MEIS investigations of model bimetallic catalysts

Chris Baddeley

EaStCHEM School of Chemistry

University of St Andrews

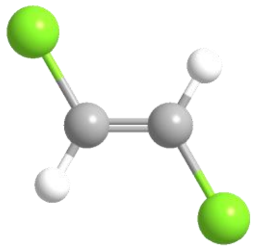
EaStCHEM

The Edinburgh and St Andrews Research School of Chemistry

Importance of bimetallic catalysis

- Many examples of bimetallic catalysts in industrial use

Hydrodechlorination catalysis (CuPd, ICI)



Trans-1,2-dichloroethene

Importance of bimetallic catalysis

- Many examples of bimetallic catalysts in industrial use

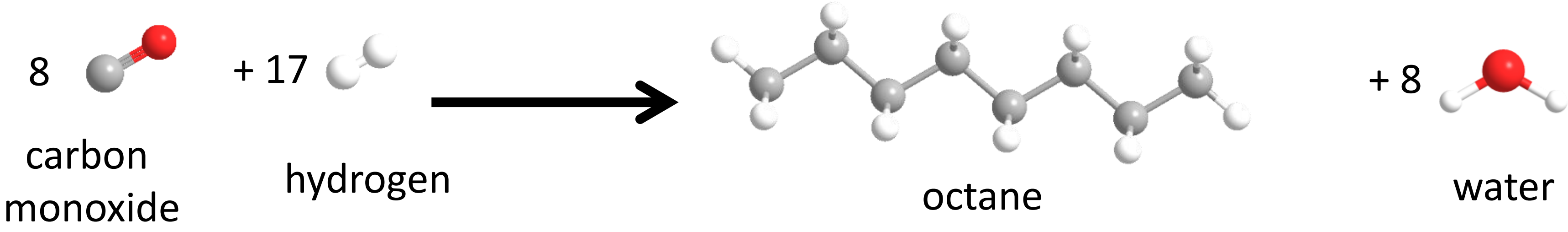
Vinyl acetate synthesis (AuPd, BP Chemicals)

ethylene acetic acid vinyl acetate

Importance of bimetallic catalysis

- Many examples of bimetallic catalysts in industrial use

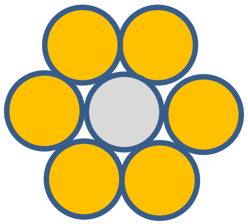
Fischer-Tropsch Catalysis (CoPd, SASOL Technology UK)

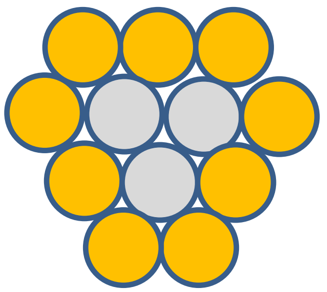


Bimetallic Catalysis – Ensemble v Ligand Effects

- The promoting effect of adding a second element is often ascribed to ensemble effects or ligand effects
  - Key issue is often SELECTIVITY towards the production of one desirable product

- 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

Influence of adsorbate on surface composition of bimetallic surfaces

EXPERIMENT

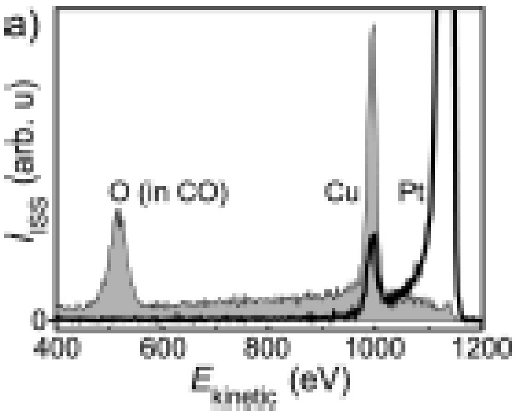
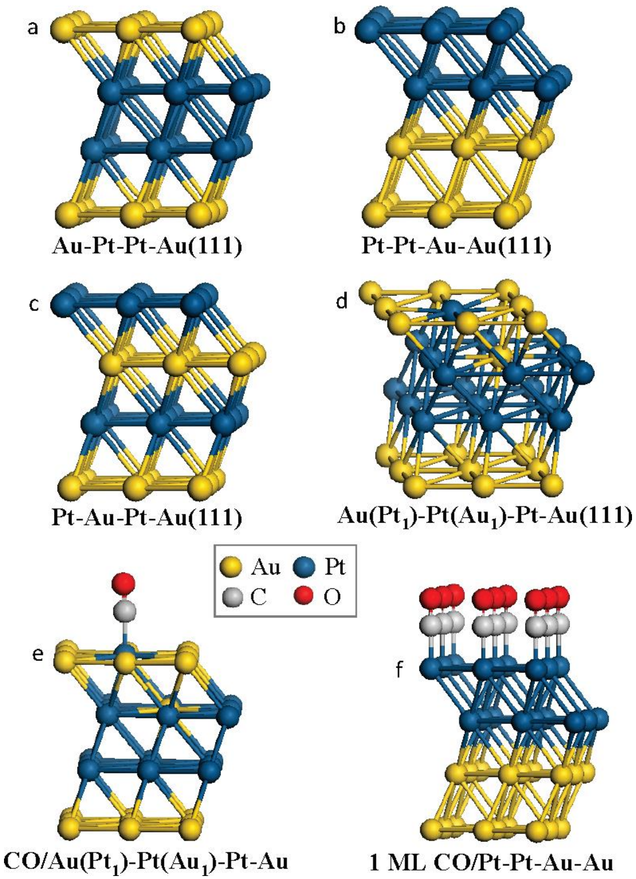


Figure 1. Illustration of (left) the CuPt NSA and (right) CO-induced Cu surface segregation and the novel SA resulting from it.

