Karlsruher Institut für Technologie

Structure and reactivity of negatively charged platinum and palladium clusters

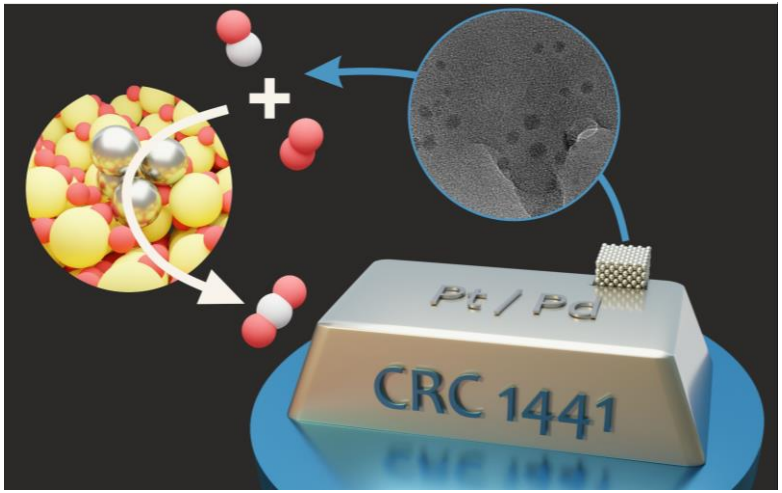
Karin Fink

CRC-1441:

Tracking the Active Site in Heterogeneous Catalysis for Emission Control

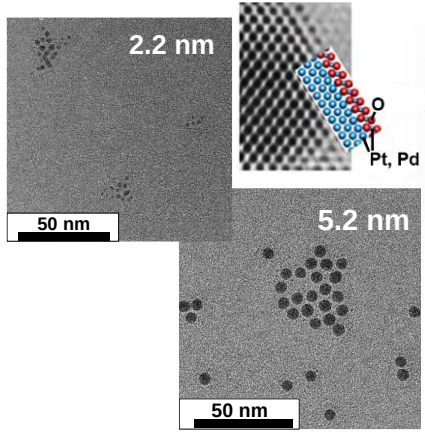
The Aim of TrackAct

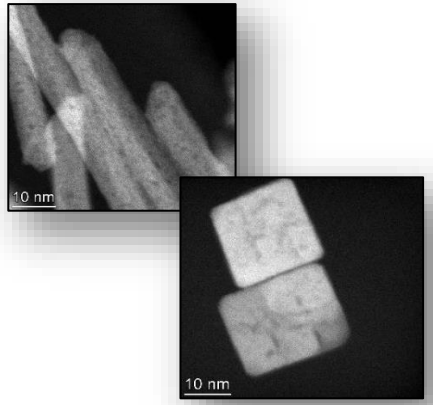
*„The goal of TrackAct is to **identify and track** the nature of the **active site**, to design and manipulate them from bottom-up across the various **length scales**, and - on a long-term vision - predict and actively control them during operation“*



