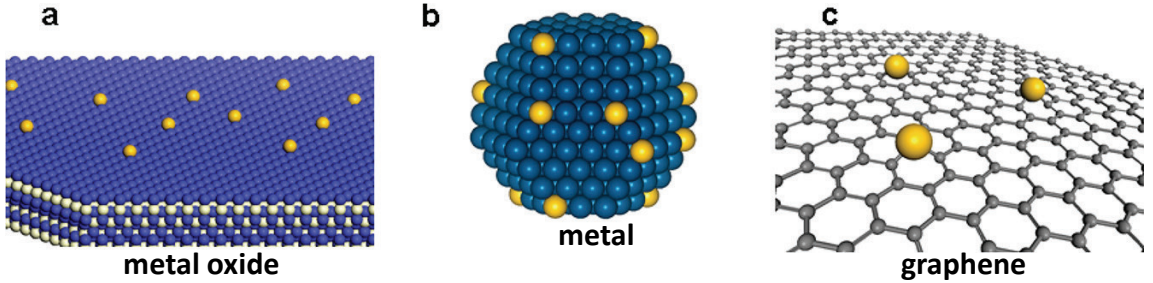
Single-atom-alloy catalysts

= dilute nanoalloys

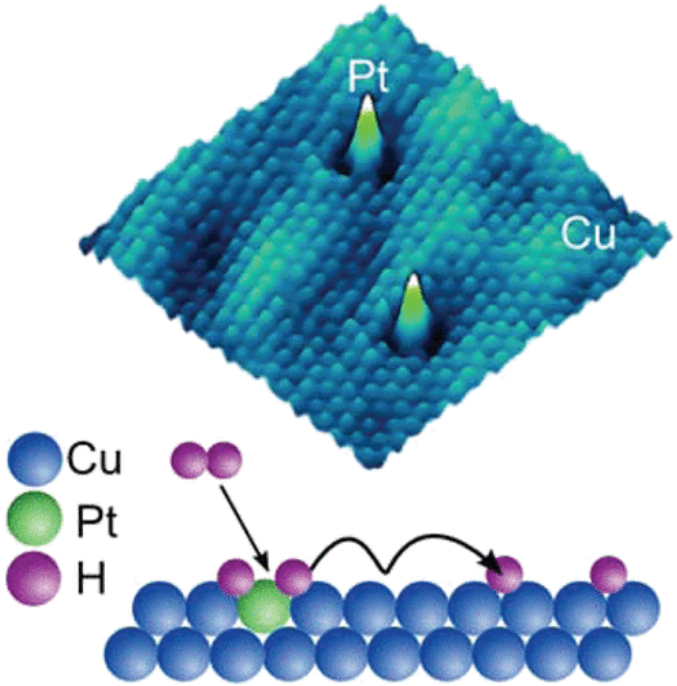
T. Zhang & coll., *Acc. Chem. Res.* **2013**, *46*, 1740