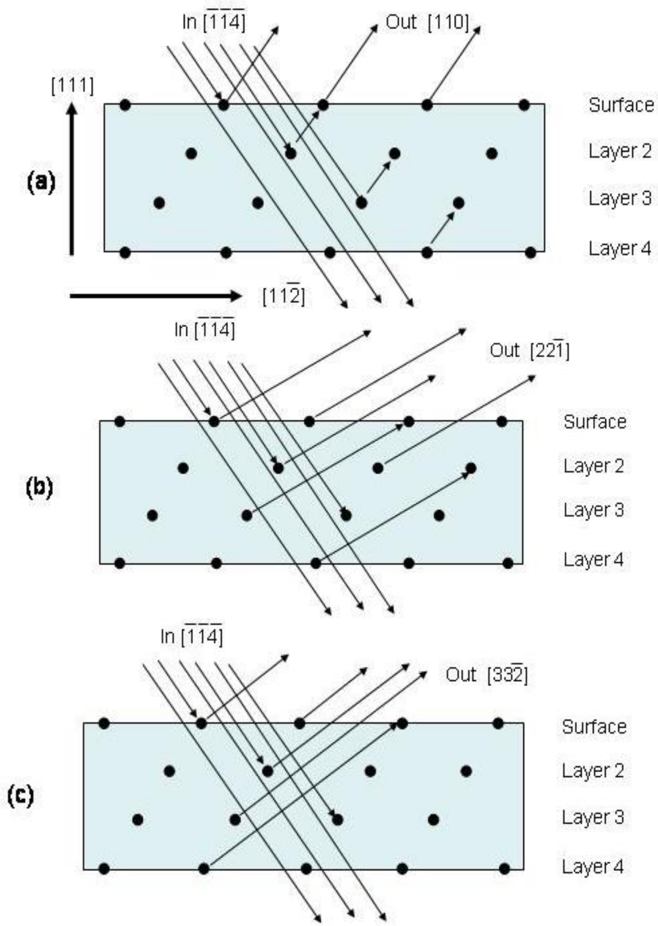
K.J. Andersson, F. Calle-Vallejo, J. Rossmeisl, L. Chorkendorff, Journal of the American Chemical Society 131 (2009) 2404

THEORY

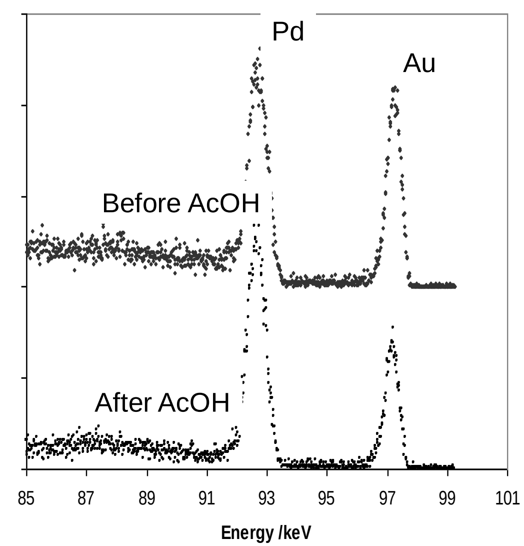


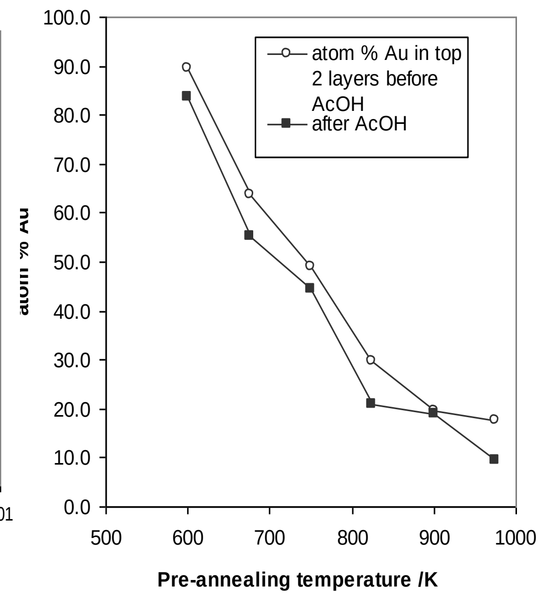
S.A. Tenney, J.S. Ratliff, C.C. Roberts, W. He, S.C. Ammal, A. Heyden, D.A. Chen, Journal of Physical Chemistry C **114** (2010) 21652

MEIS as a probe of adsorbate induced segregation



- Advantages:
  - Use of shadowing and blocking to enable selective illumination of integer numbers of layers
  - Adsorbate "invisible" in terms of shadowing underlying atoms

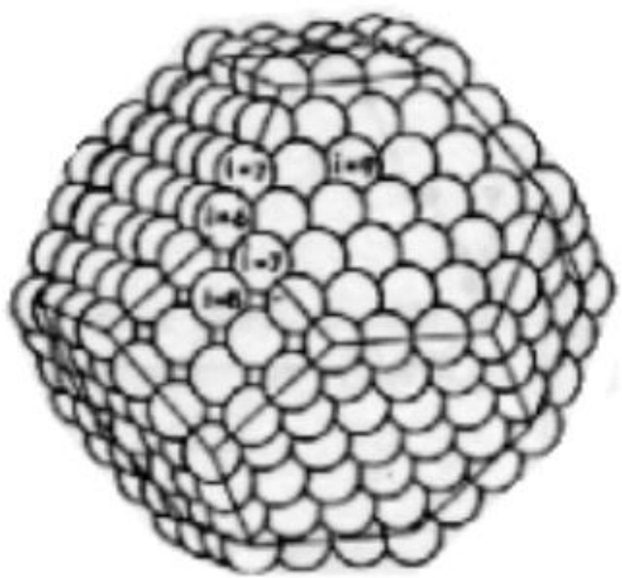




TG Owens, TE Jones, TCQ Noakes, P Bailey and CJ Baddeley; J. Phys. Chem B **110** (2006) 21152

Problems with traditional approach – structure gap

- Nanoparticles v extended surfaces
  - Different crystal planes exposed
  - Role of edges; defects
  - Differences in electronic properties