Activity depends on…

…specific particle sizes and **support interaction.**

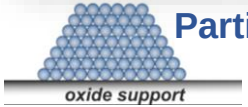




Single sites

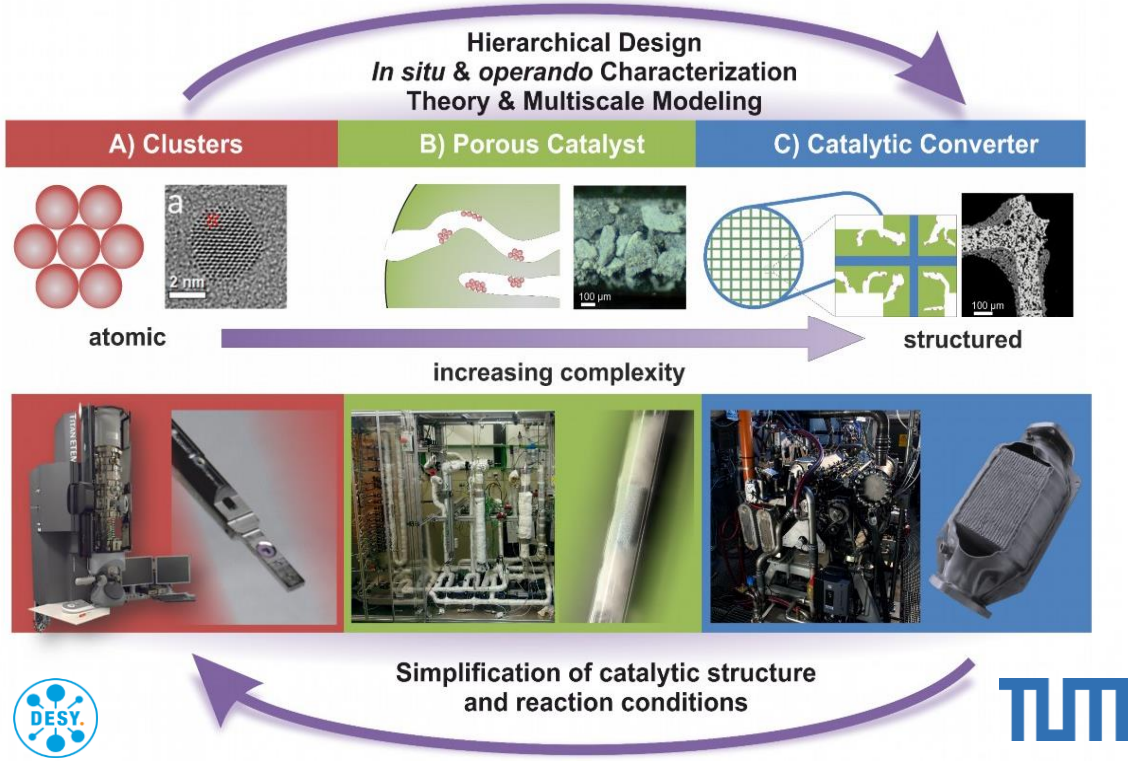
Clusters

Particles



DFG Deutsche Forschungsgemeinschaft

CRC1441: Tracking the Active Site in Heterogenous Catalysis for Emission Control



2021-2024

- Over 10 million € budget
- KIT with partners at DESY and TUM

Reactions

Emission control

- CO/NO-oxidation, NO-reduction
- CH_4- and HC-oxidation
- *Future*: VOC-oxidation, etc.

Materials

Cluster/Nanoparticles

- Platinum
- Palladium
- Platinum-Palladium

Support

- CeO_2
- TiO_2
- Al_2O_3

Outline

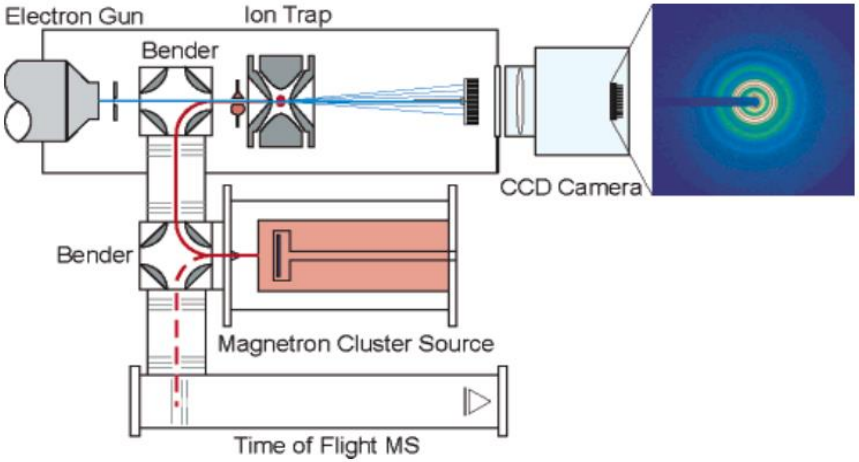
Aim: Obtain information about structure and reactivity of **Pt and Pd clusters in gas** phase from a **joint experimental and theoretical approach**.

Experiment: D. Bumüller, T. Rapps, M. M. Kappes, D. Schooss

Theory: A. G. Yohannes (INT,SCC), S. Kohaut, I. Kondov(SCC), K. Fink

- Experimental set up
- Quantum chemical methods
- Structure of small Pt_n^- clusters (n=6-13)
- Structural evolution of Pd_n^- clusters (n=55-147)
- Reaction of truncated octahedron Pt_n clusters with oxygen (n=38-201)

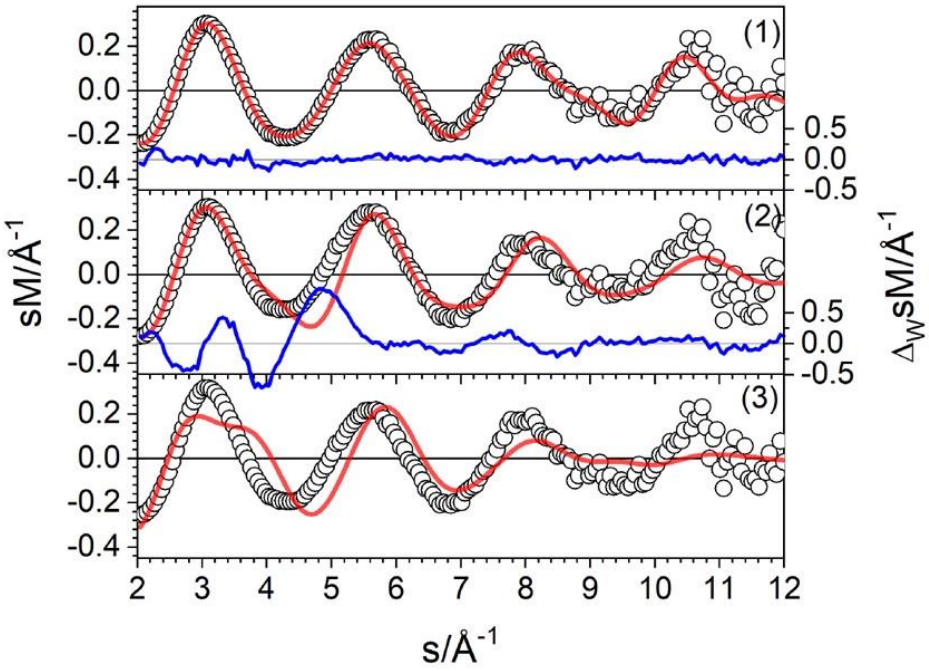
Experiment (D. Schooss, INT)



