A MEIS, STM and RAIRS investigation of the adsorption of CO on cobalt/palladium bimetallic surfaces

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Introduction – Fischer-Tropsch Catalysis

$$8CO + 17\ H_2 \xrightarrow{Cat} C_8H_{18} + 8H_2O$$

- Since the 1920s, the Fischer-Tropsch reaction[1] has been an industrially important method of converting synthesis gas ($CO + H_2$) into longer chain hydrocarbons and other high value organic chemicals
- Most F-T catalysts contain Fe or Co as the active component
- Use of bimetallic catalysts can improve catalytic performance (e.g. selectivity, activity)
- Addition of Pd to Co catalysts is thought to facilitate the reduction of cobalt oxide to allow the formation of the more active metallic Co phase[2]

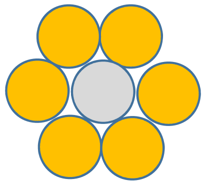
[1] F. Fischer, H. Tropsch, Brennstoff-Chemie **7** (1926) 97-104

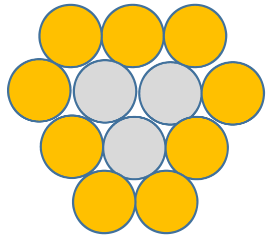
[2] M. Heemeier, A.F. Carlsson, M. Naschitzki, M. Schmal, M. Baumer, H.J. Freund, Angewandte Chemie-International Edition **41** (2002) 4073-4076

Bimetallic Catalysis – Ensemble v Ligand Effects

- Bimetallic catalysts are widely used in industry
- The promoting effect of adding a second element is often ascribed to ensemble effects or ligand effects

- E.g. ENSEMBLE EFFECT[1]
- CO adsorption on a Pd atom surrounded by 6 Au atoms in a (111) surface has a binding energy of ~0.7 eV
- CO adsorption in a hollow site surrounded by 3 Pd atoms has a binding energy of ~1.1 eV





- LIGAND EFFECT: may be ascribed to charge transfer from one element to another

[1] P. Liu, J.K. Norskov, Physical Chemistry Chemical Physics **3** (2001) 3814-3818

Adsorbate induced segregation

- The composition of a bimetallic surface is often different to the bulk
  - Relative atomic size
  - Relative surface energies
  - Exposed crystal faces
- The surface composition responds to the presence of the gas phase to produce the most thermodynamically favourable interaction

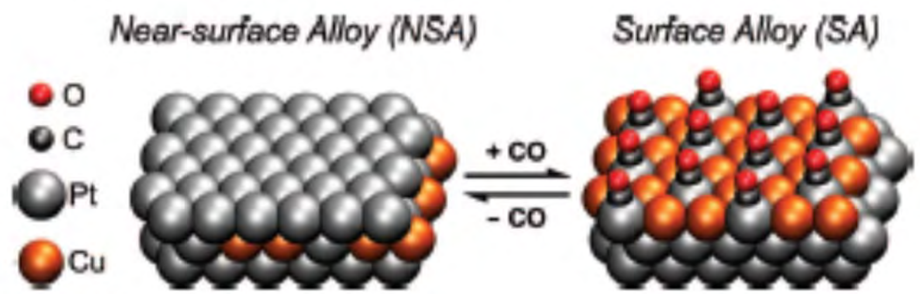
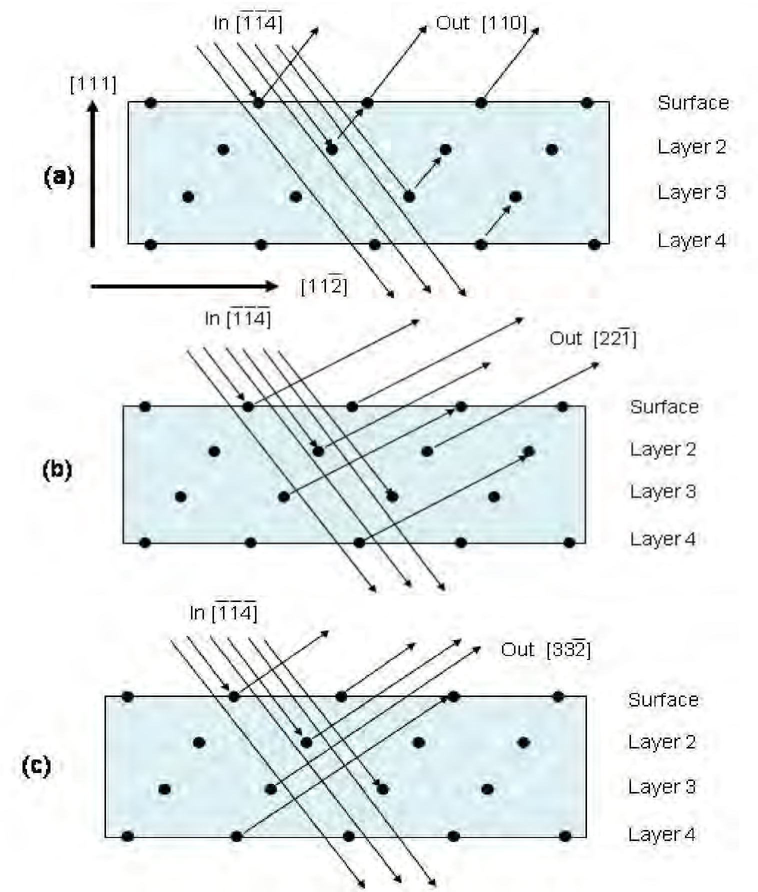


