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Clusters on surfaces:
Matter in the non-scalable size regime

Ulrich HEIZ
Technical University of Munich
Lehrstuhl fuer Physikalische Chemie 1
Lichtenbergstrasse 4
85748 Garching
GERMANY

These are preliminary lecture notes, intended only for distribution to participants
Clusters on Surfaces: Matter in the Non-Scalable Size Regime

Ulrich Heiz, Lehrstuhl für Physikalische Chemie 1
Technische Universität München
Outline

Introduction:
- Nanoparticles: The scalable size regime
- Clusters: The non-scalable size regime

Experimental Techniques

Guiding Principles for Understanding Cluster Chemistry
Mendelejev, Dmitri Ivanovitsj

8. Feb. 1834 (Tobolsk) - 2 Feb. 1907 (St. Petersburg)

In ´On the Relation of the Properties to the Atomic Weights of the Elements´, received by the Russian Chemical Society in 1869.

Mendelejev’s Periodic Table

<table>
<thead>
<tr>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
<th>Group IV</th>
<th>Group V</th>
<th>Group VI</th>
<th>Group VII</th>
<th>Group VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reihen</td>
<td>R^+O</td>
<td>RO</td>
<td>R^2O^3</td>
<td>RH^+</td>
<td>RH^+</td>
<td>RH^+</td>
<td>RH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P: 11  N: 12

11  (Au = 199)
12  -  -  -  Th = 231  -  U = 240  -  -  -  -
The 3rd Dimension of the Periodic Table
Non-Scalable - Scalable Size Regime

Vertical detachment energies

Observable

Solid

Nanoparticle:
Scalable size range

Cluster:
Non-scalable size range

Clustersize N

0 50 100 150 200
Scaling Laws

• In the regime of large sizes ($N > \sim 100$), many particle properties (e.g. ionization energy, electron affinity, melting temperature and cohesive energy) show a smooth variation with cluster size.

• The following scaling laws apply for a general property ($G$)

$$G(R) = G(\infty) + aR^{-\alpha}$$

$$G(N) = G(\infty) + bN^{-\beta}$$

Usually $\alpha = 1, \beta = 1/3$. 
Examples

- Ionization energies of potassium nanoparticles \((N \leq 100)\):

  \[
  IP(R)/eV = 2.3 + 5.35(R/\text{Å})^{-1}
  \]

  \[
  IP(N)/eV = 2.3 + 2.04N^{-\frac{1}{3}}
  \]

- Melting temperatures of gold nanoparticles:

  \[
  T_m(R)/K = 1336.15 - 5543.65(R/\text{Å})^{-1}
  \]
The Scalable Size Regime: Nanoparticles of Sodium (Na\(_n\) with \(n>2000\))

\[
\text{IP}(R) = W_{\text{inf}} + \frac{3}{8} \cdot \frac{e^2}{R}
\]

E. Schumacher, U. Heiz et al. 
Chimia 42 (1988) 357-376
Nanoparticle’s Periodic Table: Geometric Shells

<table>
<thead>
<tr>
<th>Shell (K):</th>
<th>Open Shells</th>
<th>Closed Shells</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Na\textsubscript{2870}</td>
<td>Na\textsubscript{3871}</td>
</tr>
<tr>
<td>12</td>
<td>Na\textsubscript{3872}</td>
<td>Na\textsubscript{5083}</td>
</tr>
<tr>
<td>13</td>
<td>Na\textsubscript{5084}</td>
<td>Na\textsubscript{6525}</td>
</tr>
<tr>
<td>...</td>
<td>Na\textsubscript{12431}</td>
<td>Na\textsubscript{14993}</td>
</tr>
<tr>
<td>17</td>
<td>Na\textsubscript{12432}</td>
<td>Na\textsubscript{14994}</td>
</tr>
<tr>
<td>18</td>
<td>Na\textsubscript{14995}</td>
<td>Na\textsubscript{17885}</td>
</tr>
<tr>
<td>19</td>
<td>Na\textsubscript{17886}</td>
<td>Na\textsubscript{21127}</td>
</tr>
</tbody>
</table>