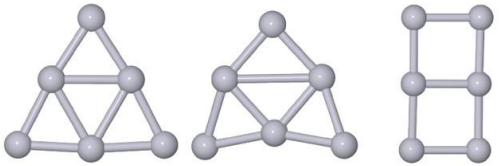
Experimental setup of Trapped Ion Electron Diffraction technique

- Clusters are produced in the selected by charge/mass ratio
- Charge is necessary to trap them in the Paul trap
- Atom precise
- Structural information from electron diffraction pattern

From scattering function to structure



Structure models



(1) D_{3h} 0.00 (0.00) eV R_w = 1.7%

(2) C_{2v} 0.11 (0.22) eV R_w = 7.8%

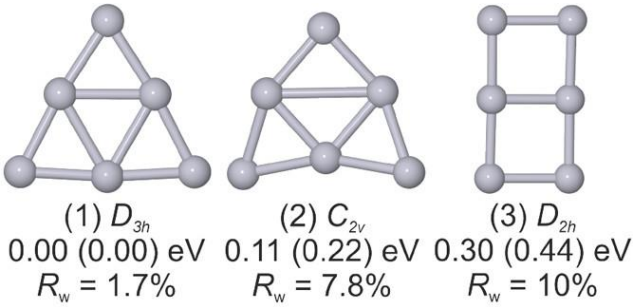
(3) D_{2h} 0.30 (0.44) eV R_w = 10%

$$sM^{theo}(s) = \frac{S_c}{N}\exp\left(-\frac{L^2}{2}s^2\right)\sum_i^N\sum_{j\neq i}^N \frac{\sin(sk_s r_{ij})}{k_s r_{ij}}$$

Weighted profile factor

$$R_w = \sqrt{\frac{\sum_i w_i\left(sM_i^{theo} - sM_i^{expt}\right)^2}{\sum_i w_i\left(sM_i^{expt}\right)^2}}$$

Obtaining structure models from Theory



DFT calculations

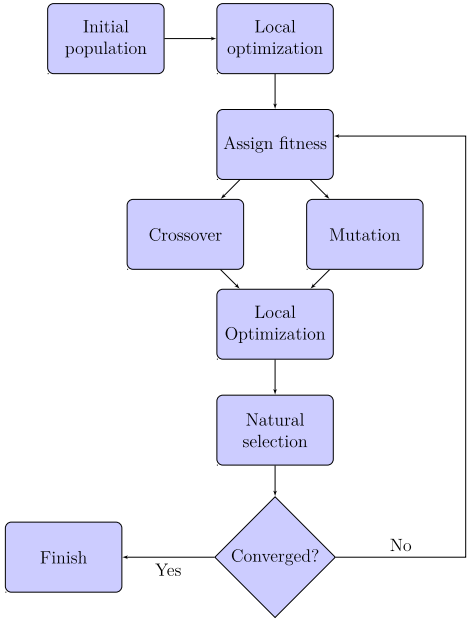
- Start from a guess structure
- Solve electronic Schrödinger equation
- Perform geometry optimization
- Converges to the next local minimum

Problems

- Several isomers with similar energy
- Problem to find all possibilities
- DFT depends on functional (GGA)
- Spin polarized calculations with different spin states necessary
- Influence of relativistic effects
- For large systems too expensive to obtain all guess structures from DFT
  → empirical potentials and semiempirical methods