Pt_1/FeO_x SAC





H_2 activation and spillover on Cu(Pt) SAAC

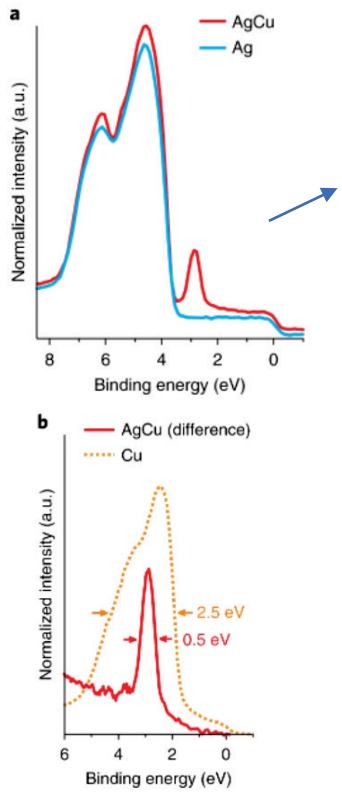


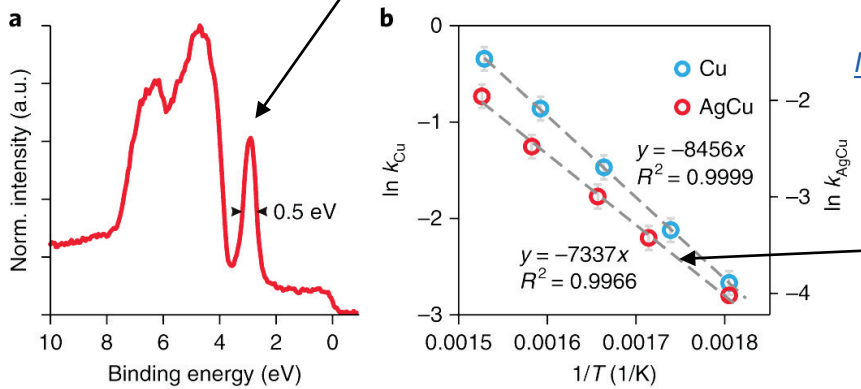
E.C.H. Sykes & coll., *J. Phys. Chem. C* **2015**, *119*, 24351

Free-atom-like Cu 3*d* state in Ag(Cu) SAAC

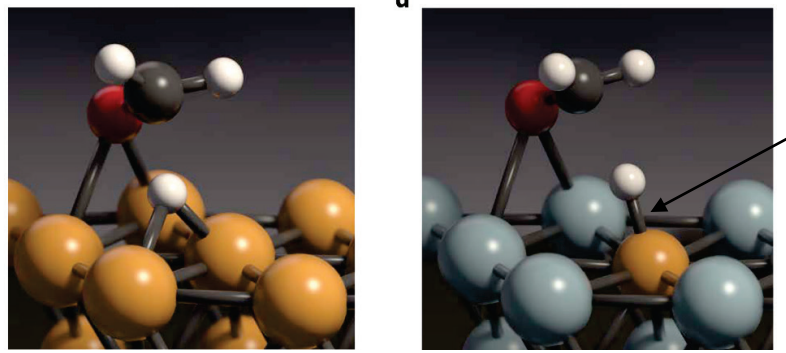
M.T. Greiner *et al.*, *Nat. Chem.* **2018**, *10*, 1008

Valence photoemission





Lower reaction activation energy



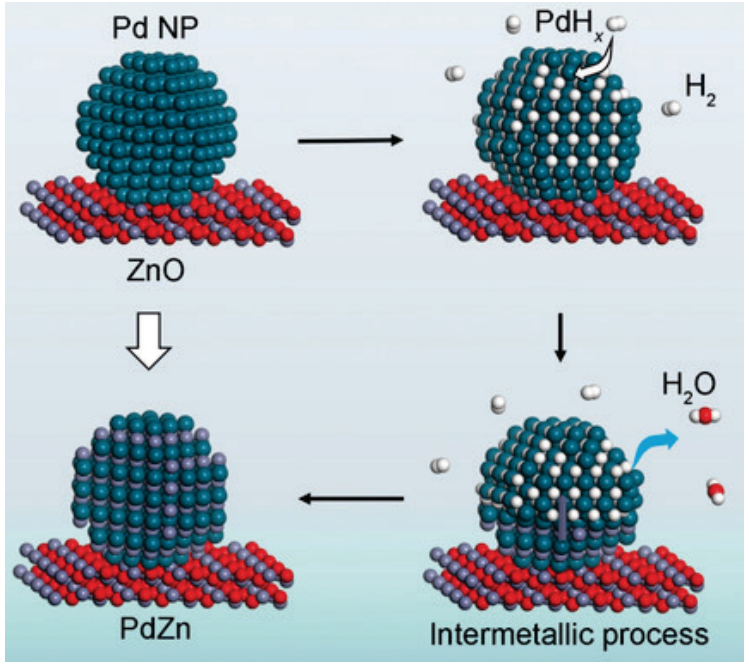
Stronger H-Cu bond

Transition state of the rate-limiting step (H abstraction from methoxy OCH_3) in methanol steam reforming

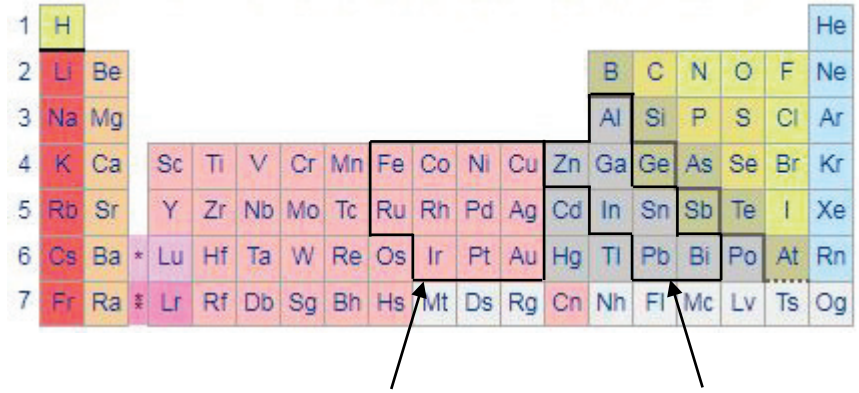
L-P intermetallic catalysts I: example of PdZn