**N=1/3 \((10K^3-15K^2+11K-3)\)**

**Mackay Icosahedra**

*Acta Cryst.* **15** (1962) 1916
Size Effects of Nanoparticles: Some Guiding Principles

- Smooth variation of intrinsic physical properties with size
- Various facets with different plane densities:
  - different reactivities
- Different proportions of facets:
  - influence on diffusion barriers
- Different coordination numbers:
  - changing electron densities, edge effects
- Substrate effects:
  - modification at the interface
  - lattice mismatch: changing lattice parameters
- Spill-over and reverse spill-over:
  - particle size and density dependent
The Non-Scalable Size Regime: Sodium Clusters ($Na_n$ with $n < 150$)


de Heer Rev. Mod. Phys. 65 (1993) 611
### Cluster’s Periodic Table: Electronic Shells

<table>
<thead>
<tr>
<th>Shell</th>
<th>Monovalent</th>
<th>Closed shells</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>Na</td>
<td>Na₂</td>
</tr>
<tr>
<td>1p</td>
<td>Na₃ Na₄</td>
<td>Na₇ Na₈</td>
</tr>
<tr>
<td>1d</td>
<td>Na₉ Na₁₀</td>
<td>Na₁₇ Na₁₈</td>
</tr>
<tr>
<td>2s</td>
<td>Na₁₉</td>
<td>Na₂₀</td>
</tr>
</tbody>
</table>

*Shell Closed shells

- Monovalent
- Closed shells
Photoelectron spectra of Na\textsubscript{n} (n=31-60) obtained with a photon energy of 6.42 eV. The peak labels give the quantum numbers of the corresponding electron shells. Closed shells are observed at:

- \( \text{Na}_{35}^+ \) (34 electrons): 1f
- \( \text{Na}_{41}^+ \) (40 electrons): 2p
- \( \text{Na}_{59}^+ \) (58 electrons): 1g

Ion mobility measurements and *ab initio* calculations reveal gold clusters to be planar up to $\text{Au}_n$ with $n \sim 10$ for the cations and $n \sim 13$ for the anions.

Strong relativistic effects in gold are responsible for these unique geometric structures.

Many clusters reveal several energetically close lying isomers. At finite temperatures these isomeric structures can be populated and interconvert into each other.

# Dynamic structural fluxionality

Cluster Properties

- Distinct, strongly size-dependent, electronic structures
- Strong impurity doping effects
- Unique structures, non-comparable to crystallites
- Manifold of energetically close-lying isomers
- Strong structural fluxionality
- Electronic and geometrical structure highly dependent on oxidation state
- Unique and size-dependent, magnetic properties
Experimental Techniques

YAG Laser

Q-mass for size-separation

Analysis chamber

Cluster source
Experimental Techniques: Cluster Preparation

**Analysis Chamber**

- FT-IR spectrometer
- Liq. N$_2$
- Electron energy analyzer for Auger/MIES/XPS
- Einzel lens
- Quadrupole mass filter
- Quadrupole deflector
- YAG laser (100 Hz)

**Cluster Source**

- Pulsed valve for He gas
- Octopole ion guide

**Mass Separation**

- Substrate MgO(100)/Mo(100)
- Molecular doser
- Pulsed valve driven by piezoelectric device

**Other Details**

- ~10^{-10} Torr (base)
- ~10^{-2} Torr
**Preparation:**

Epitaxially grown on Mo(100) or Ag(001) by evaporation of Mg in $10^{-6}$ Torr O$_2$ at RT.


**Characterization:**

- **HREELS**
- **LEED**
- **EELS, $E_p = 30$eV**
- **Detection of F-centers**


*Schaffner et al. Surf. Sci. 417 (1998) 159*
Typical cluster densities: $10^{-12} - 10^{-13}$ clusters/cm$^2$

- Detection limit of many classical surface science techniques!