Obtaining structure models from Theory

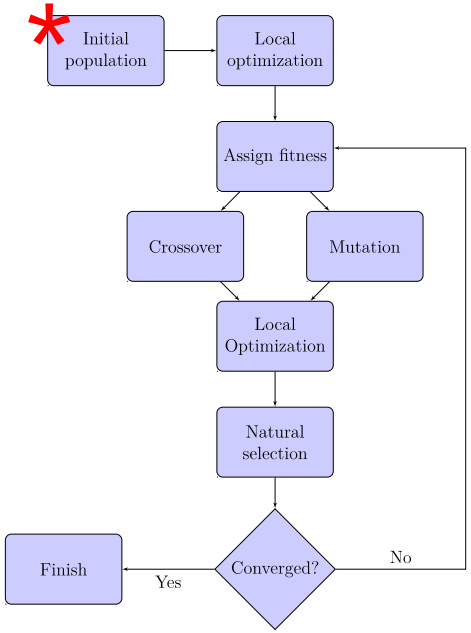
Genetic algorithm (GA) for structure search



Flow chart of the global optimization procedure

Obtaining structure models from Theory

Genetic algorithm (GA) for structure search



Flow chart of the global optimization procedure

1. Initial structures provided by the user or automatically generated.

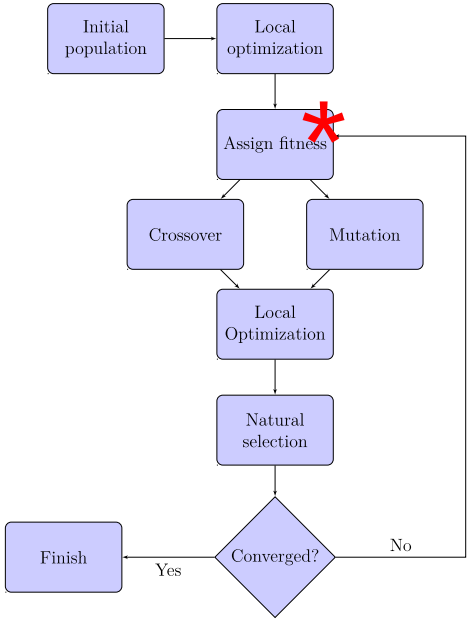
2. Initial population structures are generated by distributing atoms in space based on bonding distances in reasonable range

$$\mathbf{r_{ij} < a(\ R_i + R_j)} \qquad \mathbf{r_{ij} < b(\ R_i + R_j)}$$

R_i and R_j atomic radius of atoms i and j, respectively.
R_{ij} distance between these two atoms.
a and b being a upper and lower atomic radii multiplier, respectively.
(Default: a = 1.2 and b = 0.7)

Obtaining structure models from Theory

Genetic algorithm (GA) for structure search



Flow chart of the global optimization procedure

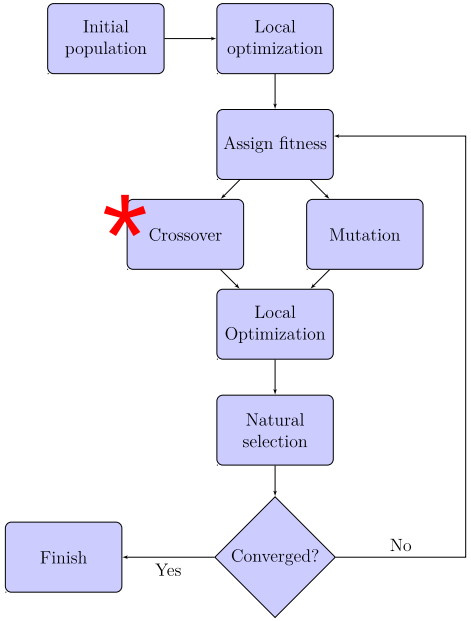
3. Population of local optimized structures is subject to evaluation based on their dynamically scaled reative energy, ε_i:

$$\epsilon_i = \frac{E_i - E_{min}}{E_{max} - E_{min}}$$

E_i total energy of the given member of the population.
E_{max} and E_{min} lowest and highest total energy of the population.

Obtaining structure models from Theory

Genetic algorithm (GA) for structure search

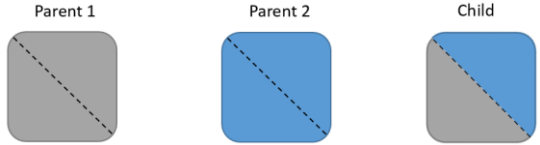


Flow chart of the global optimization procedure

4. Two clusters are selected from the population to be parents for mating, for it selection probability, p_i, is proportional to the value of the fitness function.

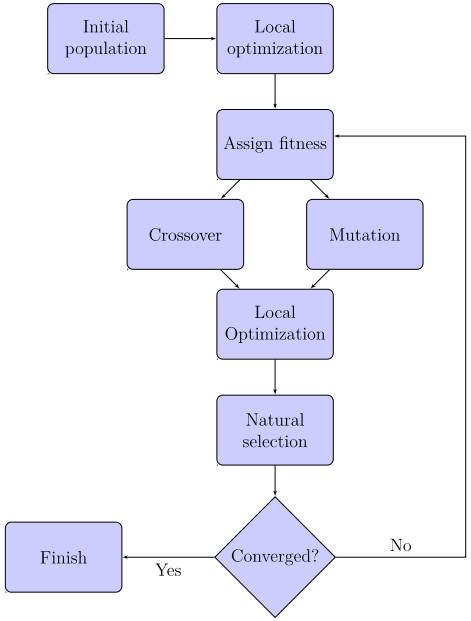
$$p_i = \left(\frac{f_i}{\sum_i f_i}\right) \quad ; \qquad f_i = e^{-a\epsilon_i}$$

Both clusters are sliced by random plane and complementeary fragments of the parents are combined together to produce a child structure.



