Dynamics and surface restructuration of gold based nanocatalysts under realistic reaction conditions

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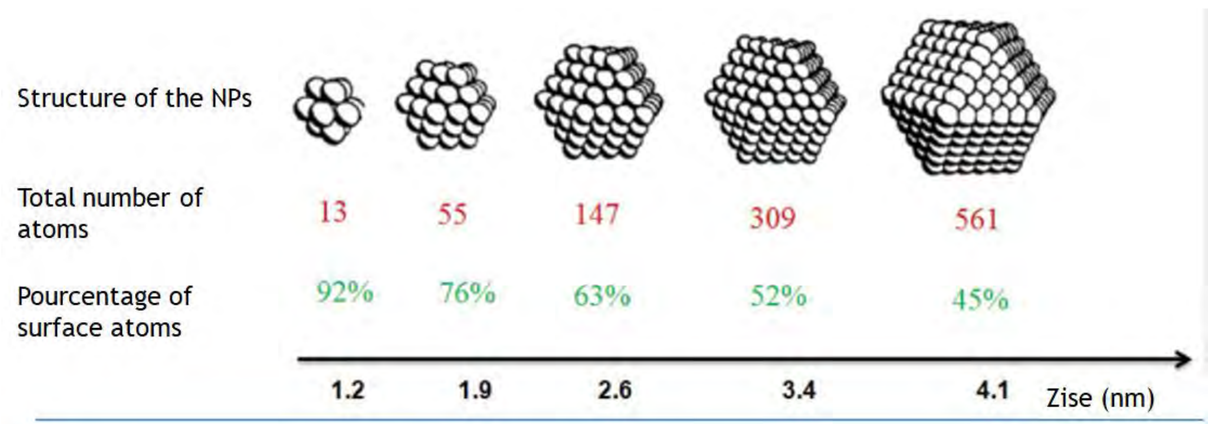
NPs improve catalytic process

Nanoparticles have unique properties that are different from their properties as compound materials.

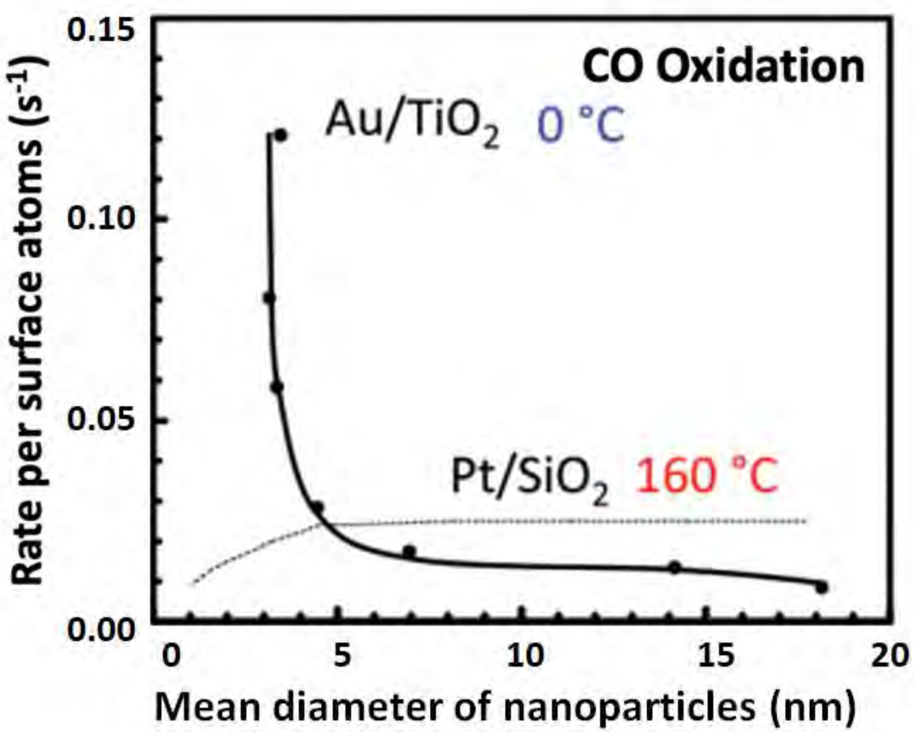
NPs improve catalysts in two main ways:

- ✓ The small size of Nps brings with it **quantum confinement effects**. These effects can directly impact the catalytic activity and selectivity.
- ✓ Due to their small size, they have a greatly **increased surface-to-volume ratio.** This strongly increases the specific catalytic activity because the chemical reactions occur on the surface of the particle.