**Integral methods:**
- Temperature programmed desorption
- Temperature programmed reaction
- Fourier transform infrared
- Electron energy loss
- Ion surface scattering
- X-ray photoelectron spectroscopy
- Ultraviolet photoelectron spectroscopy
- Metastable impact electron spectroscopy
- X-ray magnetic dichroism

**Local methods:**
- Scanning tunneling microscopy
- Scanning tunneling spectroscopy
- Atomic force microscopy
Experimental conditions:

- $p_{O_2} = 5 \times 10^{-7}$ mbar
- $p_{CO}(max) \sim 1 \times 10^{-3}$ mbar
- Repetition rate = 0.1 Hz
- $\Delta t_{pulse} = 0.07$s

Beam profile:
- 8 mm (diameter of crystal)

Time profile:
- ~70 ms
- Maximal local $p$: $1 \times 10^{-3}$ mbar

Experimental Techniques: Pulsed Molecular Beam Reactive Scattering

\[ \text{TOF} = \frac{C_{\text{calib}} \times \int_{\text{peak}} I_{CO_2}}{n[Pd_n] \times \Delta t_{pulse}} \]
Experimental Techniques: Microcalorimetry

1 mm

ON

5 mm

OFF

\[ \dot{Q} \]
Experimental Techniques: Microcalorimetry

Cantilever response to the reactive gases

[Graph showing cantilever deflection over time]
Experimental Techniques: Microcalorimetry

1% ML Pdn
H₂ Pulses
Isotropic pressure of C₄H₆

Total Released Heat
Development of a highly sensitive microcalorimeter
- Sensitive to temperature changes of \(~10^{-3} \) K
- 100 nWatt sensitivity
- Response time \(~ 0.1 - 1 \) ms
- 10 pJoule sensitivity

Study of cluster deposition
- Binding/rearrangement heats

Study of binding energies of adsorbates

Study of reaction heats on clusters on surfaces
Experimental Techniques: Cavity Ringdown Spectroscopy

- $\Lambda_0$: Intrinsic loss of the cavity (transmission of the mirror, surface scattering, ...)
- $\Lambda_s$: Additional loss due to the absorption of light by the sample

$$\tau_0 = \frac{L}{c\Lambda_0}$$

$$\Lambda_s = \frac{L}{c} \left( \frac{1}{\tau_s} - \frac{1}{\tau_0} \right)$$

$$\tau_s = \frac{L}{c(\Lambda_0 + \Lambda_s)}$$
Experimental Techniques:
Cavity Ringdown spectroscopy


Photon Energy [eV]
Loss per pass [ppm]
Experimental Techniques:
Cavity Ringdown spectroscopy

- Softlanding of size-selected clusters
- Characterization of trapping sites
- Characterization of atomic and molecular transitions
- Information of cluster structure
- Transition from atom to bulk
When Gold is not Noble

Structural, Electronic, and Impurity-Doping Effects in Nanoscale Chemistry: Supported Gold Nanoclusters

Charging Effects on Bonding and Catalyzed Oxidation of CO on Au₈ Clusters on MgO

Stéphane Abbet, Ken Judai, Anke Wörz, Jean-Marie Antonietti and Ueli Heiz

Technical University of Munich, Lehrstuhl für Physikalische Chemie, D-85747 Garching

Hannu Häkkinen, Bokwon Yoon and Uzi Landman

Georgia Institute of Technology, School of Physics, Atlanta, Georgia 30332-0430


Science 307 (2005) 403
Why is gold noble in the solid state?

Typical DOS of Metals

Why is gold noble?

Coupling of Molecular State with DOS of Metal

LDOS projected onto the \( p_x \) state of adsorbed oxygen (Dark Area)

Hammer et al., Nature 376 (1995) 238
Gold Nanocatalysts

Scalable Size Range
- Potent perimeter sites

Non-Scalable Size Range
- Sticky side
- Nonmetallic “molecule”
- Extra electron

SCIENCE, 14 March 2003
Formation of CO$_2$ on Supported Gold Clusters

$^{13}$C$^{16}$O$^{18}$O$^+$ Signal [a.u.]

Temperature [K]

0.17 % ML

$^{13}$C$^{16}$O$^{18}$O$^+$ Signal [a.u.]