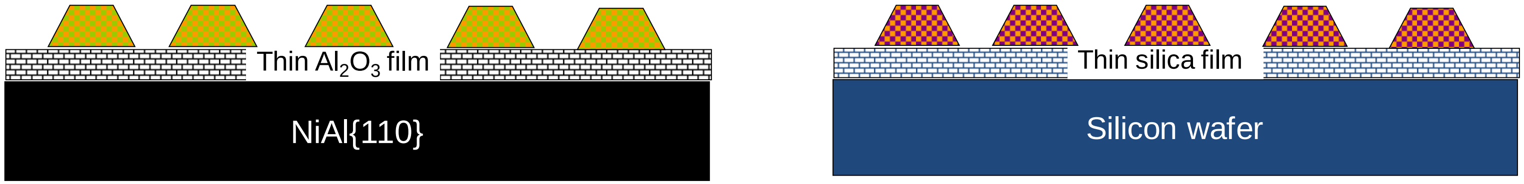


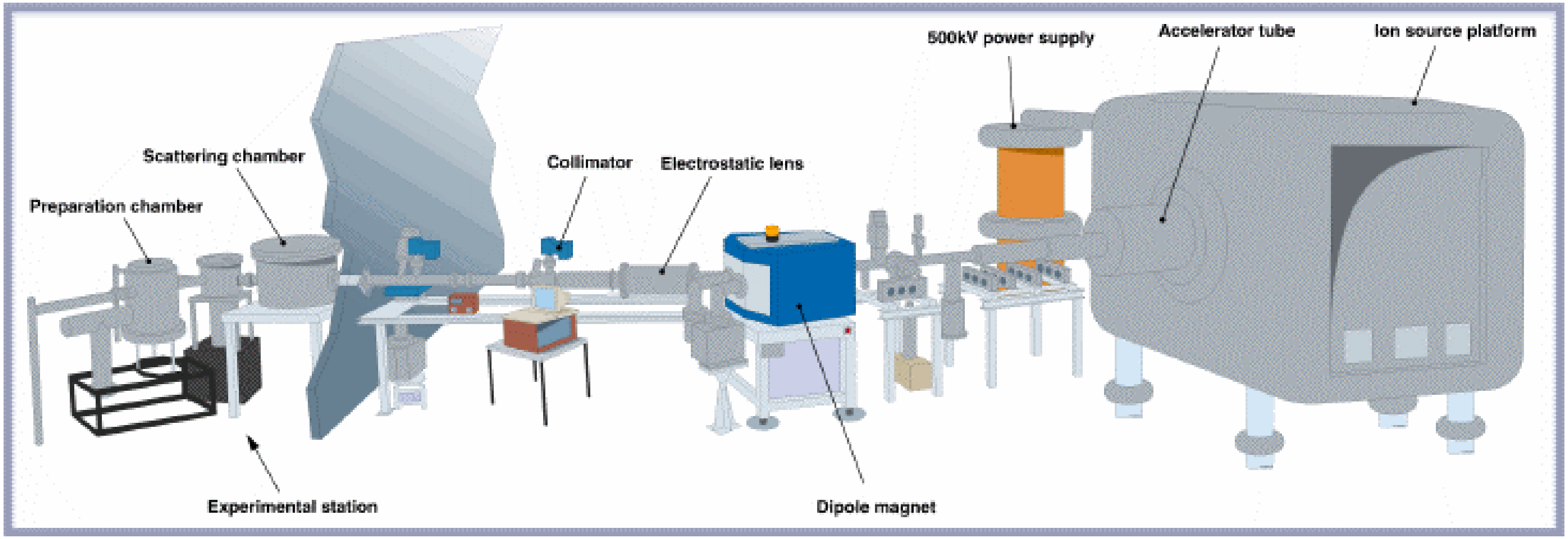
- Role of oxide support

- Better to study nanoparticles grown on oxide surfaces

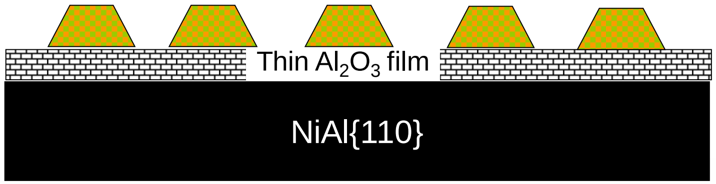
- Extend the use of MEIS to investigate bimetallic particles on oxide surfaces?

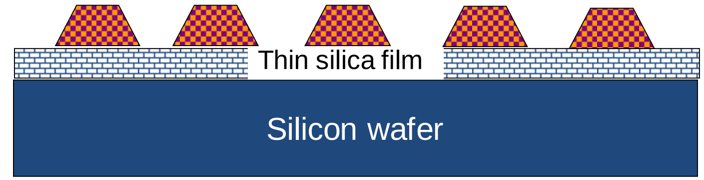
MEIS Analysis of Au/Pd Alloy Nanoparticles

