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## Spring College on Computational Nanoscience

*17 - 28 May 2010*

# Catalytic properties of nanoscale gold

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# Catalytic properties of nanoscale gold

Hannu Häkkinen
Lecture 3
Trieste 5/2010

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## Chemical and catalytic properties of gold clusters

- Bulk gold inert
- Finely dispersed gold (as nanoparticles) catalytically active, for review see eg. Haruta, Catal. Today **36**, 153 (1997)
- Oxide-supported size-selected clusters catalyze CO oxidation (Yoon, Häkkinen, Landman, Wörz, Antonietti, Abbet, Judai, Heiz, Science **307**, 403 (2005))
- Active site / charge state under debate
- Known for long: gold atom chemically active in many oxidation states (rich complex chemistry)
- Gas-phase reactivity with O2: anionic gold needed, highly size-dependent reactivity
- Reactivity associated with electron transfer to O2 $\pi^*$ orbital

Gas phase

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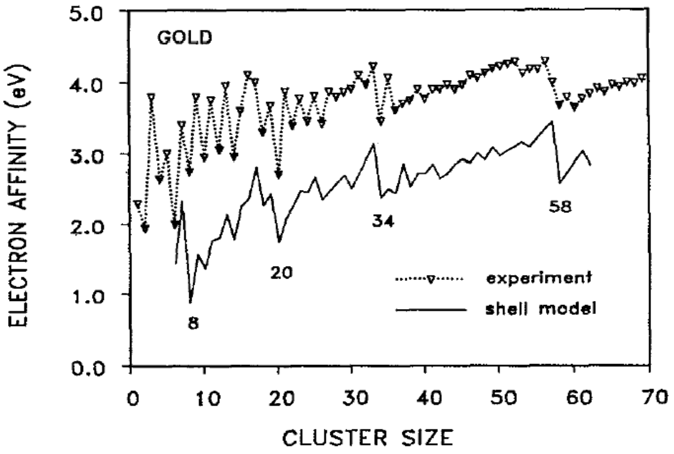
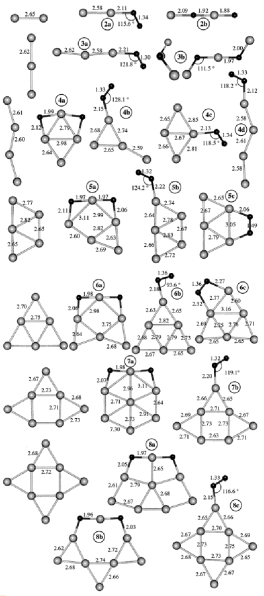
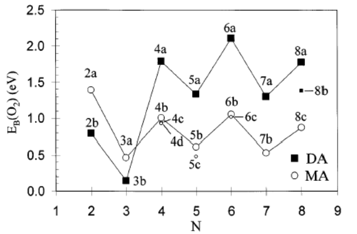
# Electron affinity of gas phase Au cluster anions from photoelectron spectroscopy



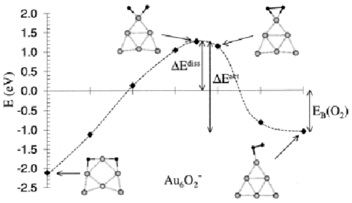
Taylor et al JCP 96, 3319 (1992)



## $Au_N^-$ anions and oxygen



Molecular adsorption for N ≤ 3
Dissociative adsorption for N > 3
High dissociation barrier !



*J. Phys. Chem. A* **2003,** *107,* 4066−4071

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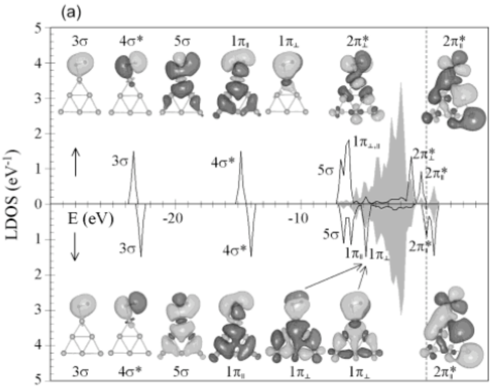
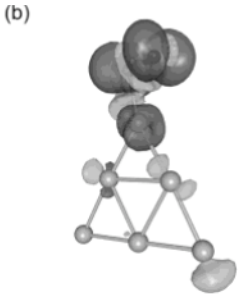
## $O_2$ is activated to superoxo-state in the $Au_6O_2^-$ complex

