

Interaction of NO and CO with surface of Pd nanoclusters studied by XRD

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Zbigniew Kaszukur

zbig@ichf.edu.pl

Institute of Physical Chemistry PAS
Warsaw, Poland

http://ichf.edu.pl/res/res_en/lab_xrd/LabXRD.html

http://acn.waw.pl/kaszukur/ZK_home_page.html



Outline

1 The method

- Combining in-situ XRD with atomistic simulations

2 Nanocrystallinity

- Peak position dependence on cluster size
- Disobeying of the Bragg law

3 Sensitivity to surface phenomena

- Interaction with oxygen
- Interaction with nitrogen monoxide
- Interaction with carbon monoxide

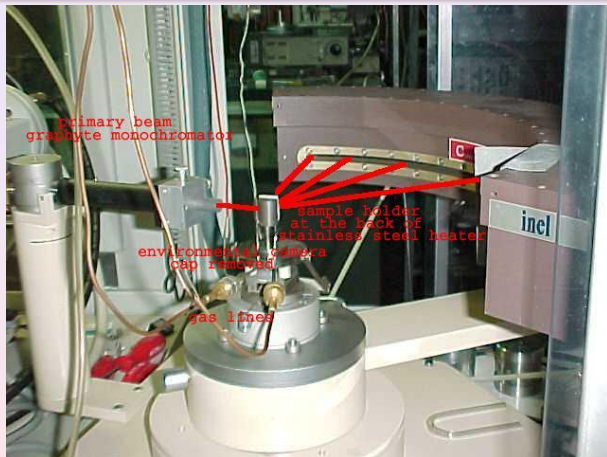


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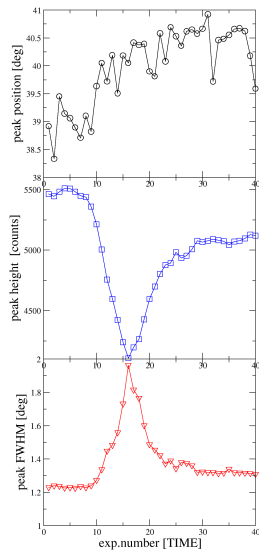
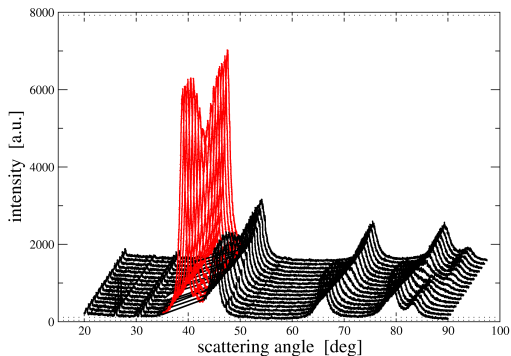
The experimental setup



The experimental setup employing INEL CPS120 and environmental, vacuum-proof chamber. Decent pattern collection time- 3-5 min.



Principles of analysis



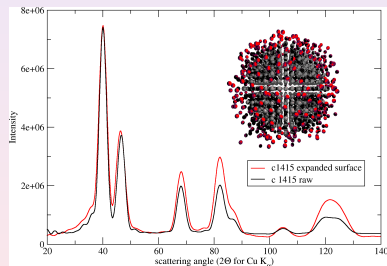
Accuracy of analysis

- Depending on counting statistics the change in peak position can be determined with accuracy 0.01deg ($\text{Cu } K_{\alpha}$) (taking into account thermal instabilities of the PSD)
- The peak intensity change can be determined down to 1% or better
- The FWHM can be determined with accuracy of few percent enabling detection of a block size (Scherrer eq.) changing by less than 1 at. layer for cluster of size $< 10\text{nm}$



Atomistic simulations

- - potentials - Sutton-Chen N-body form describing well cohesive properties of metals
- - tools - energy relaxation, molecular dynamics with constraints, configurational minimization (Monte Carlo) etc. - construction of a thermodynamically viable models, modified surface etc.