Alloy with definite stoichiometry and ordered structure

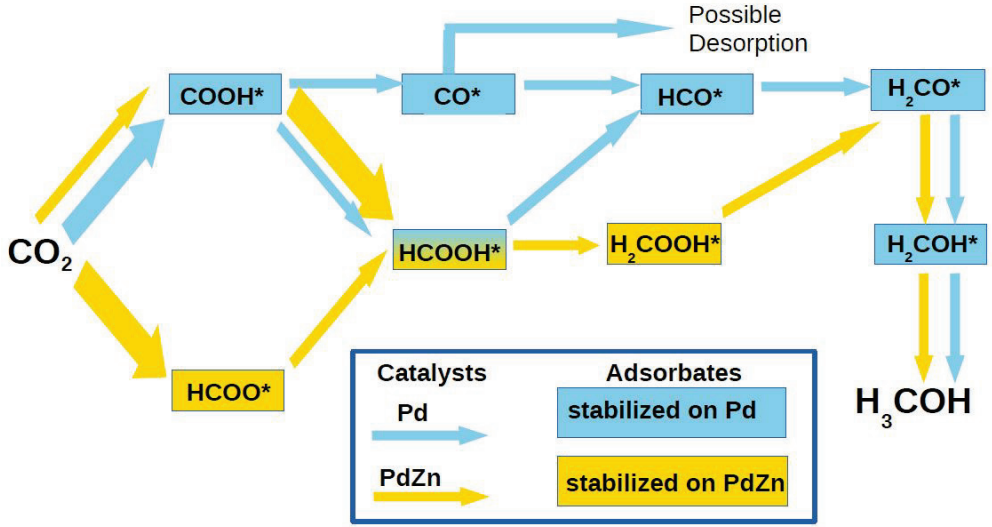
- Synthesis by reactive metal-support interaction
- Efficient in acetylene partial hydrogenation



Y. Niu *et al.*, *Angew. Chem. Int. Ed.* **2019**, *58*, 4232

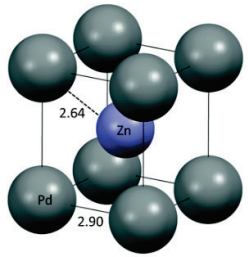


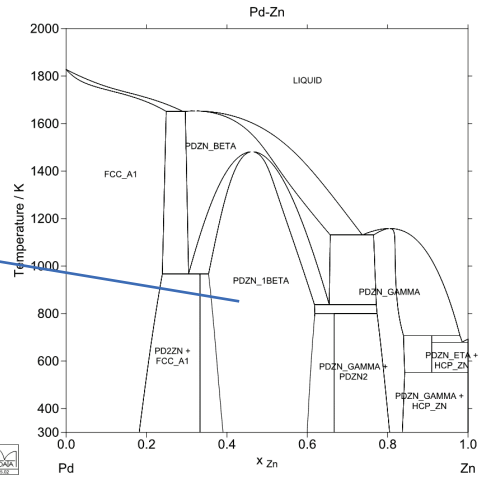
CO_2 hydrogenation to methanol: $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$