Temperature [K]
1. Guiding Principle

Each Atom Counts!
Comparison to Reactivity of Free Gold Cluster Anions

Note: No \( \text{O}_2 \) adsorption on neutral and cationic gold clusters!
Reaction Mechanism of the CO Combustion on Free \( \text{Au}_2^- \)

Elementary steps needed to fit data

\[
\begin{align*}
\text{Au}_2^- + \text{O}_2 & \rightarrow \text{Au}_2\text{O}_2^- & k_1 \\
\text{Au}_2\text{O}_2^- + \text{CO} & \leftrightarrow \text{Au}_2(\text{CO})\text{O}_2^- & k_{2,3} \\
\text{Au}_2(\text{CO})\text{O}_2^- + \text{CO} & \rightarrow \text{Au}_2^- + 2\text{CO}_2 & k_4
\end{align*}
\]

with \( k_{1-4} \) pseudo first order rate constants (pressure dependent).

J. AM. CHEM. SOC. 2003, 125, 10437
Catalytic Turn-Over Frequency (TOF)

2 nm gold particles at 273 K: TOF = 0.2 s$^{-1}$ per Au atom (Haruta et al.)
3.5 nm gold particles at 350 K: TOF = 4 s$^{-1}$ per Au atom (Goodman et al.)

TOF $\approx 0.6 \text{ CO}_2$ molecules per gold cluster per second
2. Guiding Principle

Free Clusters May Behave Differently Than Supported Clusters

Steric Hindrance

Change of Electronic Structure
Reactivity of Free and Supported Nanoscale Gold

- Adsorption of $O_2$ on free Clusters
- Combustion of CO on supported Clusters

Electron binding energy [eV]

Reactivity [a.u.]

Temperature [K]

$^{13}C$ $^{16}O$ $^{18}O$ Signal [a.u.]

0.17 % ML

$Au_{\text{Film}}$

$Au_{20}$

$Au_{18}$

$Au_{12}$

$Au_{9}$

$Au_{8}$

$Au_{7}$

$Au_{6}$

$Au_{2}$
Influence of Defect Sites: 
$\text{Au}_8$ on $\text{MgO(100)}$ F-centers

$^{13}\text{C}^{16}\text{O}^{18}\text{O}^+$ Ion Signal [a.u.]

Transmittance [%]

$\text{Au}_8/\text{MgO(100)}_{\text{defect-rich}}$

Temperature [K]

Wavenumbers [cm$^{-1}$]

$330 \degree K$

$280 \degree K$

$220 \degree K$

$13\text{CO}$

$2055$

$2049$

$2053$

$2070$

$2118$

$2000$

$2200$

$2400$

$100 \degree K$

$160 \degree K$

$140 \degree K$

$100 \degree K$

$120 \degree K$

$110 \degree K$

$100 \degree K$

$102,020,300,400,500,600,700,800$

$B. \ Yoon, \ H. \ Häkkinen, \ U. \ Landman, \ A. \ Wörz, \ J.-M. \ Antonietti, \ S. \ Abbet, \ K. \ Judai, \ U. \ Heiz, \ Science \ 307 \ (2005) \ 403$
Theoretically Proposed Structure

$^{13}$CO/Au$_8$/MgO(FC):

$\nu_{\text{theor.}}: 2018 \text{ cm}^{-1}$ (1)
$\nu_{\text{theor.}}: 1931 \text{ cm}^{-1}$ (2)
$\nu_{\text{theor.}}: 2004 \text{ cm}^{-1}$ (3)

$\nu_{\text{CO/MgO}}: 2118 \text{ cm}^{-1}$
Influence of Defect Sites: 
\( \text{Au}_8 \text{ on MgO(100)} \)

Redshift induced by F-center: 
\( \Delta \nu = 30-50 \text{ cm}^{-1} \)
CO bonding on Au$_8$O$_2$/MgO (FC)

CO on Au$_8$O$_2$/MgO:
1.18 e$^-$

CO on Au$_8$O$_2$/MgO:
1.27 e$^-$
CO bonding on $\text{Au}_8\text{O}_2$/MgO(FC)