Obtaining structure models from Theory

Genetic algorithm (GA) for structure search

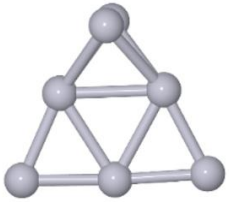


Flow chart of the global optimization procedure

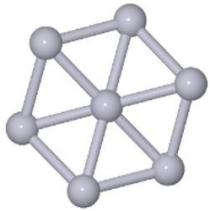
- 30 structures with 10 children were explored.
- Each structure in the population and every child requires a local structrure optimized using DFT.
  - Turbomole
  - def2-SVP basis set
  - BP86 functional

Structure of small Pt_n^- clusters (n=6-13)

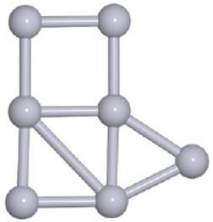
Pt_7^-



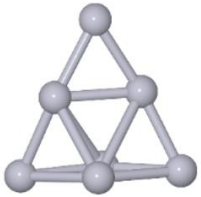
(1) C_{2v} 0.00 eV
R_w = 8.2 %



(2) D_{3d} +0.21 eV
R_w = 6.5 %



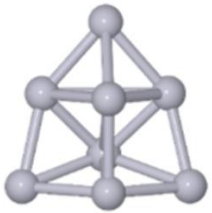
(3) C_s +0.22 eV