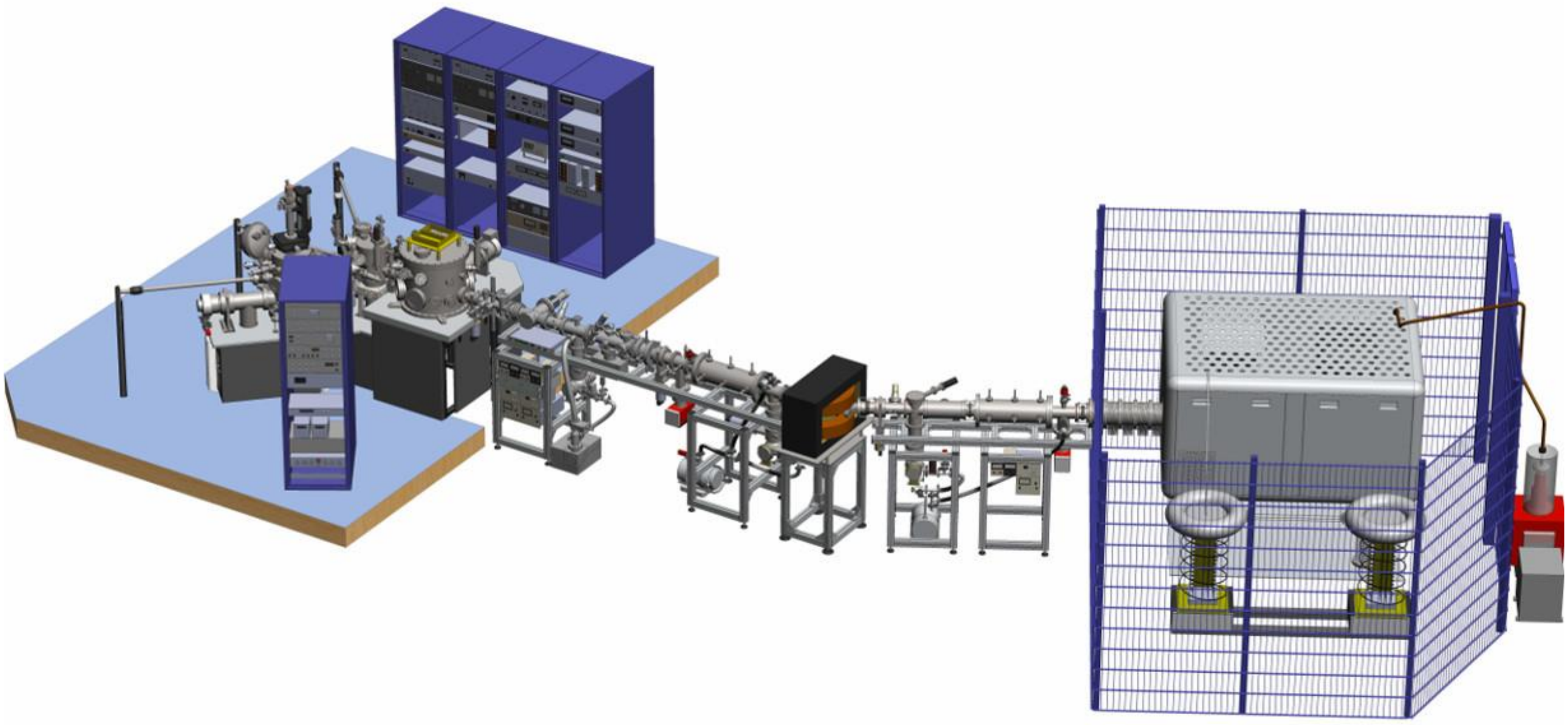




MEIS Analysis of Au/Pd Alloy Nanoparticles

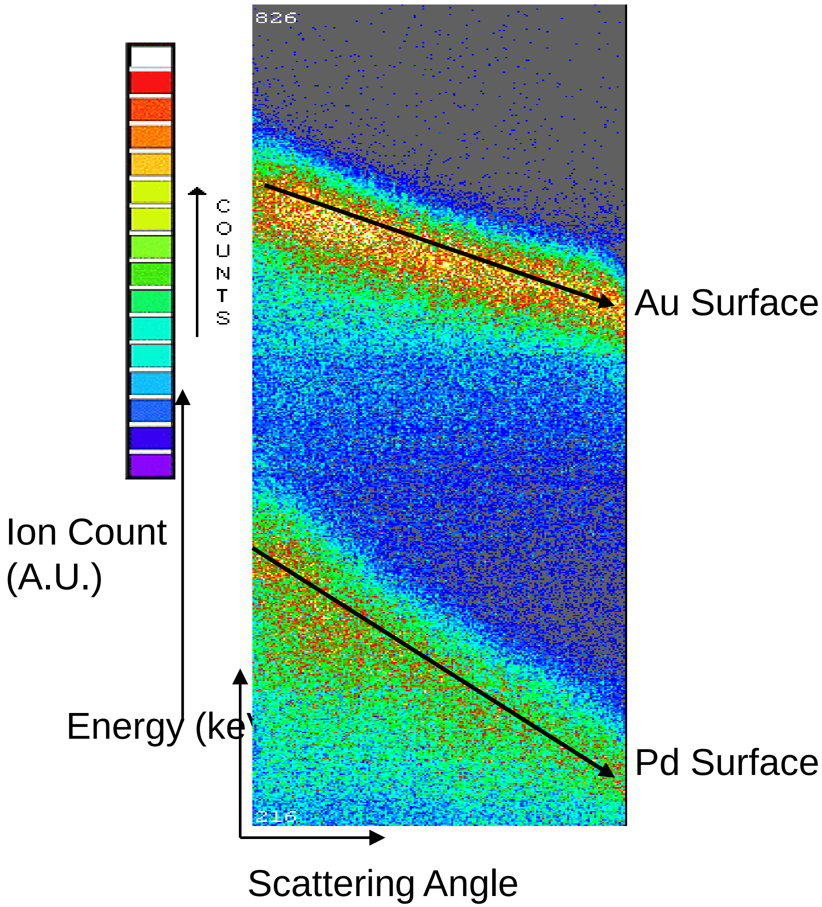


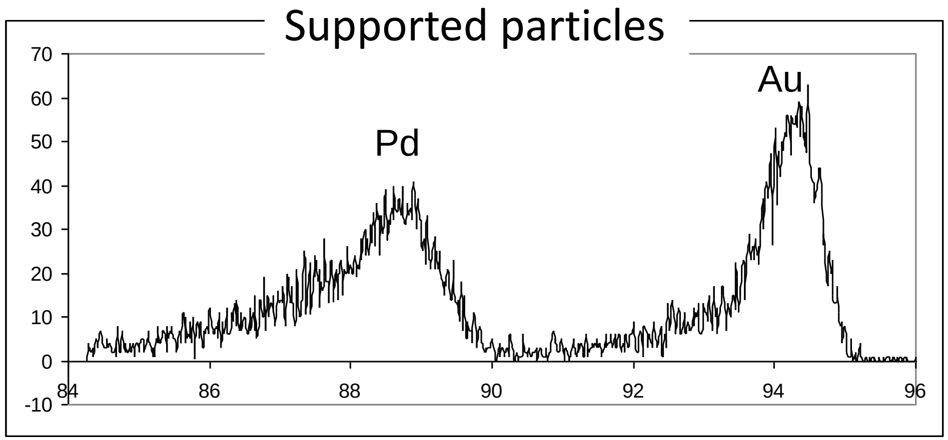


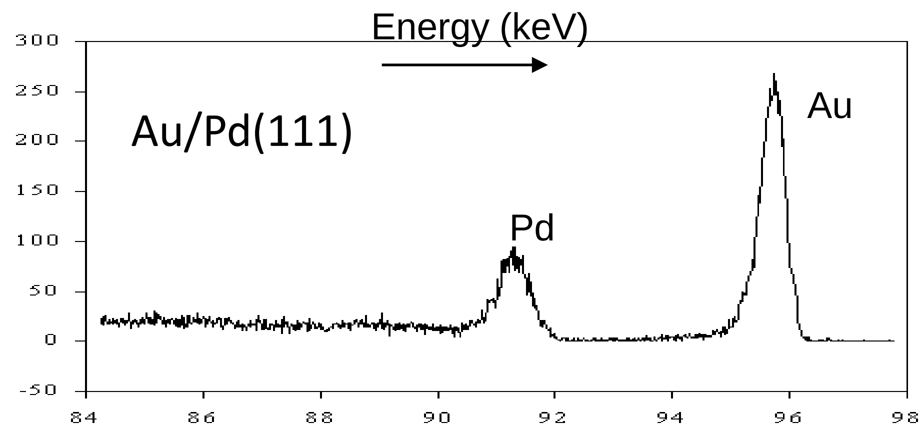


https://www.hud.ac.uk/research/researchcentres/acceleratorapplicationsinternationalinstitutefor/environment/meis/