Figure 1. Illustration of (left) the CuPt NSA and (right) CO-induced Cu surface segregation and the novel SA resulting from it.

K.J. Andersson, F. Calle-Vallejo, J. Rossmeisl, L. Chorkendorff, Journal of the American Chemical Society **131** (2009) 2404-2407

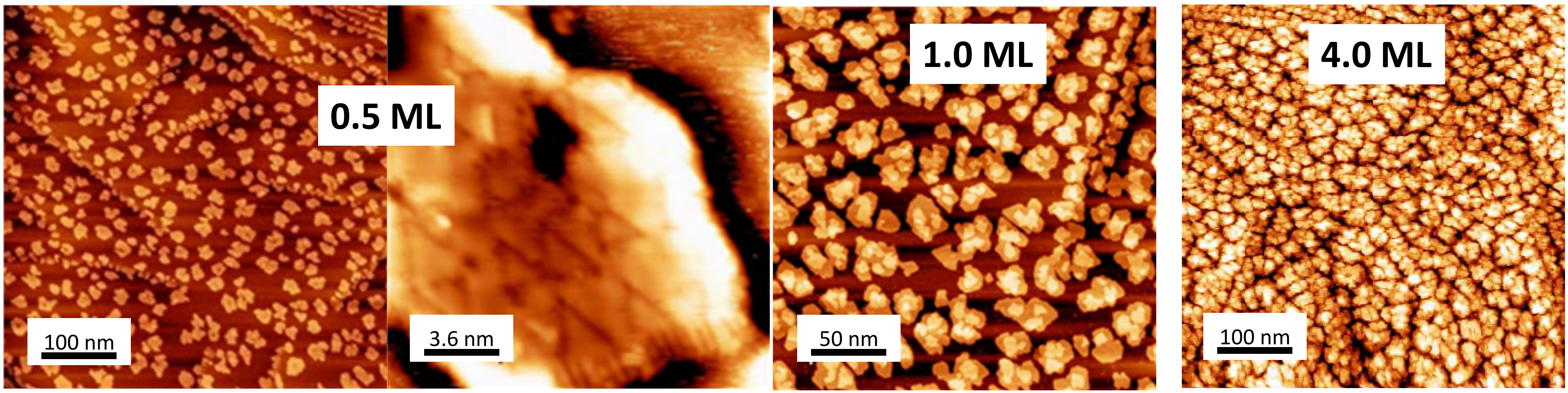
Experimental Techniques

- Scanning Tunnelling Microscopy (STM)
- Reflection Absorption Infrared Spectroscopy (RAIRS)
  - Probing composition of surface sites via CO chemisorption
- Medium Energy Ion Scattering (MEIS)
  - 100 keV He^+



Growth of Co on Pd(111)

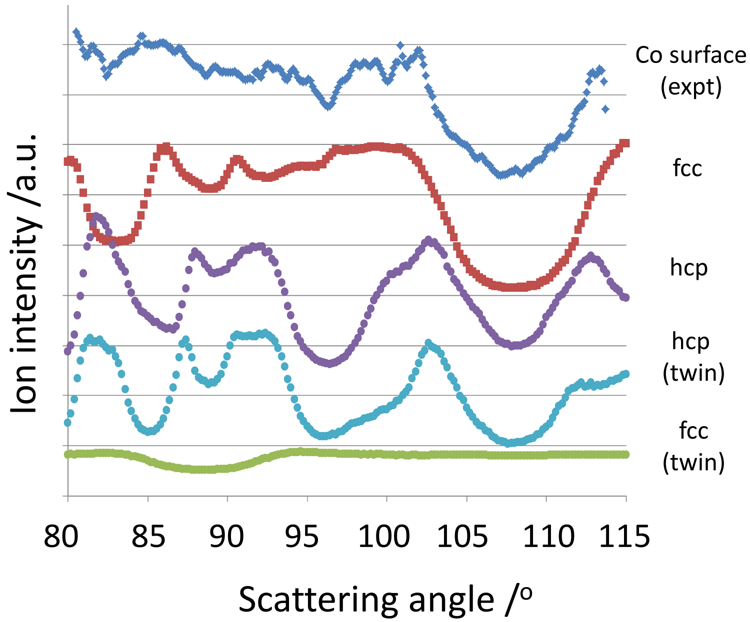
STM as a function of Co coverage (deposition at 300 K)