CO-bonding via backdonation into $2\pi^*$ and donation of $5\sigma$ into cluster
Effect of F Centers: Cluster Charging

\[ \Delta v_{\text{exp.}}(\text{cm}^{-1}): 30-50 \]

<table>
<thead>
<tr>
<th>( \Delta Q \text{ Au}_8\text{O}_2^{13}\text{CO} )</th>
<th>spin</th>
<th>( \Delta v_{\text{theor.}}(\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>0.875</td>
<td>18</td>
</tr>
<tr>
<td>0.5</td>
<td>0.75</td>
<td>37</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>34</td>
</tr>
</tbody>
</table>

\[ \Delta Q = 0.5 \]
Effect of F Centers: Cluster Stabilization

- Strong binding between cluster and F-center; 3.4 eV in comparison to 1.2 eV on regular terrace sites.
- Charge transfer to the cluster: \( \sim 0.5 \) e\(^{-}\)
CO-Oxidation on Au$_n$ on TiO$_2$
3. Guiding Principle

Cluster-Support-Interaction:

- Stabilization
- Charging
Why is Gold Active at low Temperatures?
Effect of F centers: Activation of \(O_2\) (peroxo state)
Comparison with Gas Phase Studies

Experimental Evidence of Molecular $O_2$ Adsorption

Stolcic, Fischer, Ganteför, Kim, Sun and Jena

4. Guiding Principle

Unique Activation of Reactants on Clusters!
Identification of possible Reaction Mechanisms
Oxidation of CO on Au₈ Bound to Defect-Poor and Defect-Rich MgO (100) Surfaces

Langmuir-Hinshelwood-Periphery Mechanism

Adsorption by reverse spill-over

Initial State

Transition State

Final State

Reaction Coordinate d(C-O₁)

\[ \sim 0.5 \text{ eV} \]

\[ [\sim 0.8 \text{ eV}] \]

4.5 Å  2.0 Å

A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Hakkinen, R. N. Barnett, Uzi Landman

J. Phys. Chem. A 1999, 103, 9573
Langmuir-Hinshelwood-Top Mechanism

**Oxidation of CO on Au₈ Bound to Defect-Poor and Defect-Rich MgO (100) Surfaces**

- **Initial State**: Direct Adsorption
- **Transition State**: ~ 0.1 eV
- **Final State**: 3.1 Å, 2.0 Å

**Reaction Coordinate d(C-O₁)**
Dynamic Structural Fluxionality

\[
\text{Au}_8 + \text{O}_2 + 2 \text{CO} \quad \text{Au}_8/\text{O}_2 \quad \text{Au}_8/\text{O}_2/(\text{CO})_2 \quad \text{Au}_8 + 2 \text{CO}_2
\]

Reaction Coordinate

Energy
Dynamic Structural Fluxionality
Evolution of Reactivity with Size and Elemental Composition

- Evolution of Reactivity with Size
  - Adsorption of O\(_2\)
  - Combustion of CO on supported Clusters

- Electron binding energy [eV]
  - Size evolution

- Reactivity [a.u.]

- Temperature [K]
Activation by Impurity Doping
Understanding Size-Evolution of the Reaction
Gold Cluster Reactivity

Cluster deposition of FC/MgO(100)

- $\text{Au}_n \ (n<8)$ inert
- $\text{Au}_8$ smallest gold catalyst
- $\text{Au}_3\text{Sr}$ smallest doped cluster
- $\text{MgO}$ and $\text{Au}_{\text{film}}$ inert

When gold is not noble: Nano-scale gold catalyst.

ii. H. Häkkinen, S. Abbet, A. Sanchez, U. Heiz, and U. Landman
Structural, electronic, and impurity-doping effects in nanoscale chemistry: Supported gold nanoclusters.
Optimized Atomic Structures of Pure and Mixed Gold Nanocatalysts

B.E. 3.5 eV
\( \Delta q = 0.5 \)

B.E. 4.1 eV
\( \Delta q = 0.3 \)

B.E. 2.7 eV
\( \Delta q = 0.3 \)