Data Preparation







- k^2 correction applied to both Au and Pd peaks
- Project data over a relatively wide angular range
- Inverse k^2 correction to create spectrum for fitting

Spectrum simulation

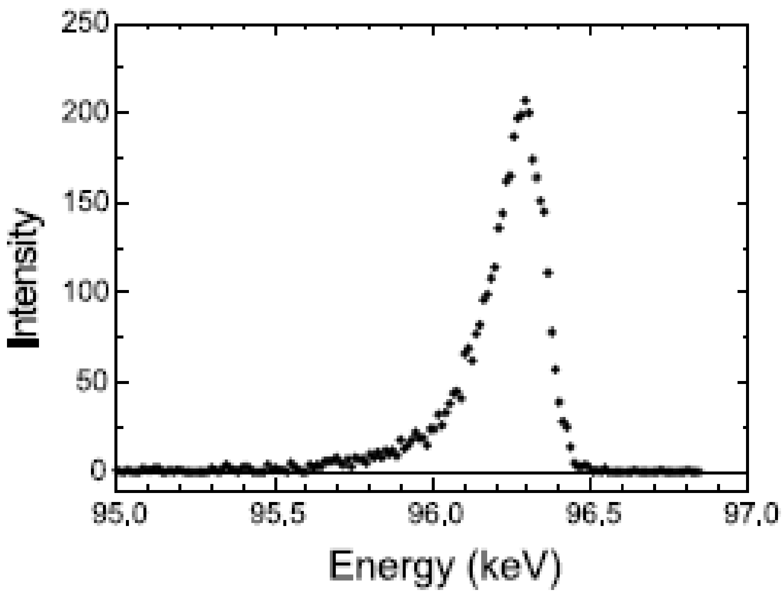


Fig. 2. Backscattering yield of 100 keV protons incident on a sub-monolayer coverage of gold.

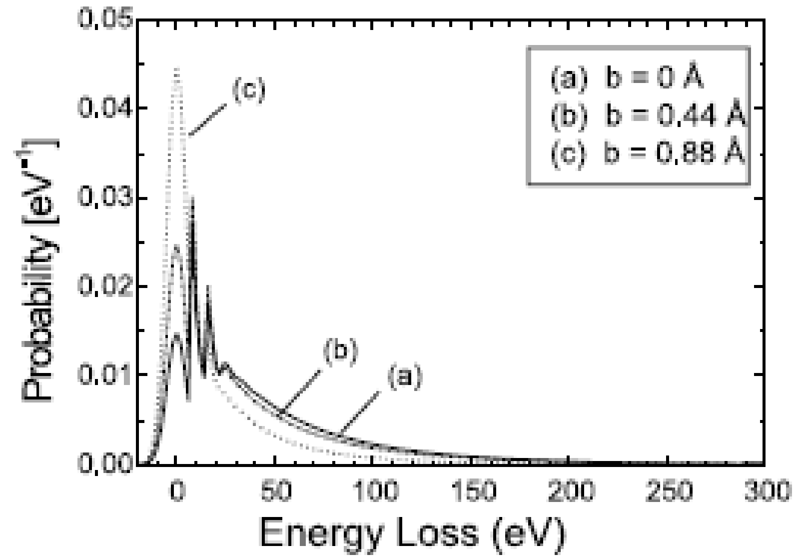


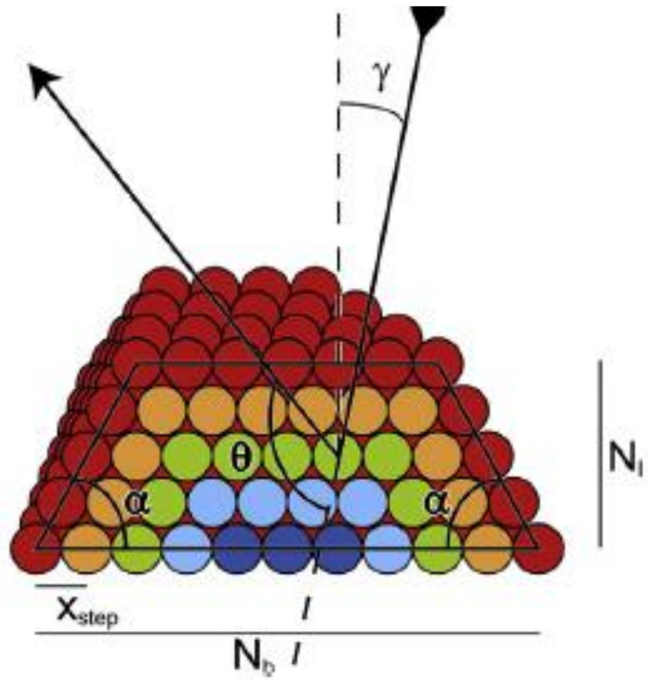
Fig. 1. Probability of energy losses as a function of the energy loss for scattering protons on carbon atoms. Spectra are shown for three different impact parameters b. The calculations are based on the SCA theory describing the collision process.

<u>Spectra of monometallic systems</u>

- Basic line shape of MEIS spectra is known to be asymmetric
- Used asymmetric Gaussian derived by fitting data from submonolayer Au on Ni{111}
- Incorporate isotopic abundance into each elemental peak