R_w = 17.8 %



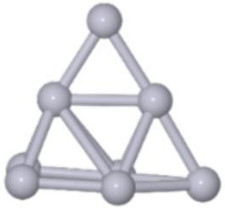
(4) C_2 +0.35 eV
R_w = 4.2 %

(5) C_s +0.90 eV
R_w = 2.6 %

Pt_8^-

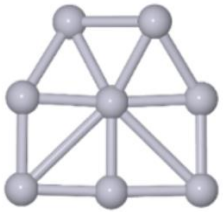


(1) C_s 0.00 eV
R_w = 8.4 %



(2) C_s 0.24 eV
R_w = 7.9 %

(3) C_1 0.29 eV
R_w = 4.8 %

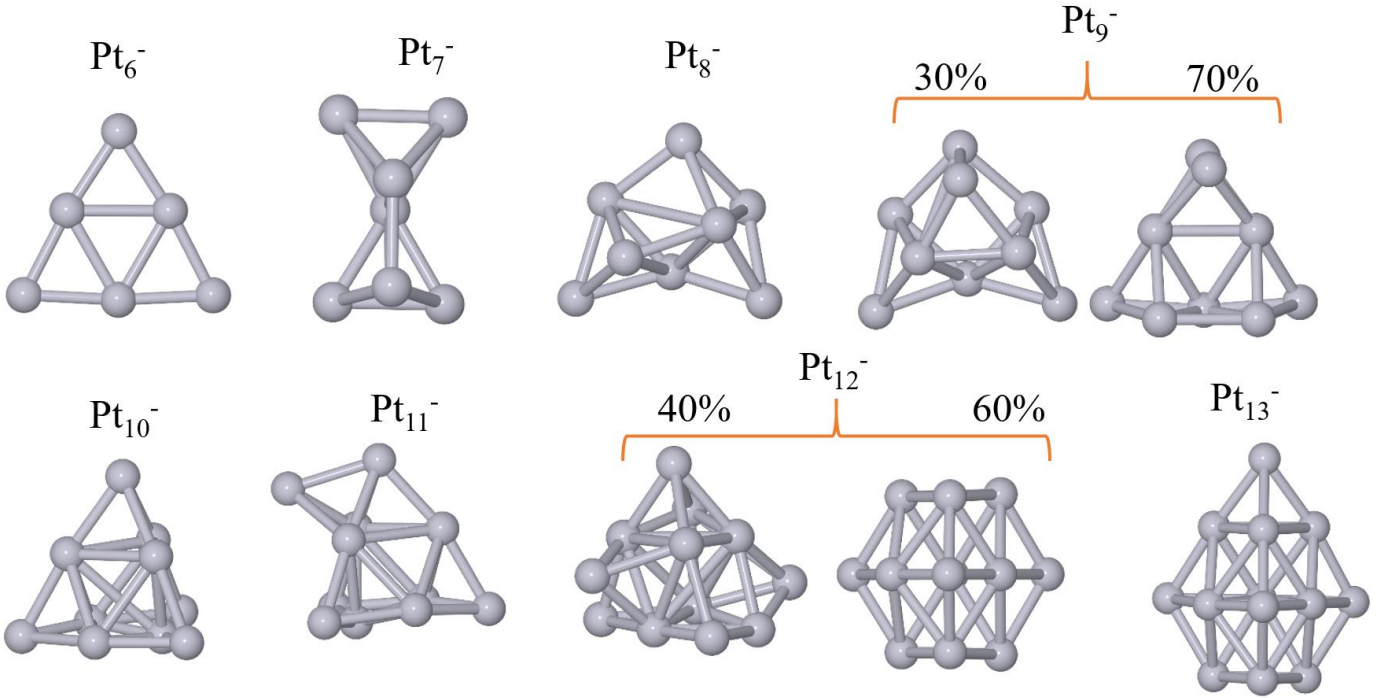


(4) C_2 0.31 eV
R_w = 13.1 %

(5) C_1 0.53 eV
R_w = 2.0 %

TPSS/def2-TZVP

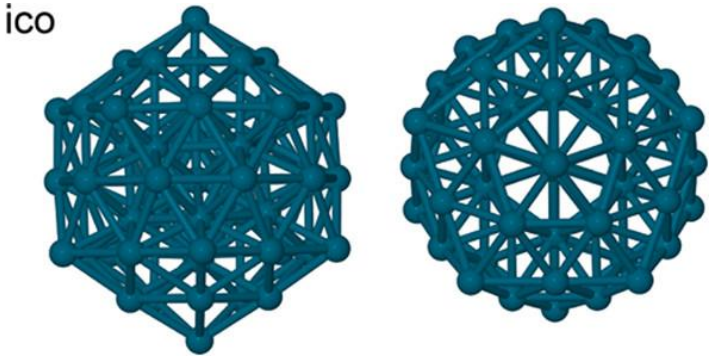
Structure of small Pt_n^- clusters (n=6-13)

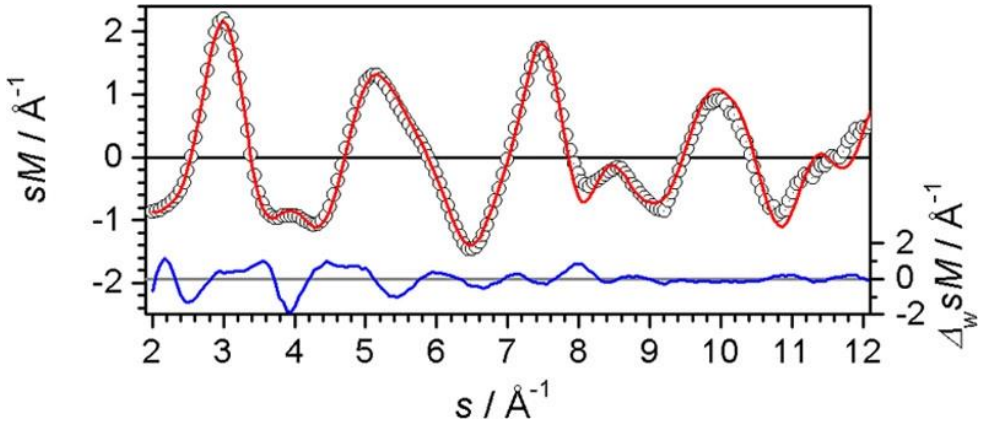


Every atom counts!

- D. Bumüller, A. G. Yohannes, S. Kohaut, I. Kondov, M. M. Kappes, K. Fink, D. Schooss, J. Phys. Chem. A 126, 3502–3510 (2022). DOI:10.1021/acs.jpca.2c02142