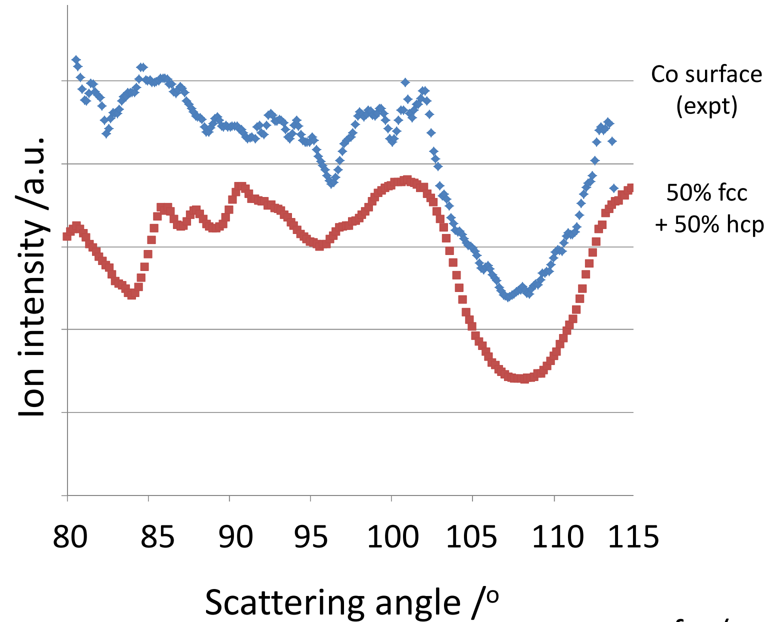


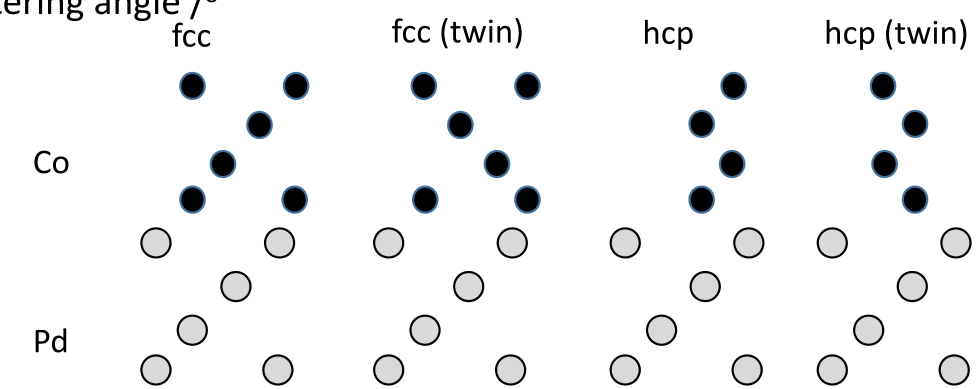
- 3D cluster growth is observed
- Evidence for surface dislocations (strain associated with 10% lattice mismatch)

A. Murdoch, A.G. Trant, J. Gustafson, T.E. Jones, T.C.Q. Noakes, P. Bailey, C.J. Baddeley; Surf. Sci. 608 (2013) 212-219

MEIS investigation of structure of Co films on Pd(111)