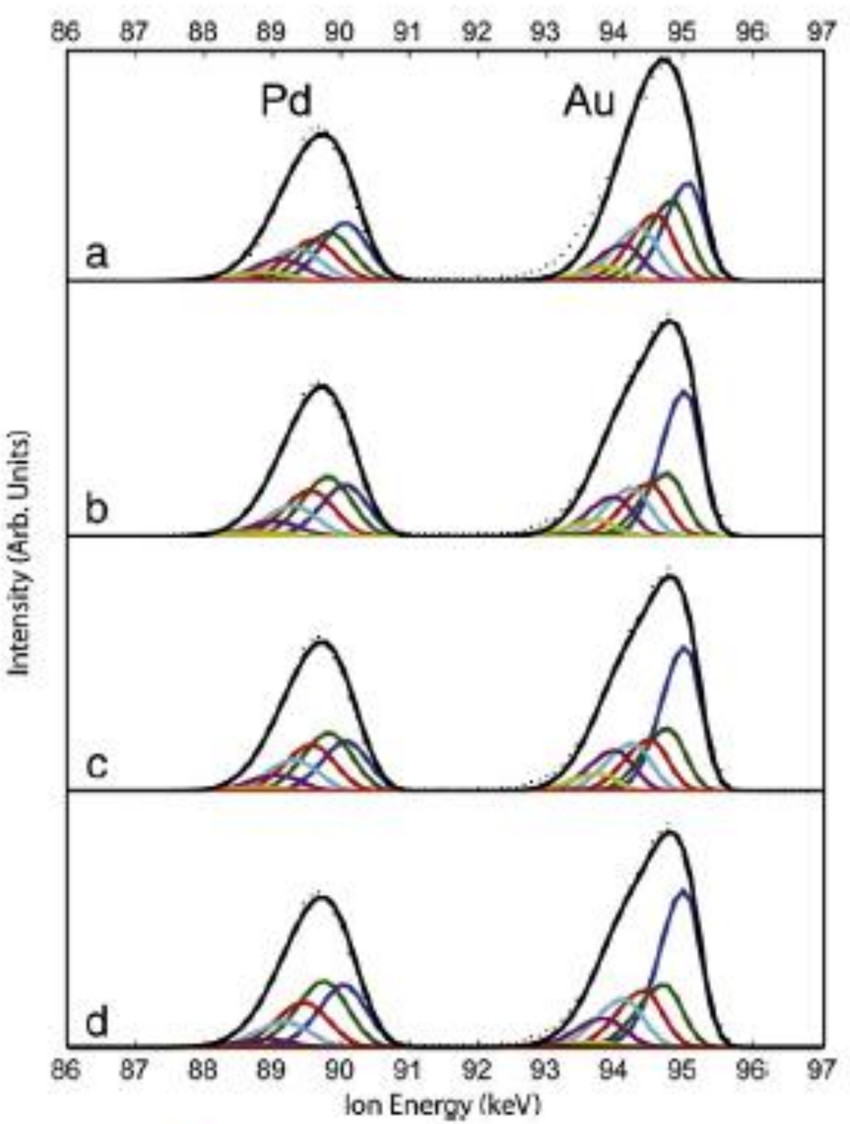
WH Schulte et al; Nuclear Instruments and Methods B **183** (2001) 16

Spectrum simulation – particle shape



- Assume hexagonal, flat-topped particle
- For each atom in a particle, take into account stopping power to determine path-dependent energy loss (SRIM) and include influence of straggling
- Shadowing and blocking
  - Used values from a psuedo-random geometry for fcc{111}
  - Needs refinement for bigger particles

Fitting results – $Pd_{60}Au_{40}$ on SiO_2/Si{100}



Homogeneous depth profile

20% top, 60% core, 20% base

Fitted % top/core/base

Particles – not flat surface

J. Gustafson, A.R. Haire, C.J. Baddeley, Surface Science **605** (2011) 220

Improved analysis tool – Pedro Grande, UFRGS, Brazil

- Parallel development of superior fitting methods for MEIS of nanostructured surfaces

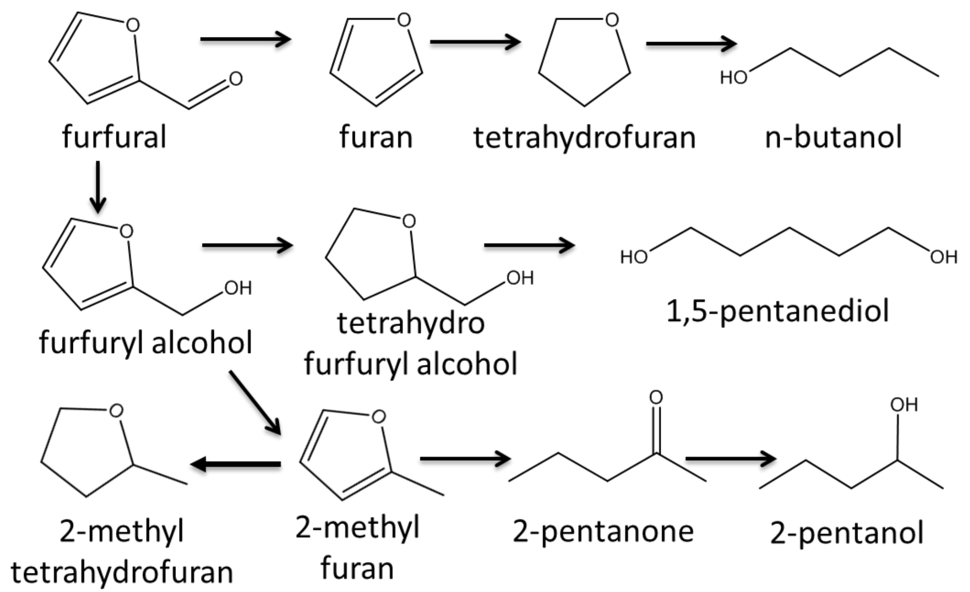
- Better modelling of peak shape

- Better capability to deal with distribution of particle shapes and sizes

- Intention is to calibrate with Grande group for data analysis

e.g. P.L. Grande and co-workers; Scientific Reports **3**, Article number: 3414 (2013)

Current MEIS project - Background



- **Furfural** regarded as a **non-oil based feedstock** [1].

- **Hydrogenation** gives **furfuryl alcohol** [2], but also **by-products**.