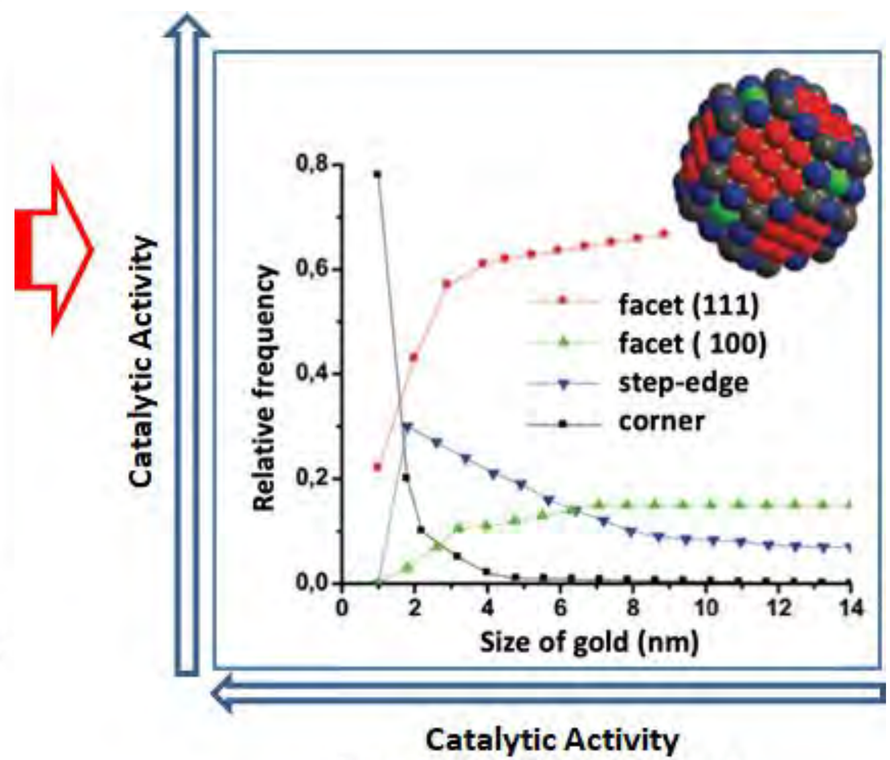


Structure-reactivity relationship

- ✓ Smaller the NPs are, higher is their reactivity
- ✓ Smaller the NPs are, higher is the proportion of under coordinated sites in the surface



M. Haruta, ChemInform 7(3), 2004, 163-172



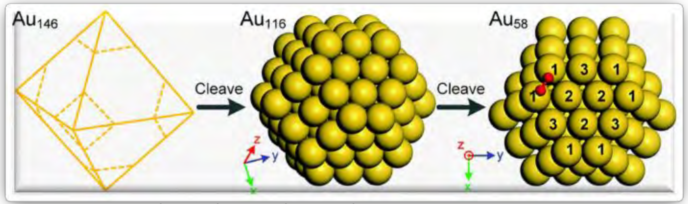
Mohr C., Claus P., *Science Prog.*, 2001, *84*.

- State of the art

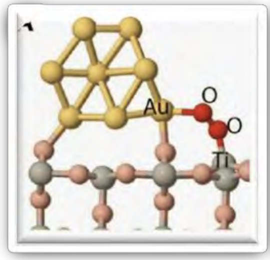
Structure-reactivity relationship

The commonly widespread paradigmatic picture

- ➢ Perfect crystal models (well-defined symmetries)
- ➢ Considered surface facets (static and rigid)
- ➢ low-coordinated surface atoms (edges, vertexes, corners, etc..)



Phys. Chem. Chem. Phys., 2020,22, 14458



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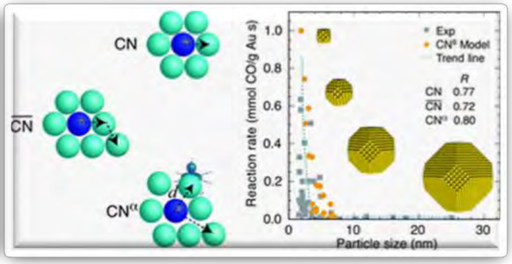

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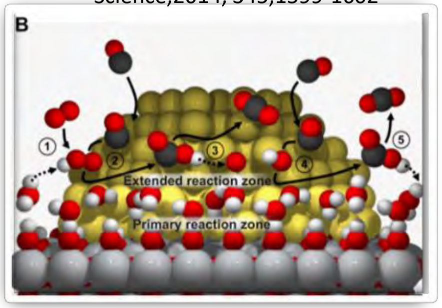