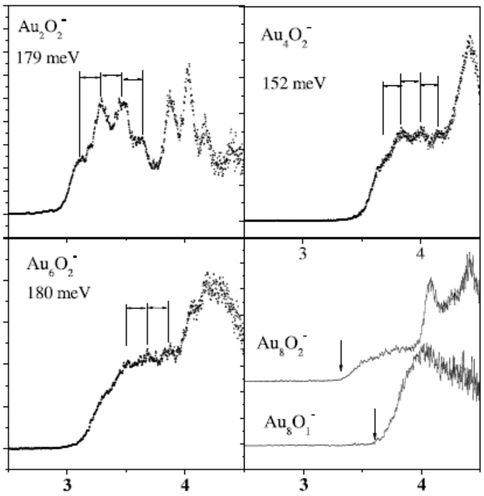


LDOS on $O_2$ part (grey area $Au_6$ part)



Spin-density

## Evidence from experiments

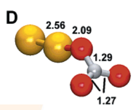


Vibrational progression of the photodetachment peak for anionic gas-phase $Au_NO_2^-$ → evidence of molecular $O_2$ adsorption for N=2,4,6 !

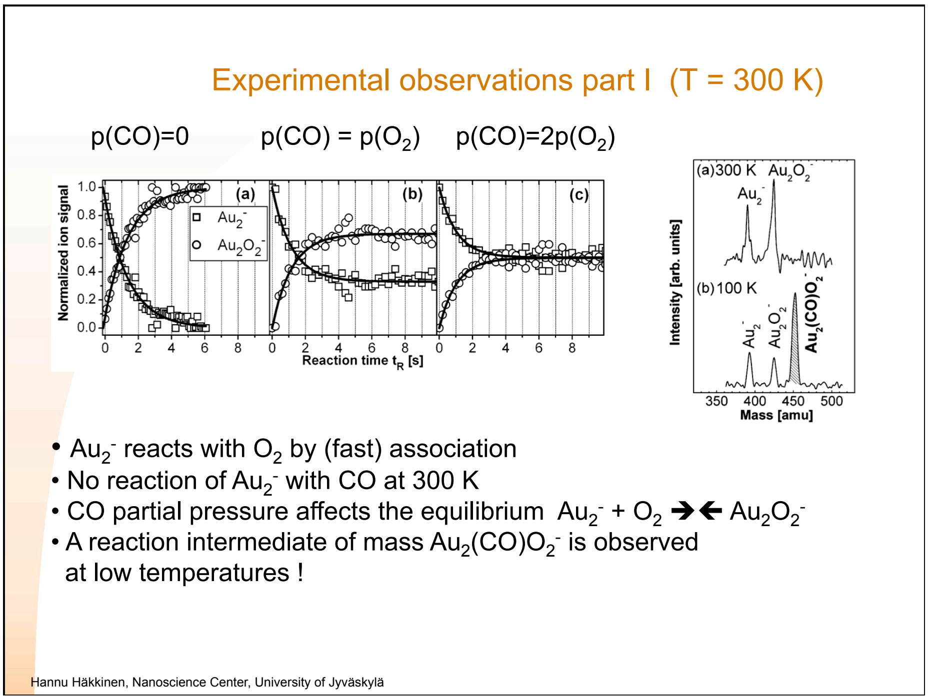
$Au_8O^-$ anion observed
→ $O_2$ can dissociate at $Au_8^-$ under exp conditions

Gantefor group
ChemPhysLet 377, 170 (2003)

## Catalytic oxidation of CO by gas-phase $Au_2^-$ Theory and Experiment (Socaciu et al, JACS 125, 10437 (2003))



- $Au_N^- + O_2 + 2CO \rightarrow (Au_NO_2^*)^- + ? \rightarrow Au_N^- + 2CO_2$
- $Au_2^-$ is the smallest non-trivial case ! Can it bind $O_2$ and CO, activate the O-O bond and produce $CO_2$?
- Theoretical prediction 2001 (Häkkinen, Landman, JACS 123, 9704): yes it can, a *carbonate* species $Au_2CO_3^-$ is the key intermediate → experimental verification?
- Experiments in FU Berlin (Wöste) in an ion trap setup
- $10^4$ mass-selected $Au_2^-$ anions per $mm^3$
- 1 Pa He buffer gas
- Controllable partial pressure of CO and $O_2$
- Temperature control 20 K – 350 K
- Steady state, kinetics, extraction of product (ions)