- **Supported Au can operate** with a very high selectivity to furfuryl alcohol [3]
- reaction rate is very slow
  - high activation barrier for dissociative adsorption of H_2
  - Needs very high H_2 pressures

[1] Y. Yang *et al. ChemSusChem* **2012**, *5*, 405;
[2] H. T. Wang *et al. Ind. Eng. Chem. Res.* **2006**, *45*, 6393;
[3] M. Li *et al. Catal. Commun.* **2015**, *69*, 119;

Background

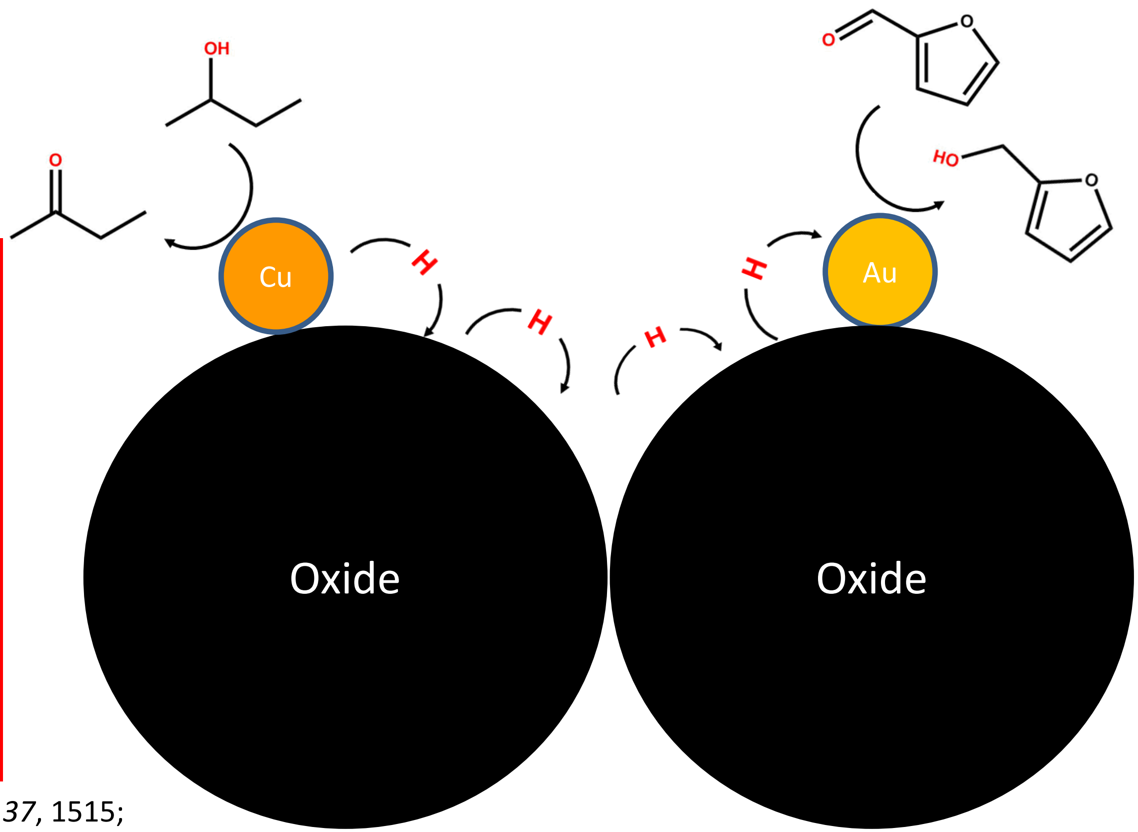
- **Atomic hydrogen may be generated** *in situ via* a parallel dehydrogenation reaction [1].
- **Au** is **inactive** toward dehydrogenation, therefore another catalyst is needed.
- **Hydrogen-free hydrogenation** of nitrobenzene coupled with 2-butanol dehydrogenation over **supported Cu** has been successfully demonstrated [2].
- **Possibility** of using **supported Cu/Au** as catalysts for a coupled dehydrogenation /hydrogenation reaction.

100% selectivity to furfural

Full utilisation of hydrogen

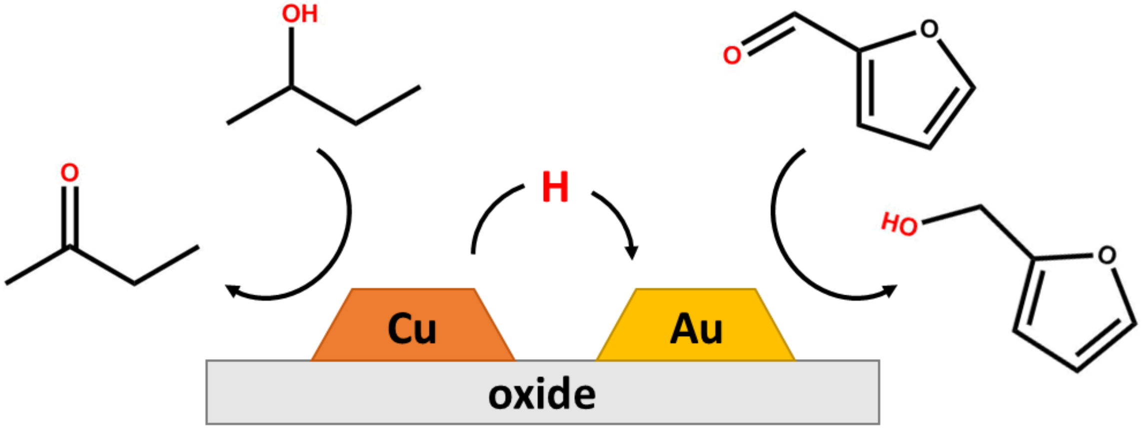
Operates at 1 bar pressure

Order of magnitude increase in reaction rate vs high pressure H_2 over Au catalyst



[1] A. Javaid *et al. Chem. Eng. & Technol.* **2014**, *37*, 1515;
[2] M. Li *et al. Top. Catal*. **2015**, *58*, 149.

Target catalyst



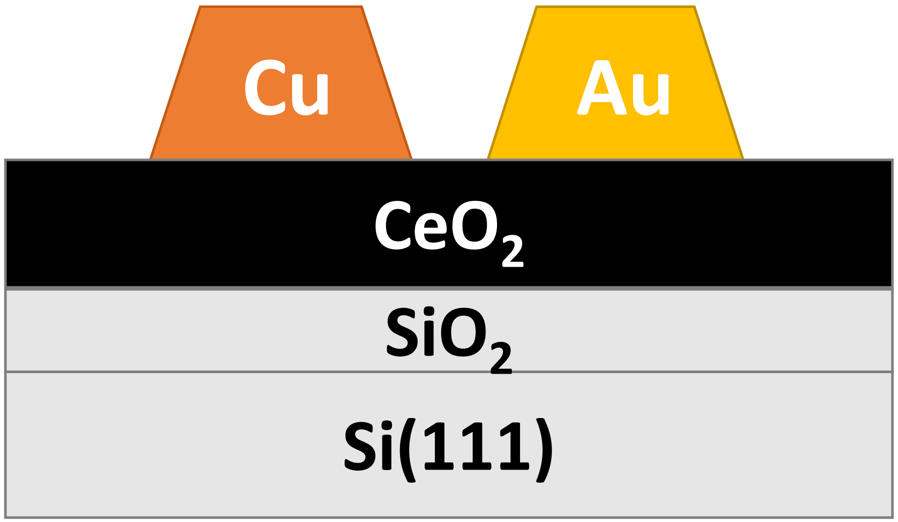
- Aim to gain a mechanistic understanding of coupled dehydrogenation/hydrogenation over supported Cu/Au catalytic systems.
  - In situ DRIFTS/MS on real systems
  - STM, TPD, vibrational spectroscopy on UHV model systems