Pd_n^- clusters: Transition to bulk Pd_{55}^-

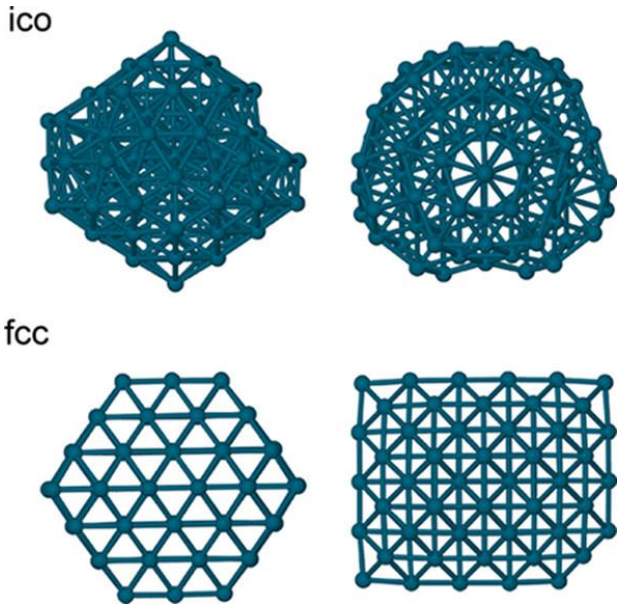




Siesta software package

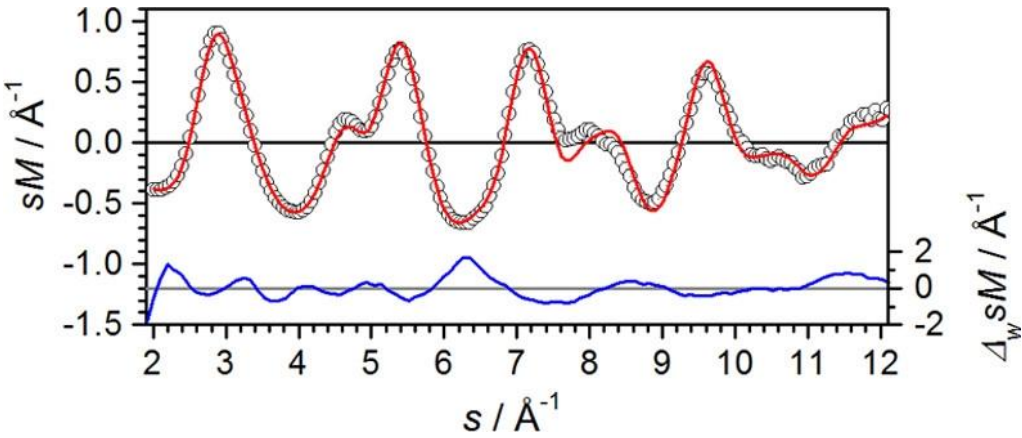
- S. Kohaut, T. Rapps, K. Fink, D. Schooss, J. Phys. Chem. A. 123, 10940-10946 (2019).

Pd_n^- clusters: Transition to bulk Pd_{105}^-



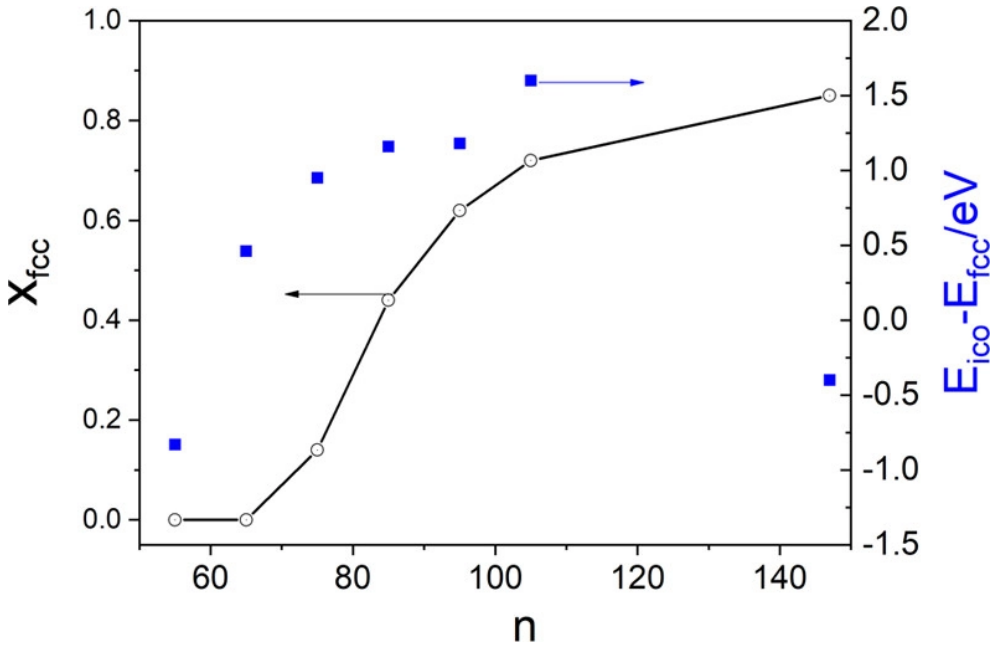
30%

70%

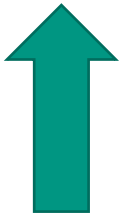


- S. Kohaut, T. Rapps, K. Fink, D. Schooss, J. Phys. Chem. A. 123, 10940-10946 (2019).