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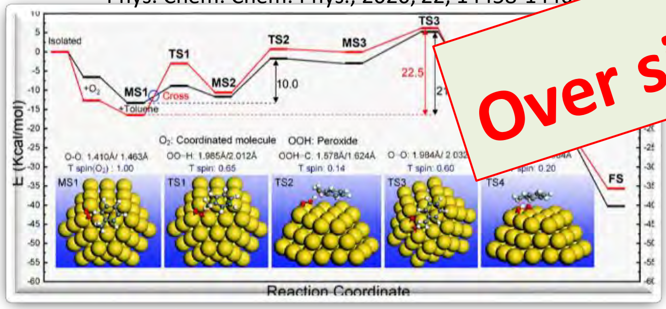
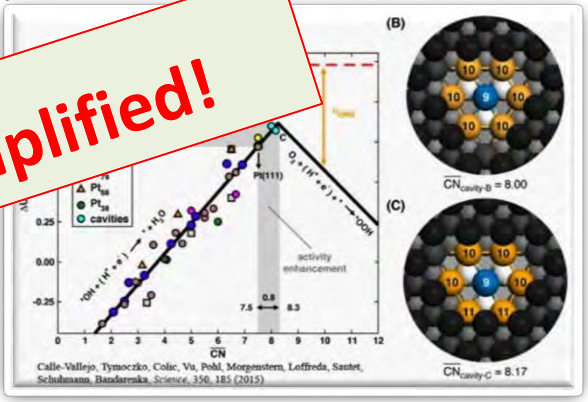


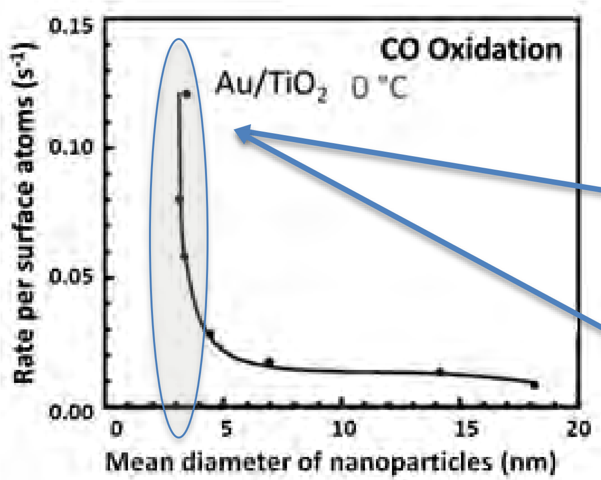


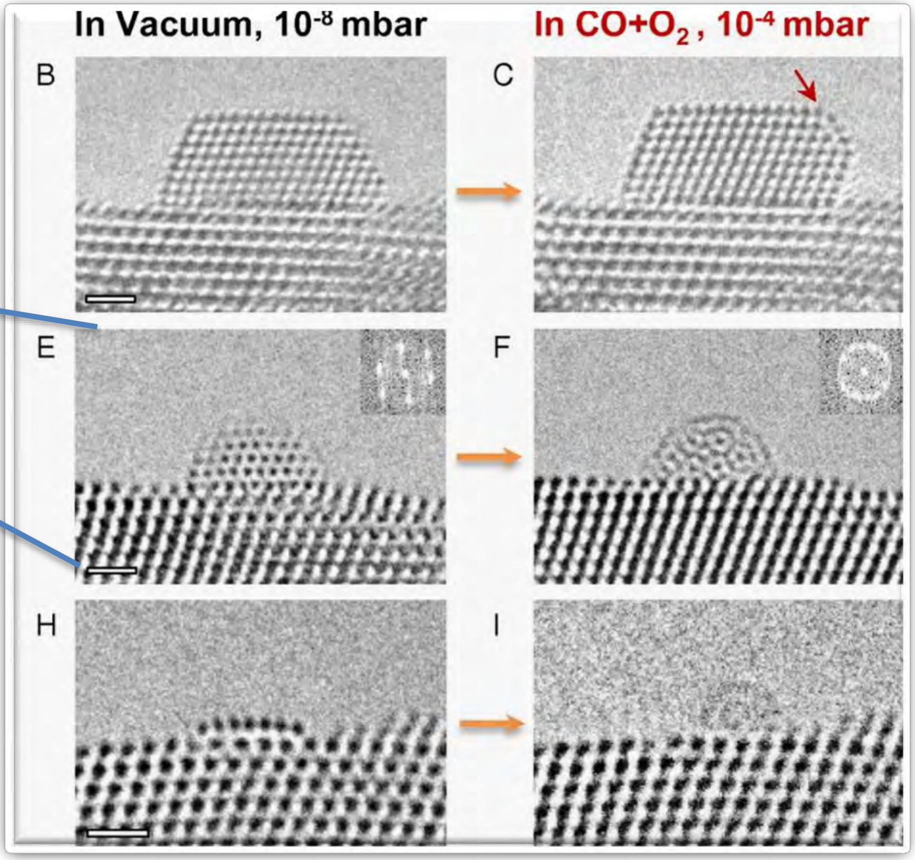
Over simplified!