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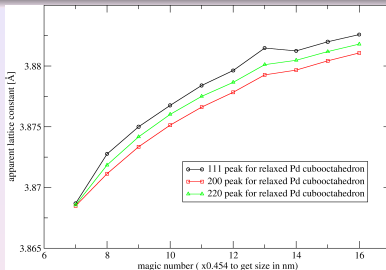
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Does lattice constant depend on the crystallite size ?

Evidence

- Theoretical suggestions (Pauling)
- Many literature observations for transition metals, alkali metals.
- Growing dependence on the state of surface (vacancies, adsorption etc.)
- Some literature data obscured by non clean surface



Theory

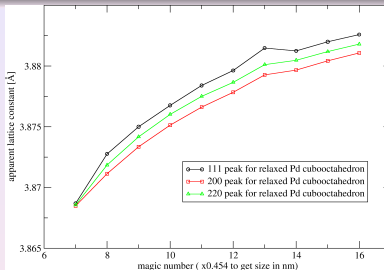
Powder diffraction peak shifted with multiplication by square of the atomic factor, measuring geometry...

Peak position to determine on $I(2\theta)\sin^2(\theta)/F^2(\theta)$

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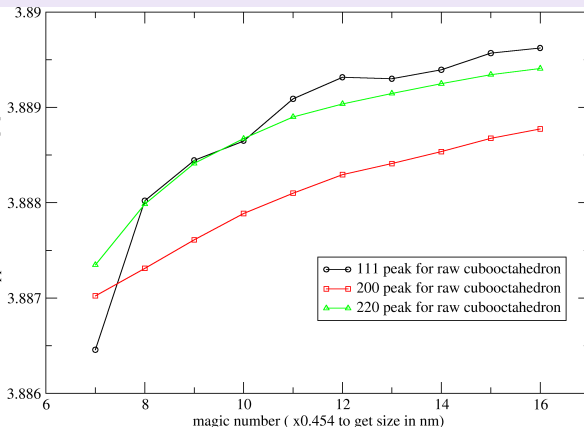


Theory

Powder diffraction peak shifted with multiplication by square of the atomic factor, measuring geometry...

Peak position to determine on
 $I(2\theta)\sin^2(\theta)/F^2(\theta)$

For nanocrystals the peak position does not show the real atom spacing

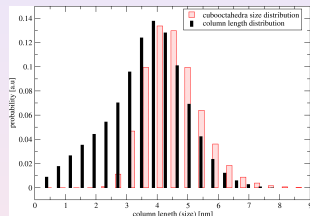
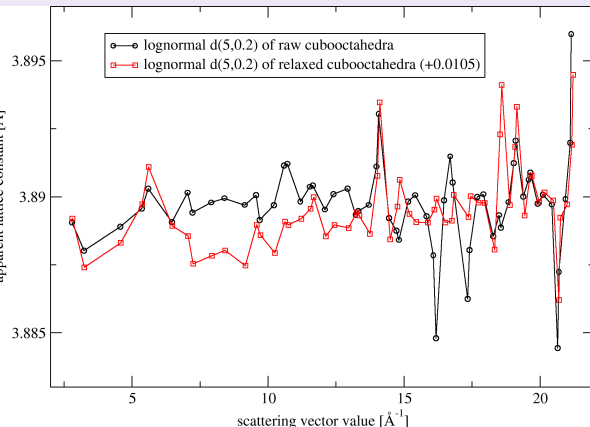


All clusters have the same real lattice constant

The peak shift - the effect of a limited length Fourier series.



Apparent lattice constant from diffraction peaks of a model distribution of palladium cluster size