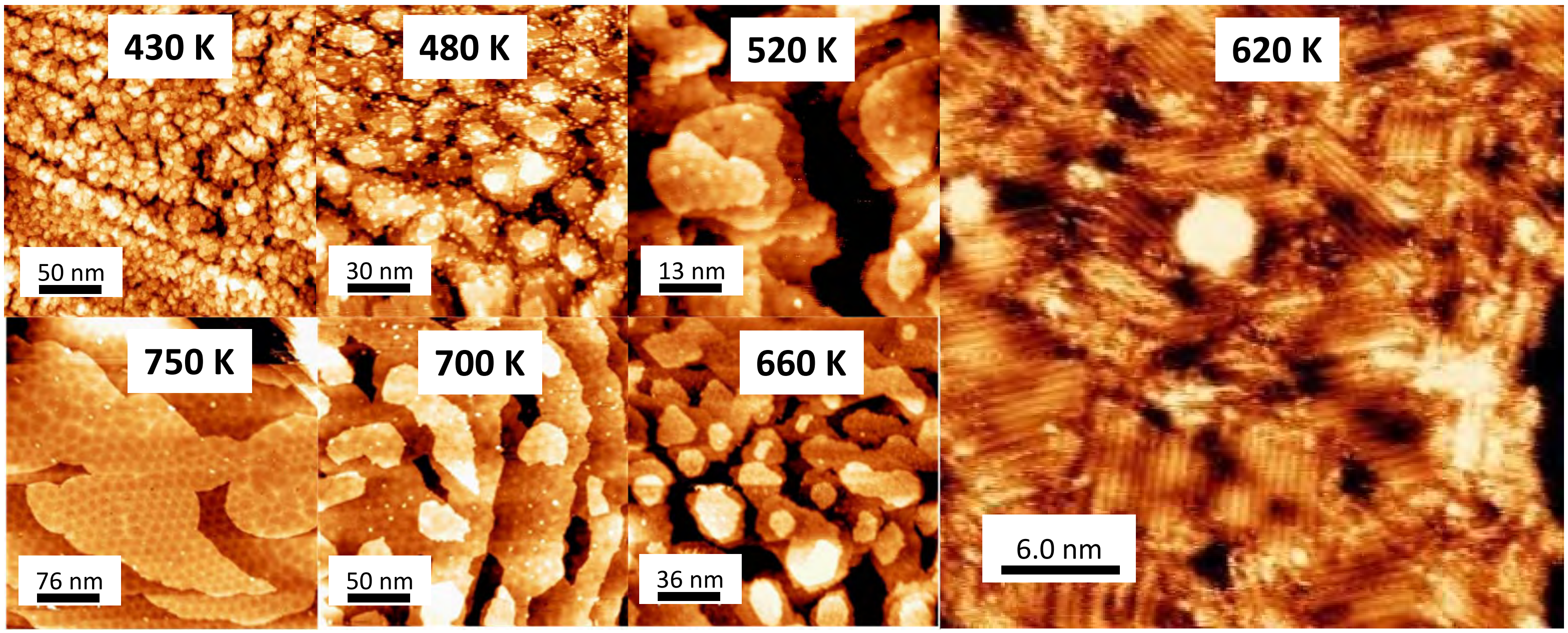


- VEGAS simulations of a (13x13) overlayer of 6 ML Co on Pd(111)
- Best (qualitative) fit is for a 50:50 fcc:hcp mixture

A. Murdoch, A.G. Trant, J. Gustafson, T.E. Jones, T.C.Q. Noakes, P. Bailey, C.J. Baddeley; Surf. Sci. 608 (2013) 212-219

Annealing behaviour of Co/Pd(111)

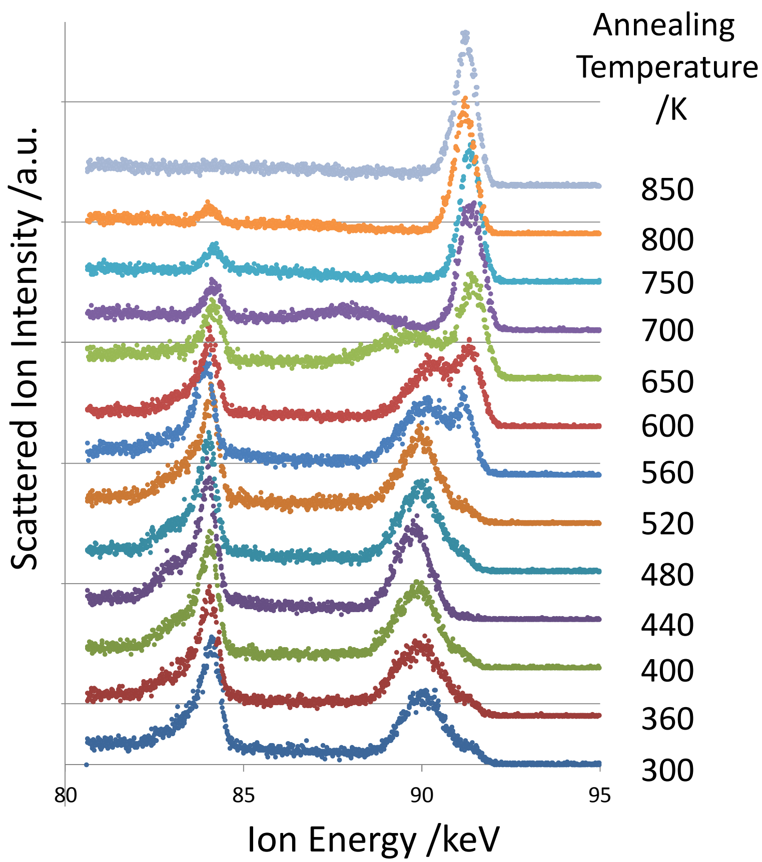
STM of 4 ML Co on Pd(111) as a function of annealing temperature



- Annealing in the ~600 K regime, results in striped phase.
- LEED gives "2x2" pattern [actually 3 domains of p(2x1)]