B.E. 0.7 eV
\( r_{O2} = 1.44 \text{ Å} \)

B.E. 0.2 eV
\( r_{O2} = 1.28 \text{ Å} \)

B.E. 1.9 eV
\( r_{O2} = 1.37 \text{ Å} \)

Peroxo

Molecular

Superoxo
Au₈/Mg(100)/FC: LDOS Projected on the O₂ Molecule and the Metal Part
Au$_4$, Au$_3$Sr/Mg(100)/FC: LDOS Projected on the O$_2$ Molecule and the Metal Part
6. Guiding Principle

Electronic Structure (Au₈, Au₄, Au₃Sr) Impurity Doping Effects
Heterogeneous Catalysis

Vital Role of Moisture in the Catalytic Activity of Supported Gold Nanoparticles**

Masakazu Datê,* Mitsutaka Okumura, Susumu Tsubota, and Masatake Haruta

Why can inert gold become catalytically active only when dispersed in the form of nanoparticles?—This simple question has attracted growing interest in the field of not only catalytic and industrial chemistry,[1–4] but also cluster and theoretical science.[5–7] To answer this question, CO oxidation has been intensively studied as a model reaction.[8–14] The reaction is known to be greatly influenced by moisture in the reactant gas.[10,15] However, only a few recent studies discuss the reaction mechanisms taking water into account.[16,18] Even in these studies on the effect of moisture, for practical reasons, the addition of water vapor has been examined only at high concentrations.
**Figure 2.** Turnover frequencies per surface gold atom at 273 K for CO oxidation over a) Au/TiO$_2$, b) Au/Al$_2$O$_3$ and c) Au/SiO$_2$ as a function of moisture concentration. Upright arrow indicates the saturation of CO conversion.
Mechanism Predicted by Theory

Angelo Bongiorno & Uzi Landman

Cooperative Adsorption of $\text{H}_2\text{O}$ and $\text{O}_2$

TABLE I. Energies (in eV) for the adsorption and coadsorption of $\text{O}_2$ and $\text{H}_2\text{O}$ on free ($\text{Au}_8$ and $\text{Au}_{30}$) clusters and on a gold octamer supported on MgO(100), i.e. $\text{Au}_8$/MgO. In the case of the $\text{Au}_8$/MgO system, results are given for both the adsorption on the top-facet of the gold cluster cluster (-T) and at the peripheral interface of the cluster with the substrate (-P).

<table>
<thead>
<tr>
<th></th>
<th>$\text{O}_2$</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{O}_2\text{-H}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}_8$</td>
<td>unbound</td>
<td>$\sim0.3$</td>
<td>0.4–0.9</td>
</tr>
<tr>
<td>$\text{Au}_{30}$</td>
<td>$\leq0.4$</td>
<td>0.3–0.6</td>
<td>0.7–0.9</td>
</tr>
<tr>
<td>$\text{Au}_8$/MgO-T</td>
<td>$\leq0.1$</td>
<td>0.2–0.3</td>
<td>0.5–1.2</td>
</tr>
<tr>
<td>$\text{Au}_8$/MgO-P</td>
<td>0.3–0.8</td>
<td>0.4–0.6</td>
<td>1.3–2.1</td>
</tr>
</tbody>
</table>
7. Guiding Principle

Cooperative Adsorption and Activation by Coadsorbants
Chemical Properties in the Nonscalable Size Regime: Reverse Spill-Over