- Optimise support
  - initial catalytic measurements have identified cerium oxide as best support

- Decrease Cu – Au particle separation to enhance transfer of atomic hydrogen

Future MEIS experiments

- Deposit thin (~5 nm) cerium oxide films on silicon wafer
- Deposit Cu and Au from solution
- Use AFM and XPS to optimise sample preparation
- Use MEIS to characterise thermal behaviour focussing on alloying and adsorbate induced segregation
- For analysis, collaborate with group of Professor Pedro Grande (Federal University of Rio Grande do Sul, Brazil)



HERIOT WATT UNIVERSITY

Acknowledgements

EaStCHEM School of Chemistry, St Andrews

Dr Federico Grillo

Rory Megginson

Dr Johan Gustafson

Dr Tim Jones

Dr Aoife Trant

Dr Andrew Haire

Dr Tom Owens

Dr Alex Murdoch

Chemical Engineering, Heriot Watt University

Prof Mark Keane

Dr Fernando Cardenas-Lizana

MEIS facility, STFC Daresbury Laboratory

Dr Tim Noakes

Dr Paul Bailey

MEIS facility, University of Huddersfield

Prof Jaap van den Berg

Dr Andrew Rossall

sasol reaching new frontiers

bp

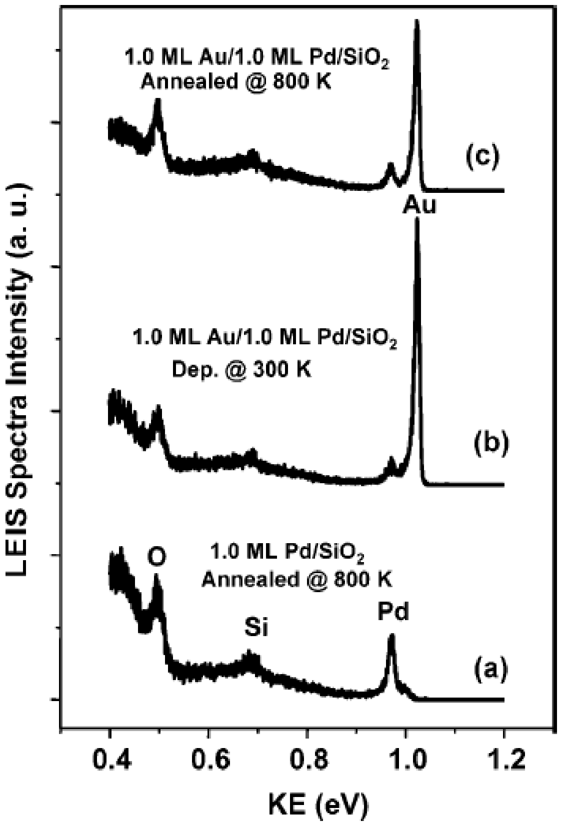
EPSRC

Science & Technology Facilities Council

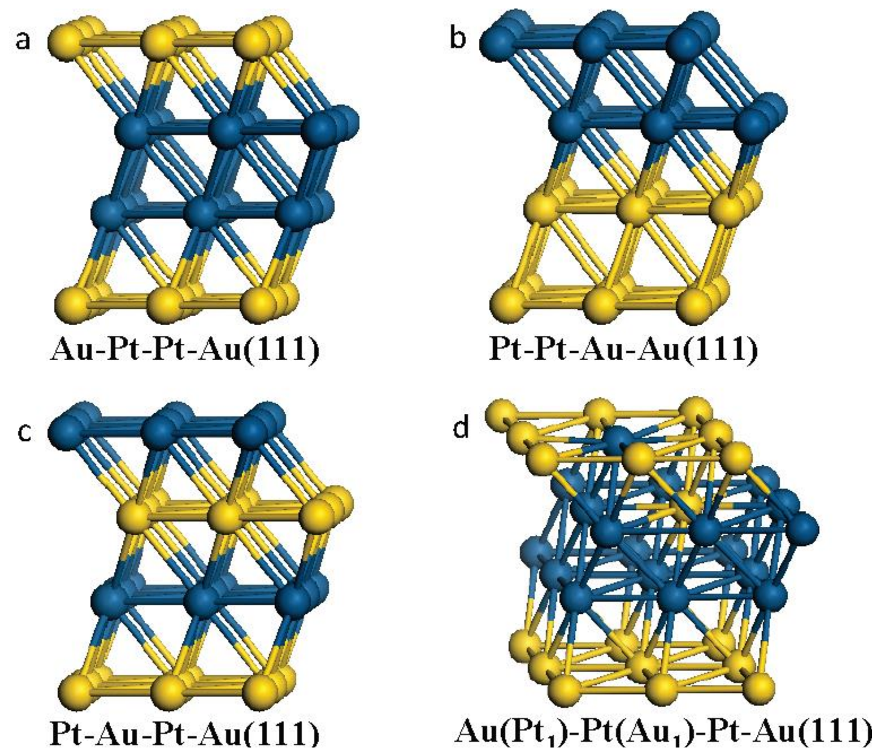
The Knut and Alice Wallenberg Foundation

Surface composition of bimetallic particles on oxide supports

EXPERIMENT



THEORY



- Detailed composition of surface of particles on planar oxide supports from LEIS
- Segregation phenomena well described by DFT etc

K. Luo, T. Wei, C.W. Yi, S. Axnanda, D.W. Goodman, Journal of Physical Chemistry B **109** (2005) 23517

S.A. Tenney, J.S. Ratliff, C.C. Roberts, W. He, S.C. Ammal, A. Heyden, D.A. Chen, Journal of Physical Chemistry C **114** (2010) 21652