- Problematic

Structural evolutions under gas

Observations of dynamic changes of metallic catalysts towards reaction conditions





Au NPs supported on TiO_2
Y. He PNAS, 2018 115 (30) 7700-7705

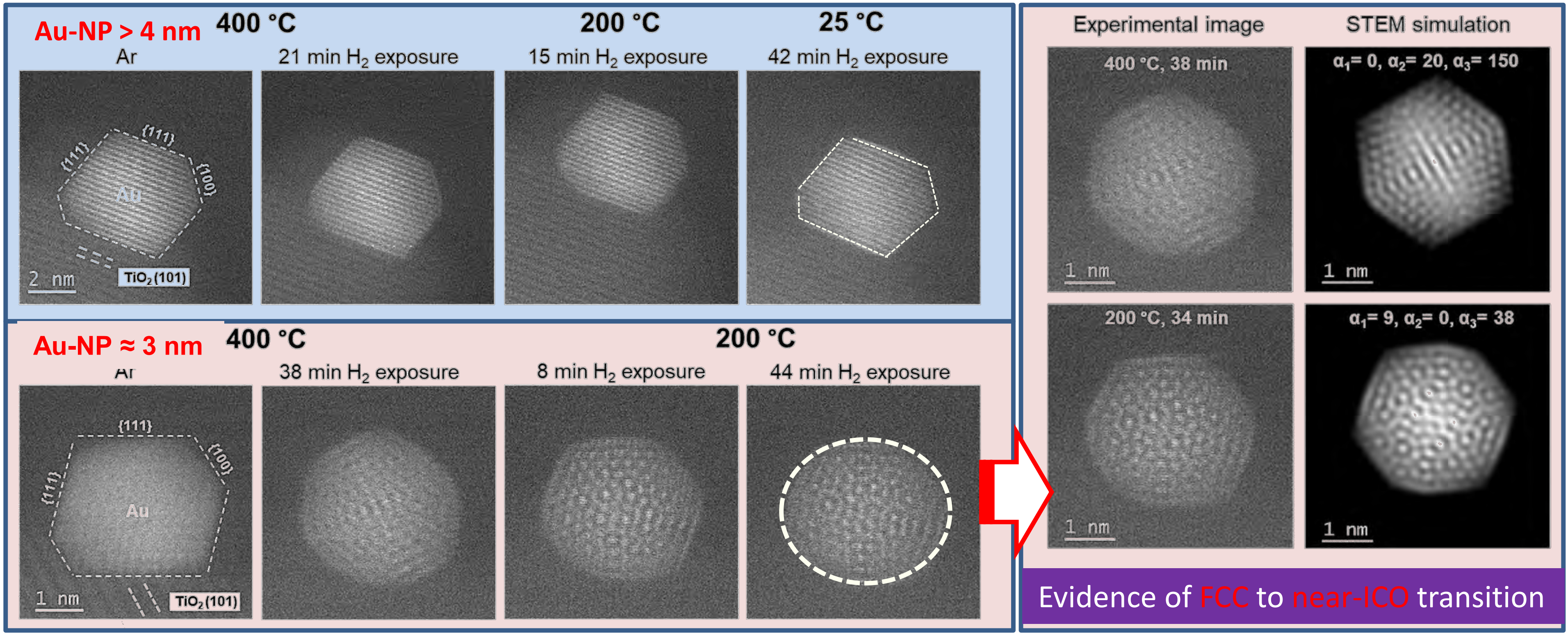
The **understanding** of catalytic properties of Au NPs requires access with **atomic resolution** to the evolution of their structure under relevant conditions of temperature and pressure.

- Exp. Results

Au NPs under hydrogen atm. P

Experimental observations

***in situ* HADF STEM images of Au/TiO_2 at H_2 atmospheric pressure:**

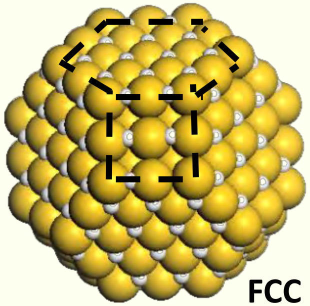


Images provided by A. Nassereddine and J. Nelayah; Laboratoire Matériaux et Phénomènes Quantiques, Univ. Paris, CNRS, F-75013, Paris

Au NPs in presence of hydrogen

Theoretical approach: DFT + AIMD

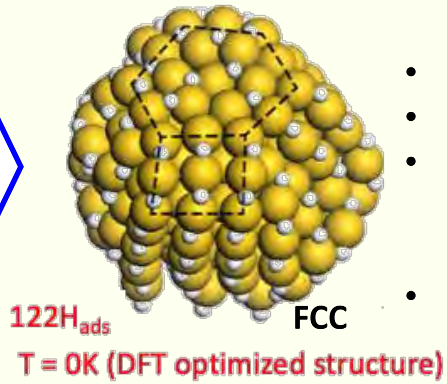
(1) Au NPs model preparation:



TOH_Au_{201} H_{122}

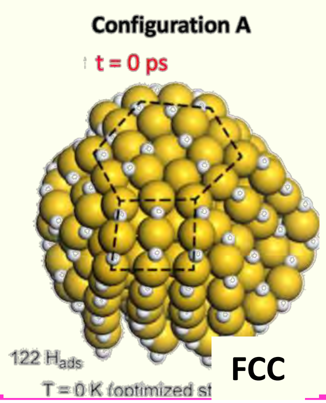
- Shape: truncated octahedron (TOH); FCC symmetry
- Size: ~1.8 nm
- 1ML of H-atoms
- Periodic box: $(30 \times 30 \times 30)$Å

(2) DFT optimization:

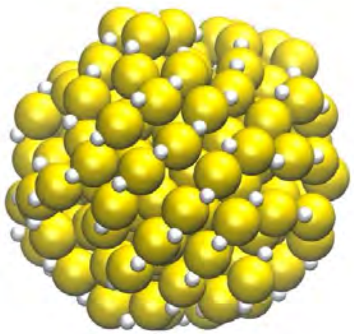


- VASP; DFT_GGA/PBE (DFT-D3)
- No Hydrogen-desorbed
- Optimized structure: TOH shape (slightly disturbed); FCC symmetry
- Cut-off: 400 eV

(3) AIMD calculations:



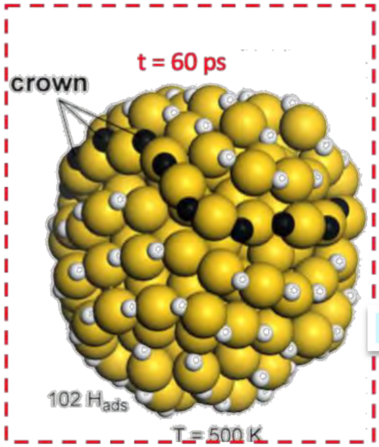
- Born-Oppenheimer approximation
- Canonical (NVT) ensemble
- Nosé-Hoover thermostat
- Time-step: 1.5 fs
- T = 500K