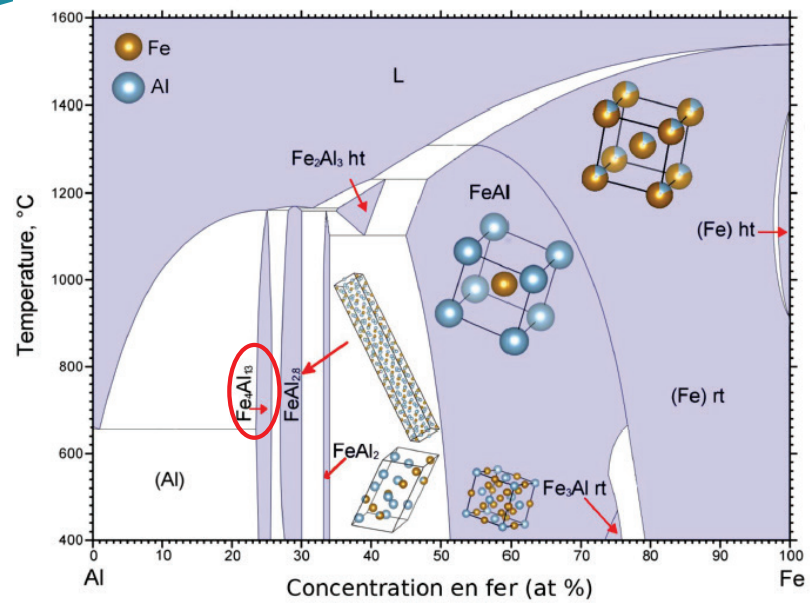
É. Gaudry & coll., *J. Phys. Chem. Lett.* **2020**, *11*, 7672

Tetragonal L1$_0$ structure of β1-PdZn:

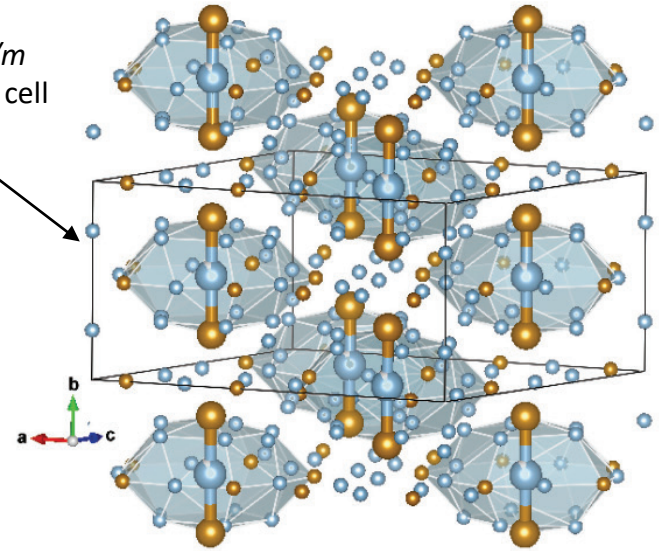


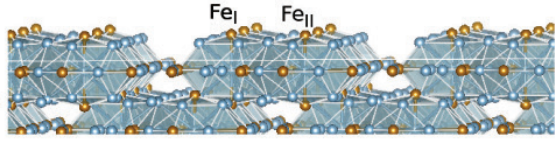


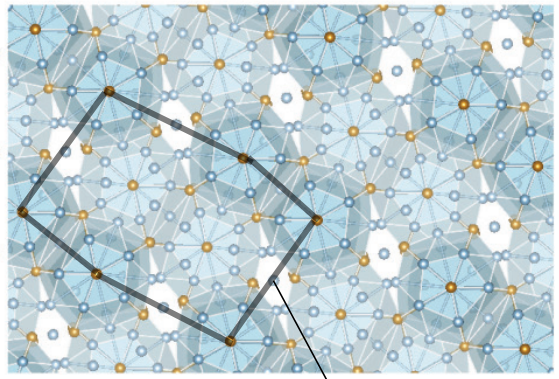
L-P intermetallic catalysts II: example of Fe_4Al_{13} = ordered SAAC