A. Murdoch, A.G. Trant, J. Gustafson, T.E. Jones, T.C.Q. Noakes, P. Bailey, C.J. Baddeley; Surf. Sci. 608 (2013) 212-219

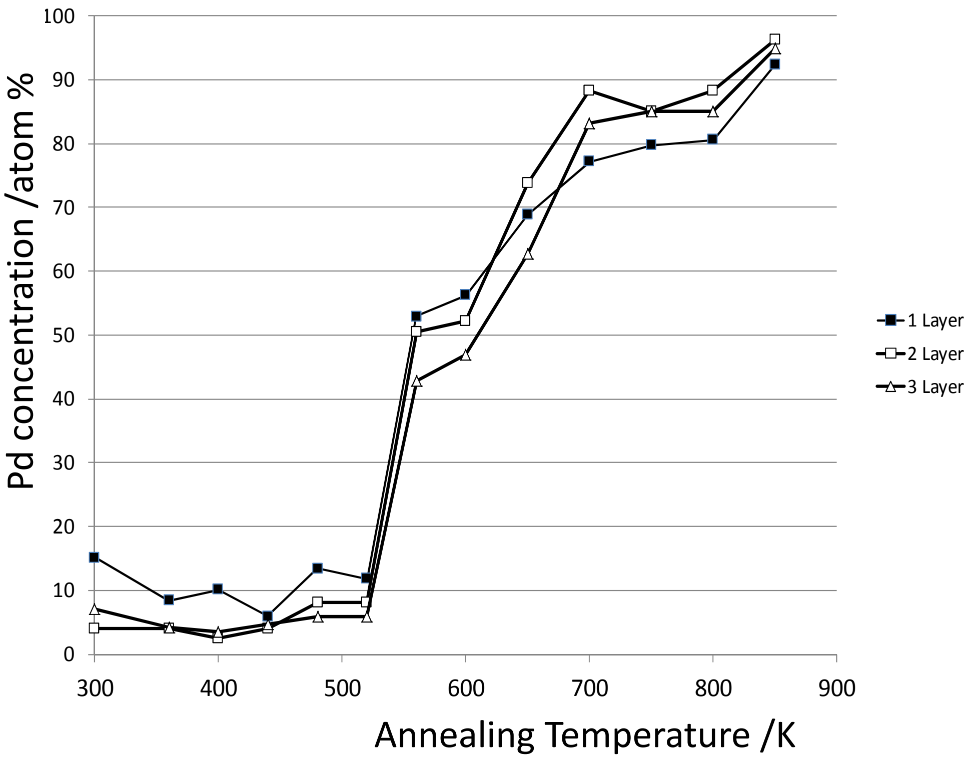
MEIS of 6 ML Co/Pd(111) as a function of annealing temperature

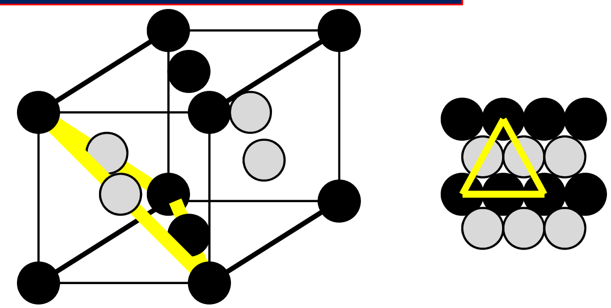


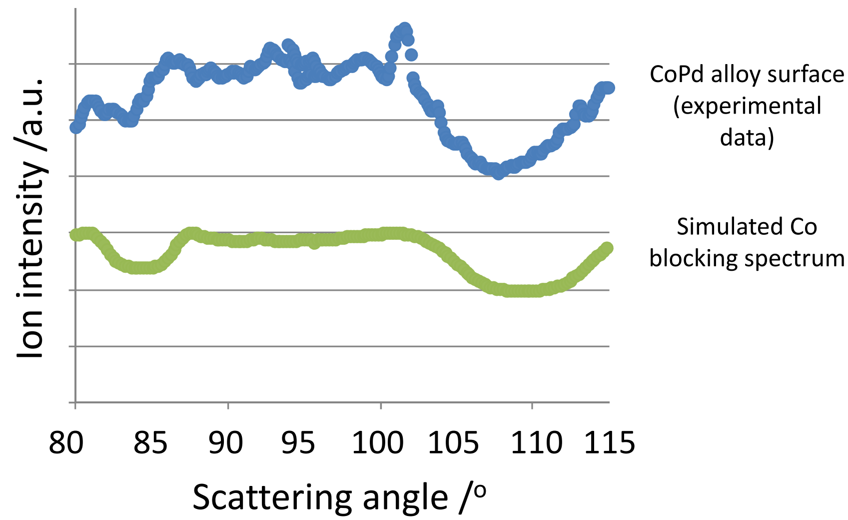
- 1-layer blocking direction
- Further evidence of non-pseudomorphic growth (appearance of sub-surface Pd peak)
- Gradual depletion of near-surface Co with increasing annealing temperature