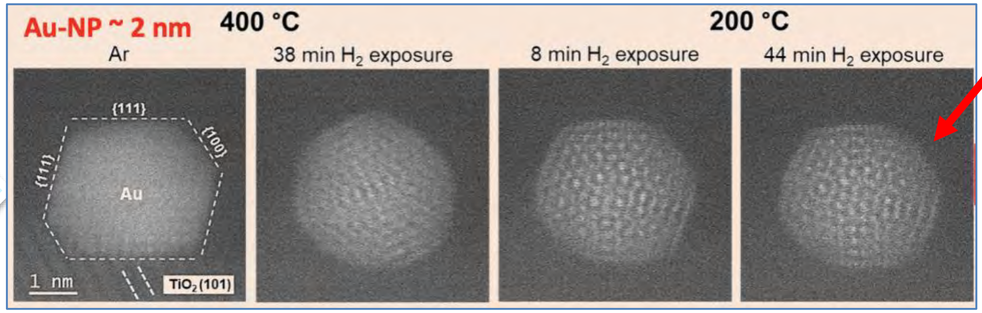
Theo. Results

Au NPs in presence of hydrogen

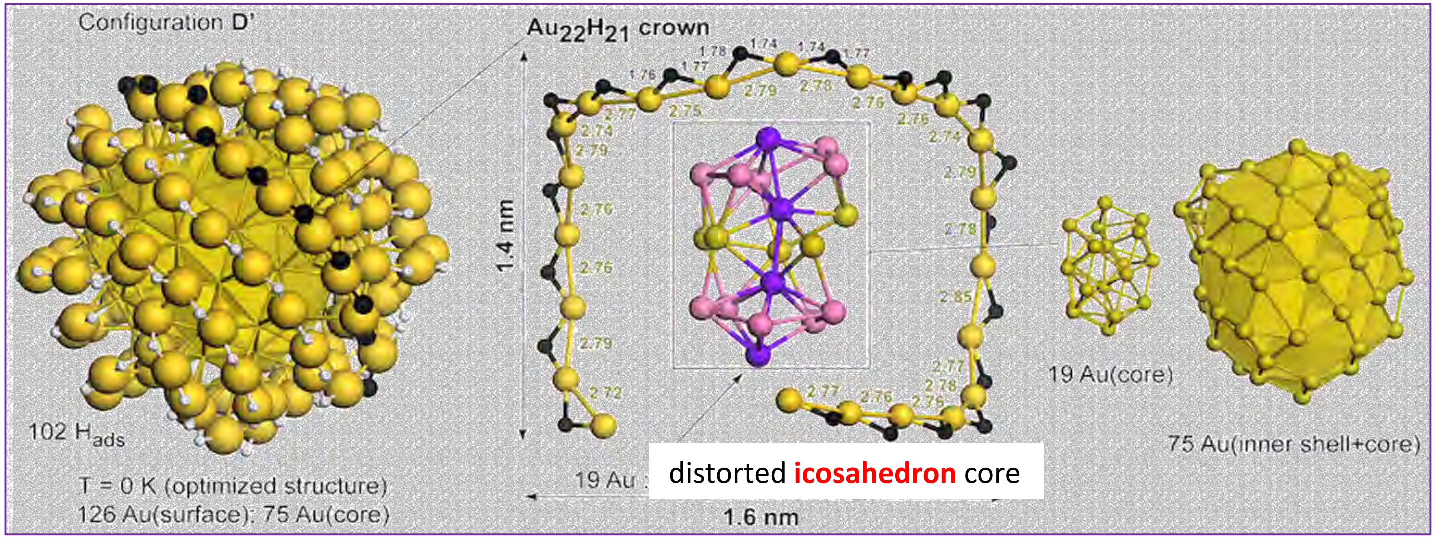
AIMD simulations evidence



- ✓ Original surface restructuration
- ✓ The beginning of phase transition from CFC to ICO



DFT optimizations

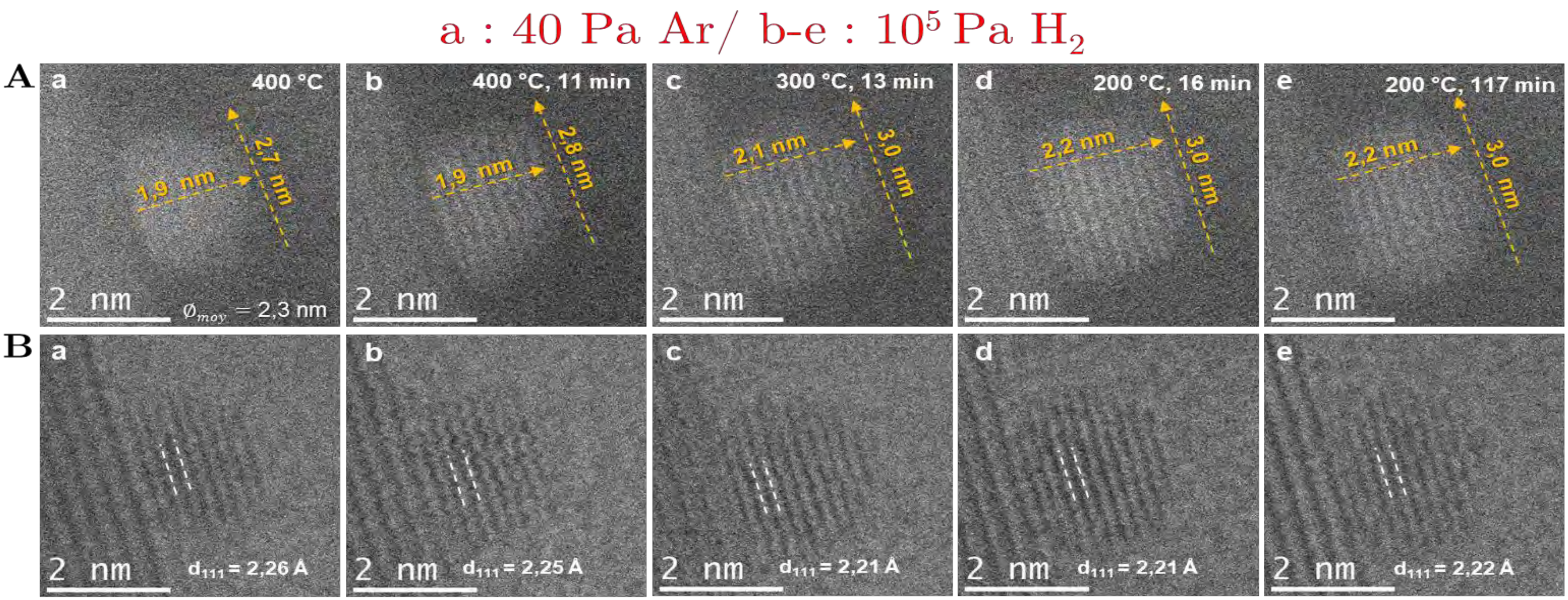


H. Guesmi et al. *Small* **2021,** 2104571

Predicting realistic shape and structure of bimetallic catalysts under working conditions: Increasing the complexity!