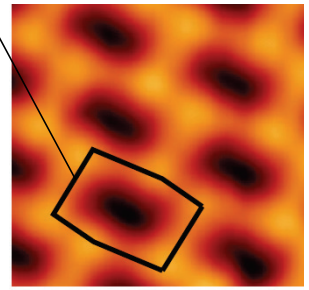
Monoclinic, *C2/m*
102 atoms/unit cell





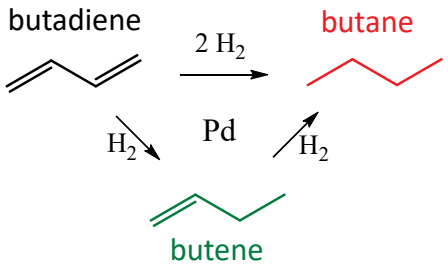


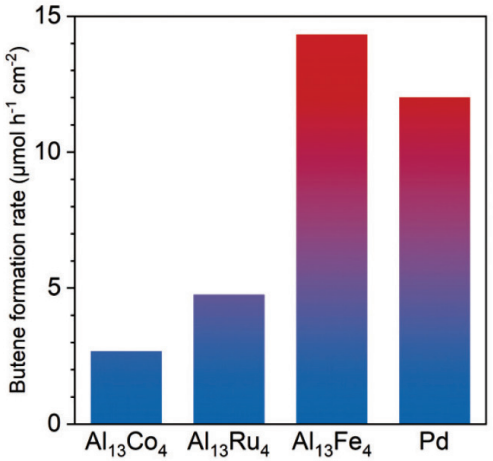
STM



$Fe_4Al_{13}(010)$

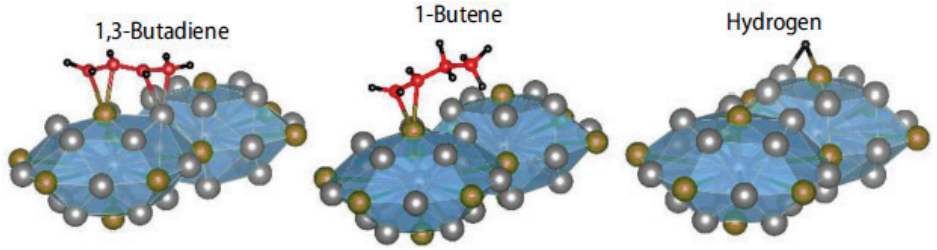
Adapted from
J. Ledieu *et al.*, *PRL* **2013**, *110*, 076102





Acetylene hydrogenation:

Armbrüster *et al.*, *Nat. Mater.* **11**, 690 (2012)



	1.3	0.9	0.4
E_{ads} (eV)	1.2	0.8	0.4
	1.1	0.6	0.2

$Al_{13}Fe_4$
$Al_{13}Ru_4$
$Al_{13}Co_4$

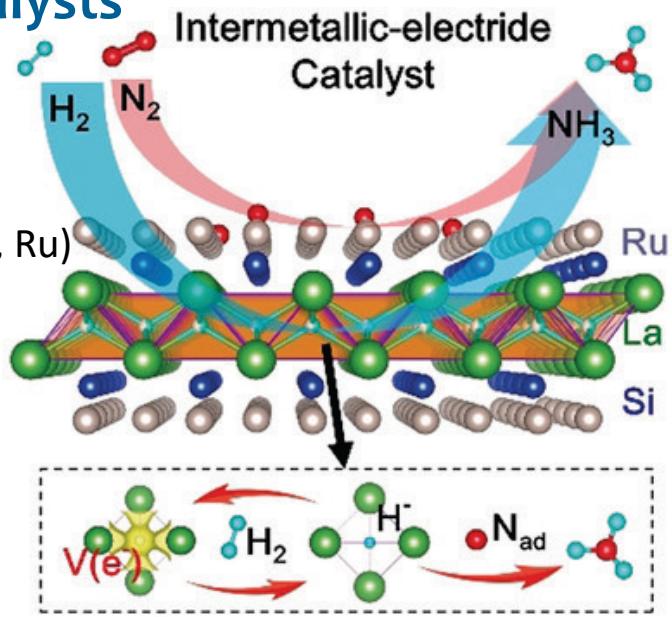
Site isolation in Fe-Al: strong ensemble & ligand effects

L. Piccolo, É. Gaudry & coll., *Sci. Technol. Adv. Mater.* **2019**, *20*, 557 + *L'Actualité Chimique* **June 2022**, in press

Exotic alloy catalysts

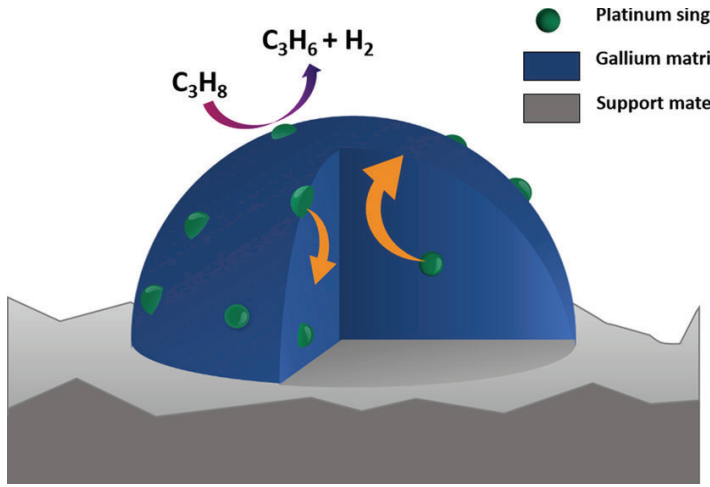
Electrides: ionic compounds with anionic e-
Ln-TM-Si (*Ln* = La, Ce, Pr, Nd | *TM* = Co, Ni, Cu, Ru)
Ammonia synthesis