A. Murdoch, A.G. Trant, J. Gustafson, T.E. Jones, T.C.Q. Noakes, P. Bailey, C.J. Baddeley; Surf. Sci. 608 (2013) 212-219

MEIS – composition as a function of annealing temperature







- Striped phase consistent with formation of $L1_0$ CoPd structure

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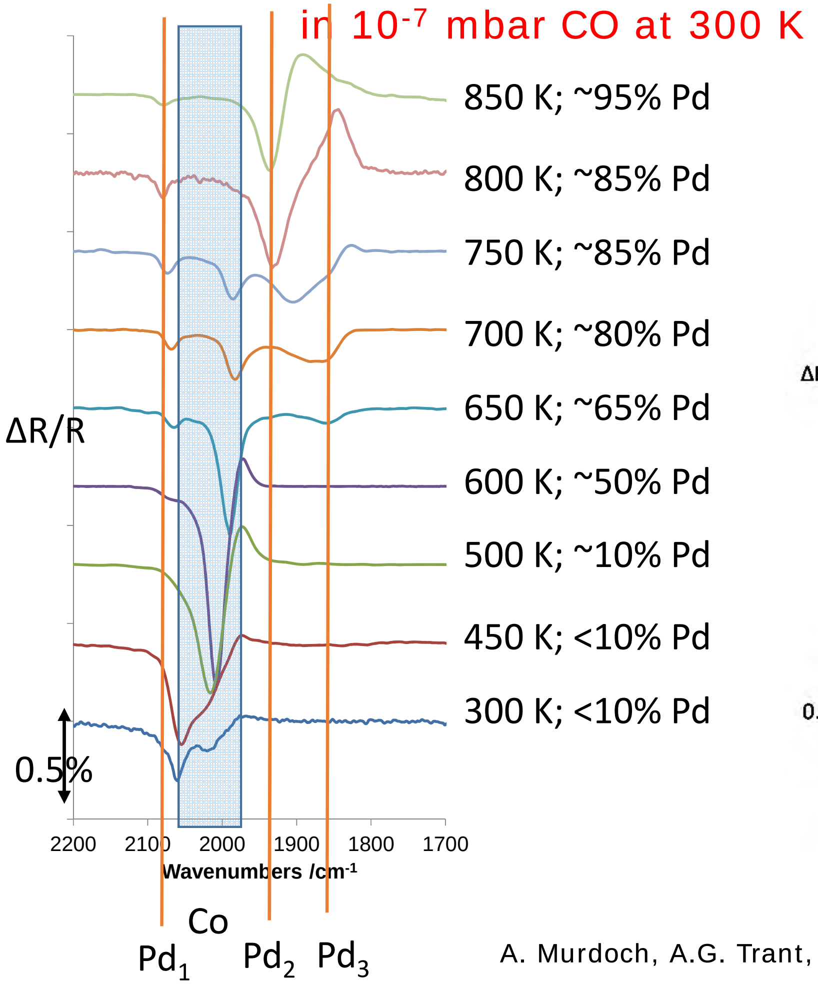
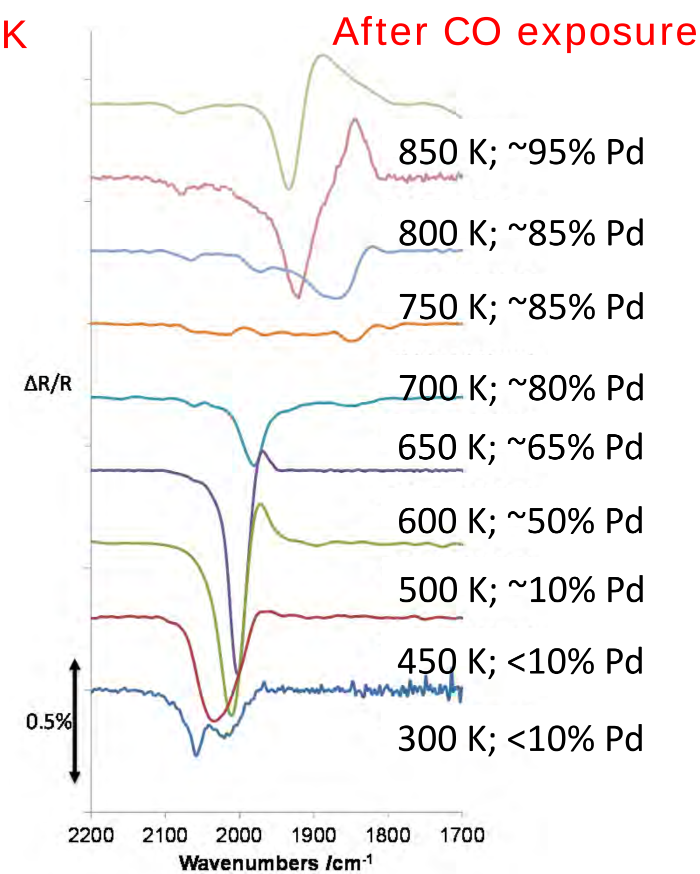
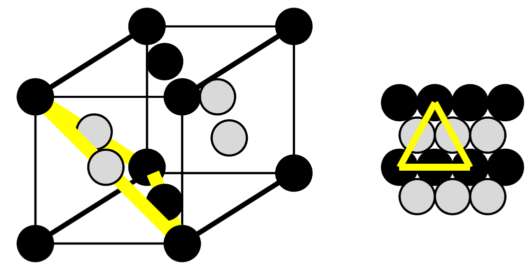
CO adsorption on Co/Pd surfaces