Pd_n^- clusters



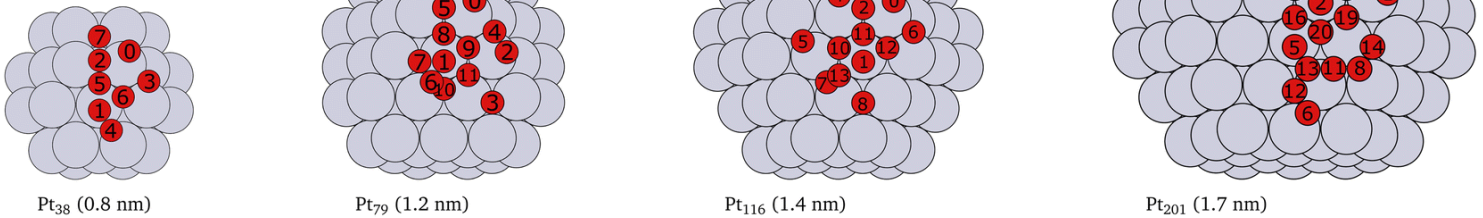
fcc structures



icosahedral cluster

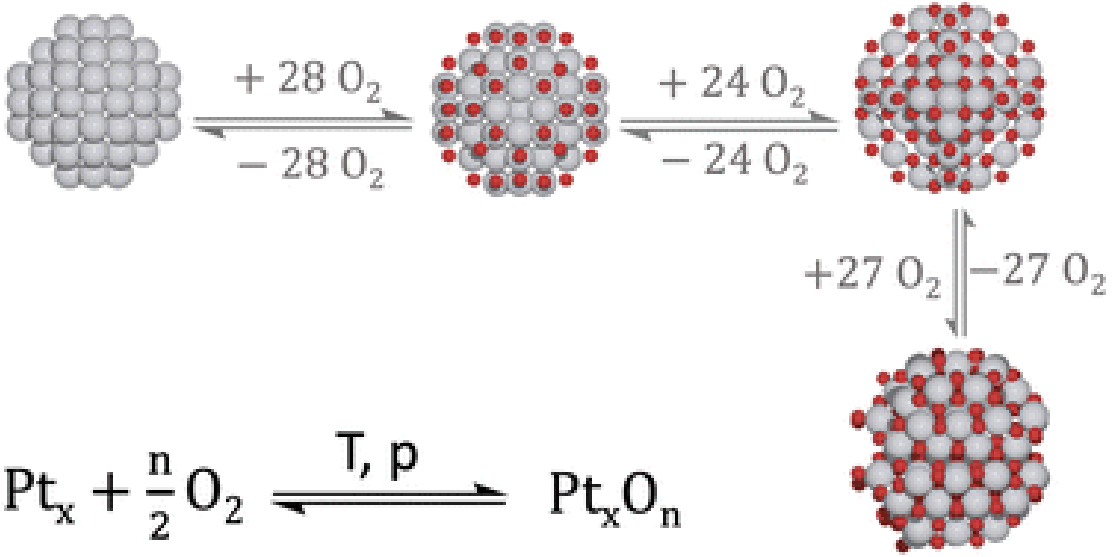
- S. Kohaut, T. Rapps, K. Fink, D. Schooss, J. Phys. Chem. A. 123, 10940-10946 (2019).

Reaction of Pt clusters with oxygen



- In general fcc and bridge most stable
- relation between coordination number and binding energy for same site
- VASP software package PBE functional, Cut off energy 450 eV
- A. G. Yohannes, K. Fink, I. Kondov, Nanoscale Adv. 10.1039/D2NA00490A (2022).

Reaction of Pt clusters with oxygen

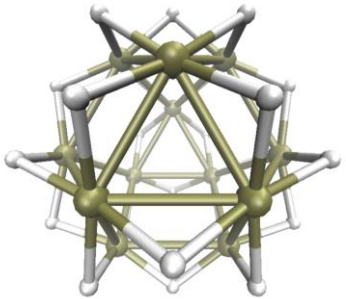


$$Pt_x + \frac{n}{2} O_2 \underset{}{\overset{T,\,p}{\rightleftharpoons}} Pt_xO_n$$

- Partial oxidation
- A. G. Yohannes, K. Fink, I. Kondov, Nanoscale Adv. 10.1039/D2NA00490A (2022).
- Large data set, reusable for maschine learning

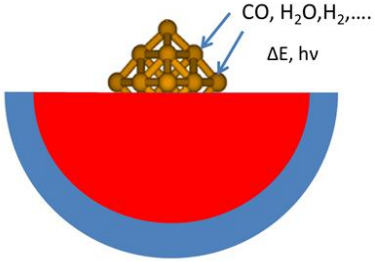
Summary and Outlook

- Several isomers for small Ptn- clusters
- Transition from cluster structures to bulk structures
- Reaction with oxygen



Next steps

- Reaction with hydrogen
- Considering oxide support CeO_2, Al_2O_3



Siddhi Gojare, Juana Vázquez Quesada, Chengyu Jin

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Theory

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Experiment

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Manuel Renz
Manfred Kappes
Detlef Schooss