Structural evolutions under gas: the case of bimetallics

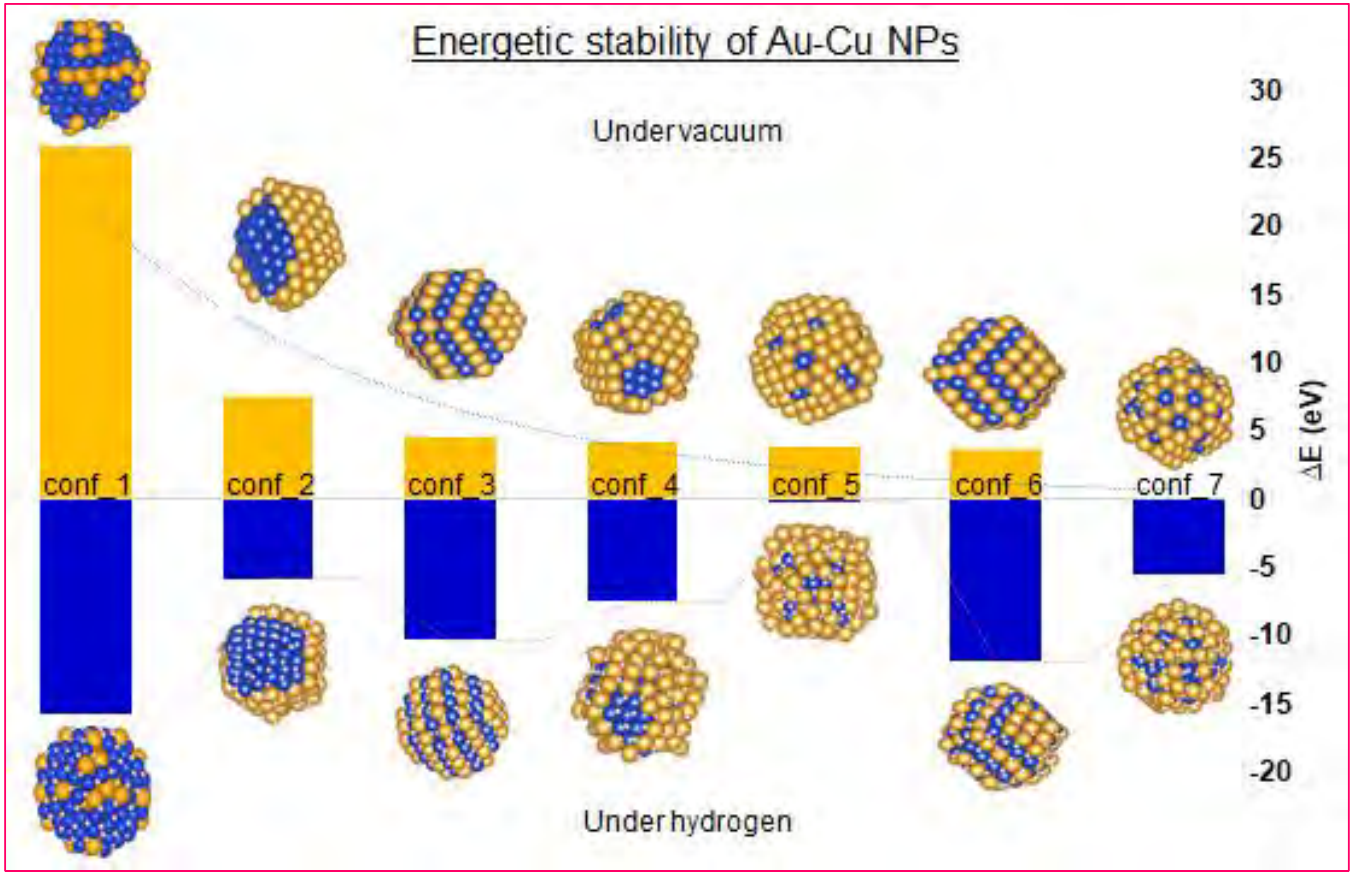
Au-Cu NPs: ordered alloy

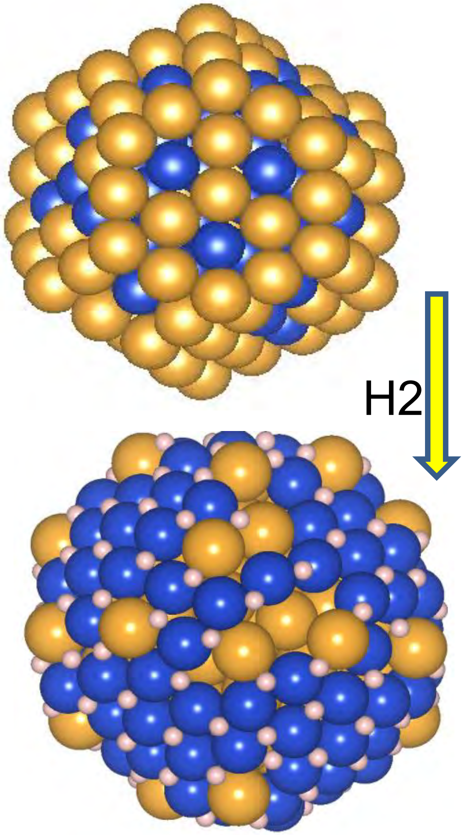


✓ For **Au-Cu NPs**, no size-dependent reactivity exists. In situ ETEM observations showed that the Au-Cu NPs, whatever their size, **maintain their initial fcc** structure under H2.