RAIRS – CO adsorption on CoPd surfaces







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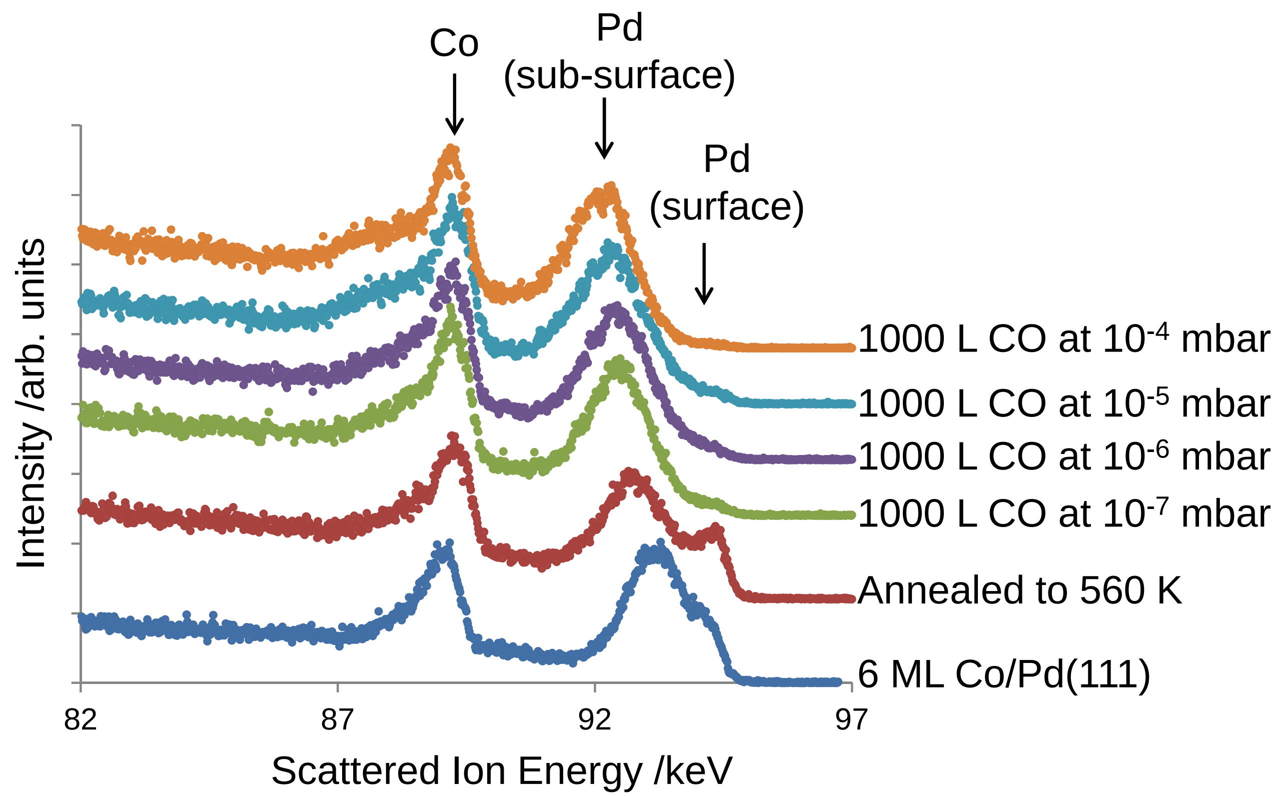
MEIS as a function of CO exposure at 300 K

- After annealing, the surface is a Co rich bimetallic surface
- CO adsorption removes Pd from the surface layer