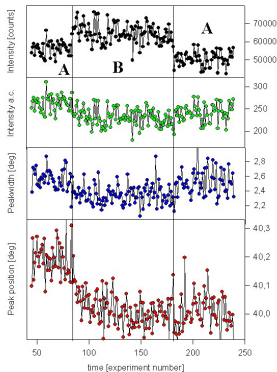


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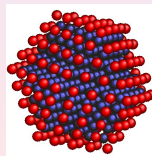
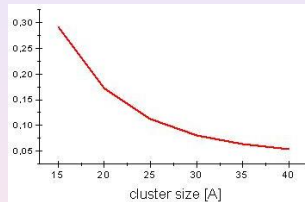
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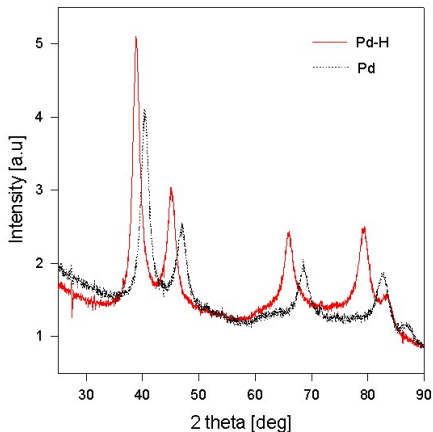
Change of XRD pattern on nanoparticle exposition to oxygen



Example for 111 peak of 10%(wt) Pd/SiO_2 of crystallite size $< 2.5nm$ (Scherrer). For chemisorption of oxygen the peak shift agrees with the surface relaxation effect



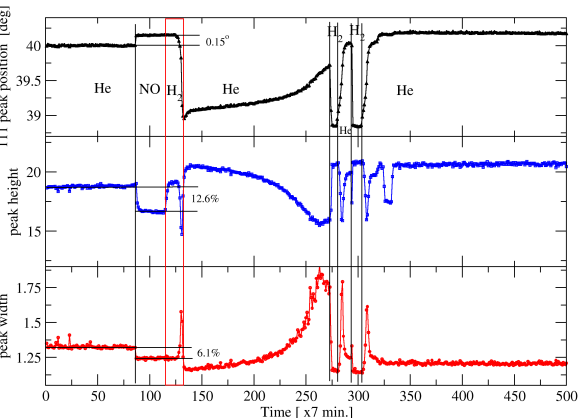
Policrystalline transition to β – hydride



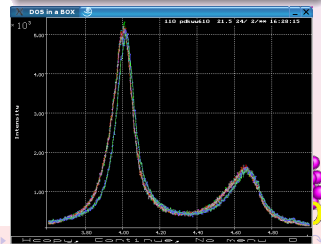
In situ transition to β -hydride for $D \approx 6.5 \text{ nm}$ Pd crystallites of 10% Pd/SiO₂.



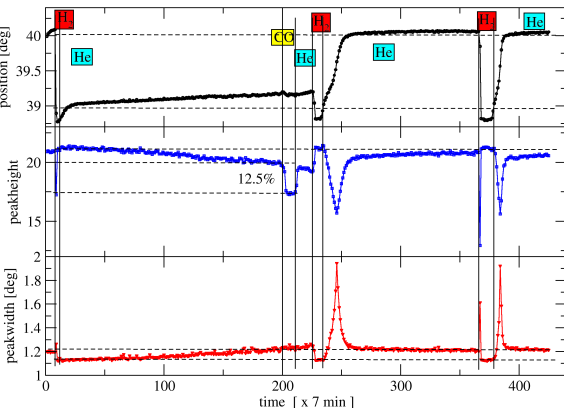
Change of XRD pattern on nanoparticle exposition to NO



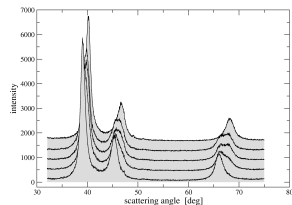
Example for 111 peak of Pd black of crystallite size 6.9nm (Scherrer) prepared by chemical reduction method at RT from Pd nitrate and formaldehyde-sodium hydroxide solution.



Change of XRD pattern on nanoparticle exposition to CO



Example for 111 peak of Pd black of crystallite size 6.9nm (Scherrer).



XRD

Summary

- The apparent lattice constant of nanoclusters commonly depends on their size and state of the surface

Small nanoclusters violate the Bragg law

The degree of the violation, evolution of peak intensity and width can be indicative of the surface reconstruction or chemical transformation of the surface layer.

- Chemisorption of NO and CO (1 atm) causes deep surface reconstruction
- NO chemisorption delays formation of PdH and hinders recombination of H to H_2 slowing down PdH decomposition
- Right tool for structure identification = diffraction in-situ + atomistic simulations.

A way to bridge the pressure gap in catalysis ? (surface science techniques- real industrial processes).