(a) \[ T = 147K \quad T = 327K \quad T = 351K \]
(b) \[ T = 377K \quad T = 450K \quad T = 709K \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{LH} ) [kJ/mol]</th>
<th>Conditions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>105 59</td>
<td>Low O(_2) cov., T&gt;500K high O(_2) cov., T&lt;420K</td>
<td>[18]</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>45 – 64</td>
<td>High O(_2) cov., T&lt;500K</td>
<td>[17]</td>
</tr>
<tr>
<td>Pd ([a]) (27nm)</td>
<td>32 – 45</td>
<td>High O(_2) cov., T&lt;500K</td>
<td>[13]</td>
</tr>
<tr>
<td>Pd ([b]) (5-6nm)</td>
<td>57 ± 8 62 ± 9</td>
<td>CO rich regime, low T O rich regime, low T</td>
<td>[17]</td>
</tr>
<tr>
<td>Pd ([a]) (2.5nm)</td>
<td>19 - 20</td>
<td>High O(_2) cov., T&lt;500K</td>
<td>[13]</td>
</tr>
<tr>
<td>Pd(_{30}) ([c])</td>
<td>36 ± 3</td>
<td>O saturated, T&lt;400K</td>
<td></td>
</tr>
<tr>
<td>Pd(_8) ([c])</td>
<td>25 ± 3</td>
<td>O saturated, T&lt;400K</td>
<td></td>
</tr>
</tbody>
</table>
Chemical Properties in the Non-scalable Size Regime: Reverse Spill-Over

Reaction probability: TOF normalized by total flux.
Low cluster coverage: High contribution of reverse spill-over (F_{diff})

Pd_8: No discrimination between F_{direct} and F_{flux} → a) identical activation energies at periphery and on cluster; b) no diffusion barrier at periphery.
Pd_{30}: F_{diff} less effective for reactivity → a) different activation barriers at periphery and on cluster; b) high diffusion barrier at periphery.

≠ Effect of reverse spill-over is size dependent!
8. Guiding Principle

Effect of Reverse Spill-Over is Cluster Size Dependent
1. Each cluster has its characteristic electronic structure: Intrinsic quantum size effects

2. Each cluster size has characteristic cluster-support interaction (stability, mobility, charging, steric effects ...)

3. Clusters are fluxional: Low-temperature reactivity

4. Effect of reverse spill-over is size dependent
Thank You

**Present team:**

Dr. M. Arenz  
Dr. S. Gilb  
Dr. M. Michalski  
Dr. M. Pivetta  
M. sc. V. Habibpour  
M. sc. A. Kartouzian  
dipl. chem J. Kungl  
dipl. chem. M. Röttgen  
dipl. phys. V. Teslenko  
Katrin Hartl

**Former collaborators:**

Dr. S. Abbet  
Dr. J.-M. Antonietti  
Dr. A. Sanchez  
Dr. F. Vanolli  
Dr. A. Wörz  
dipl. phys J. Gong

**Present collaborations:**

Prof. U. Landman  
Dr. H. Häkkinen  
Prof. G. Pacchioni & coworkers  
Prof. C. Henry  
Prof. Ch. Gerber  
Prof. L. Wöste  
Dr. Th. Bernhardt  
Prof. V. Kempter  
Prof. H. Jones  
Dr. H.-G. Boyen  
Prof. P. Ziemann  

(Simulations)

(Pulsed molecular beams)

(Microcalorimetry)

(Gas phase reactivities)

(Metastable impact spectroscopy)

(Cavity ring-down spectroscopy)

(Nanocrystals)

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Post-Doctoral Position in Cluster Chemistry and Surface Science at the Technical University of Munich

A post-doctoral position is available in the group of Prof. Ueli Heiz at the Technical University of Munich in the field of Cluster Chemistry and Surface Science. In this project the size evolution of the chemical and catalytic properties of size-selected clusters at oxide surfaces will be studied by state-of-the-art surface science techniques (microcalorimetry, pulsed molecular beams, Fourier transform infrared spectroscopy, thermal desorption and reaction spectroscopy, metastable impact electron spectroscopy). There is an exceptional infrastructure available in the group to study other properties of nanostructures at surfaces as for instance with local probes or cavity ringdown spectroscopy. In addition, the Technical University of Munich offers a very active and stimulating scientific environment.

The successful candidate is expected to have experiences in at least one of the used experimental techniques as well as in UHV technology. The position is open in September 2006 and can be occupied for one year with an option of a second year.

Further details are available from Dr. Matthias Arenz (matthias.arenz@mytum.de) or Prof. Ulrich Heiz (ulrich.heiz@mytum.de), Lehrstuhl für Physikalische Chemie, Technische Universität München, Germany.