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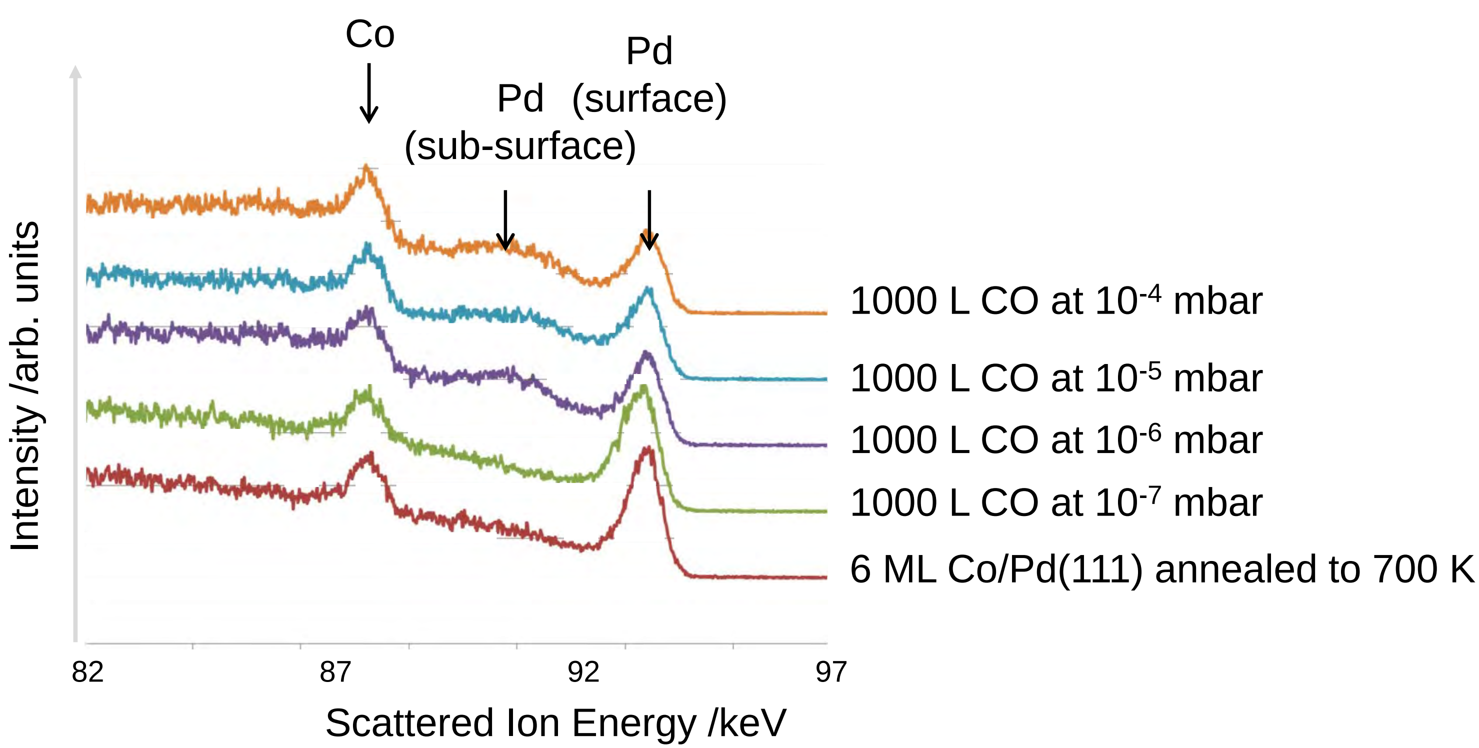
MEIS as a function of CO exposure at 300 K

- Annealed to produce a Pd rich CoPd surface
- CO adsorption reduces Pd surface signal – surface composition heads towards 50:50



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Discussion

- CO adsorption on:
  - an isolated Pd atom ~0.7 eV[1]
  - a Pd_3 cluster ~1.1 eV[1]
  - an isolated Co atom ~1.2 eV[2]
- When the surface is Co rich, most Pd exists as isolated atoms. Exposure to CO leads to Pd being excluded from the surface layer
- When the surface is Pd rich, the surface restructures to a 50:50 composition, but evidence of CO adsorption in 3-fold hollows from RAIRS. Similar in-plane segregation has been observed in the CO/PdZn(111) system[3]

[1] P. Liu, J.K. Norskov, Physical Chemistry Chemical Physics 3 (2001) 3814-3818
[2] J. Lahtinen, J Vaari, K. Karuala, E.A. Soares, M.A. van Hove; Surface Science 448 (2000) 269
[3] C Weilach, S.M. Kozlov, H.H. Holzapfel, K Foettinger, K.M. Neyman, G Rupprechter; J. Phys. Chem. C 116 (2012) 18768

Conclusions

- MEIS and RAIRS are a powerful combination of techniques to characterise adsorbate induced segregation effects at bimetallic surfaces
- Segregation effects occur at 300 K more rapidly than either the RAIRS or MEIS data collection timescales
- For real catalytic significance, need to extend to bimetallic nanoparticles on oxide surfaces.

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