H. Hosono & coll., *Angew. Chem. Int. Ed.* **2018**, *58*, 825



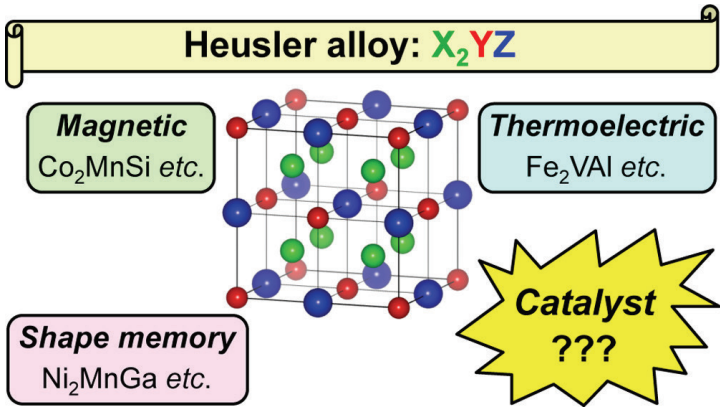
SCALMS: Supported Catalytically Active Liquid Metal Solutions
Late TM dissolved in post-TM solution = liquid SAAC
Alkane dehydrogenation

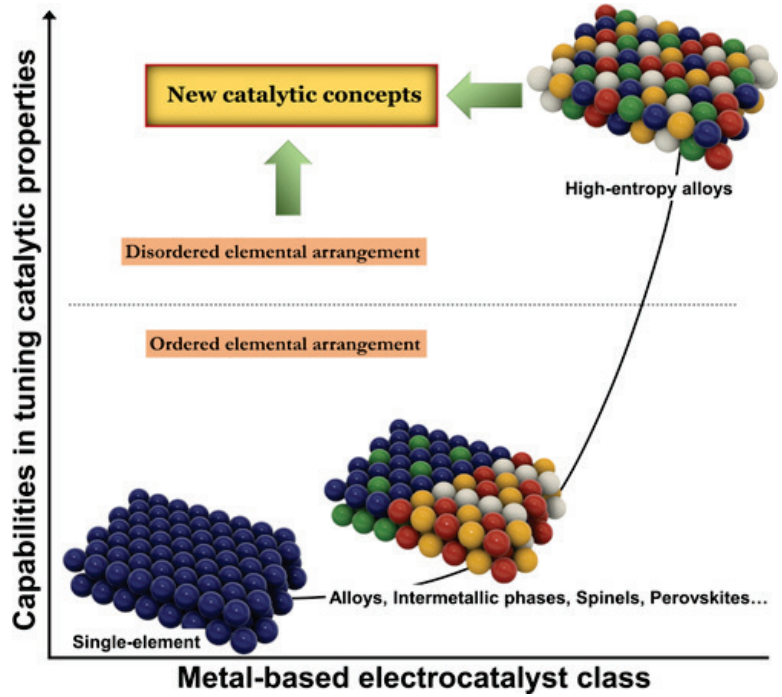
P. Wasserscheid & coll., *ACS Catal.* **2021**, *11*, 13423



Heusler alloys
X_2YZ, $L2_1$ structure
Selective hydrogenation of alkynes

T. Kojima *et al.*, *ACS Omega* **2017**, *2*, 147





High-entropy alloys
Solid solution of at least 5 metals
Electrocatalysis

T. Löffler *et al.*, *Angew. Chem. Int. Ed.* **2021**, *60*, 26894

Conclusions

1. **Nanoalloys promise infinite catalytic possibilities**

Challenges in nanocatalyst design

2. **Nanoalloy catalysts at work are highly dynamical**

Challenges in nanocatalyst characterization

3. **Alternatives to LTM-LTM alloys have high potential**

Challenges in nanocatalyst synthesis