Structural evolutions under gas: the case of bimetallics

Exploring the different Au-Cu structures : DFT energetic calculations

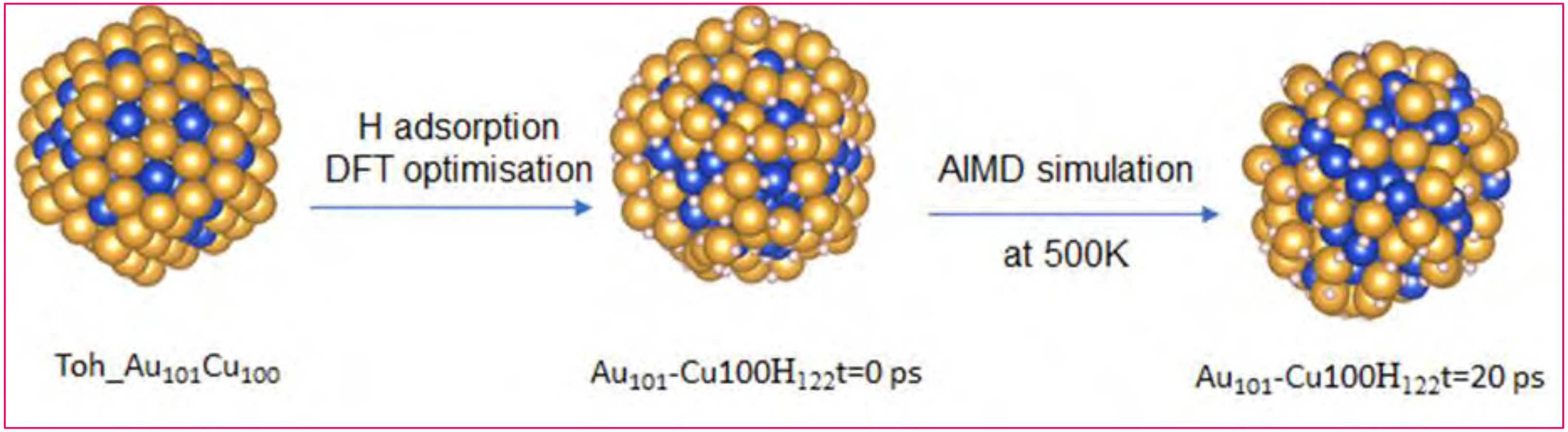




Q Wang et al. Faraday Discussions 242 (2023) 375-388

Structural evolutions under gas: the case of bimetallics

Dynamic changes of Au-Cu structures : AIMD simulations



- ✓ Segregation of Cu from the subsurface layer is confirmed (reversed seg. of Au)
- ✓ The evolving surface seems to organize in the form of linear chains of H-Cu-H-Cu with hydrogen in bridge sites separated by H-Au-H-Au chains encircling the core, which may explain the rounded particle shape observed experimentally.
- ✓ The **tendency** of Au-Cu core to form hetero-atomic Au-Cu bindings.

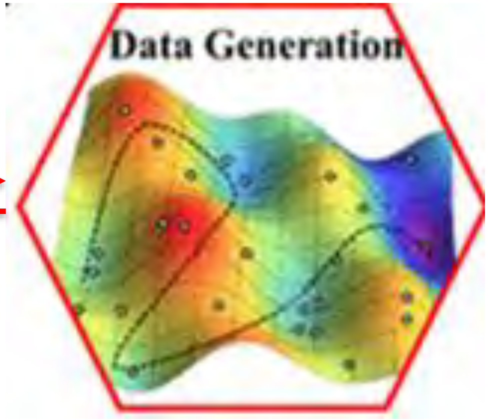
Modelling the structural dynamics

Because of scaling issues and the high cost of QM calculations, it has always been necessary to sacrifice either **accuracy or time** when performing large-scale atomic simulations.

The solution:

Classical molecular dynamics & QM based interatomic potential

DFT/AIMD data



Machine Learning Interatomic potential
MLIP

Conclusions

- ✓All these results open the way for a deep investigations of the reactivity of these revealed surface active sites to understand the “real” reaction mechanisms occurring over hydrogenated gold nanocatalyst.

- ✓Controlling dynamic changes of heterogeneous catalysts under working condition remains a challenging task and systematic modelling approach should be undertaken.

Acknowledgments

Performed and participated to this work

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Or-Nano 2024 in Montpellier