## Experimental observations part I (T = 300 K)

$p(CO)=0$ $p(CO) = p(O_2)$ $p(CO)=2p(O_2)$

- $Au_2^-$ reacts with $O_2$ by (fast) association
- No reaction of $Au_2^-$ with CO at 300 K
- CO partial pressure affects the equilibrium $Au_2^- + O_2 \rightarrow\leftarrow Au_2O_2^-$
- A reaction intermediate of mass $Au_2(CO)O_2^-$ is observed at low temperatures !

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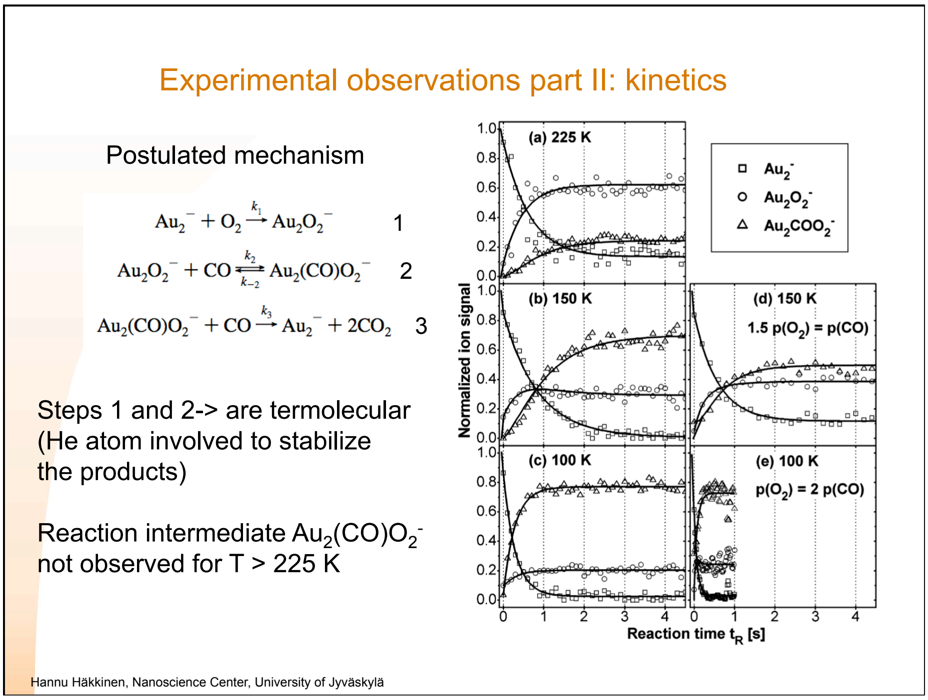


## Experimental observations part II: kinetics

Postulated mechanism

$$Au_2^- + O_2 \xrightarrow{k_1} Au_2O_2^- \quad 1$$

$$Au_2O_2^- + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Au_2(CO)O_2^- \quad 2$$

$$Au_2(CO)O_2^- + CO \xrightarrow{k_3} Au_2^- + 2CO_2 \quad 3$$

Steps 1 and 2-> are termolecular (He atom involved to stabilize the products)

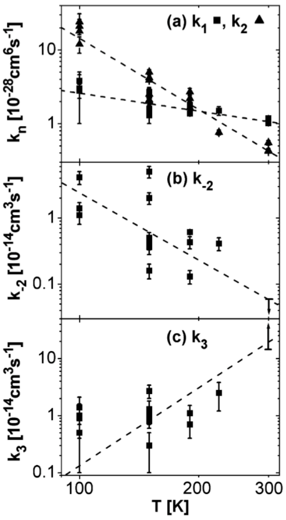
Reaction intermediate $Au_2(CO)O_2^-$ not observed for T > 225 K

## Experimental observations part III: Rate constants vs temperature

$$Au_2^- + O_2 \xrightarrow{k_1} Au_2O_2^-$$

$$Au_2O_2^- + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Au_2(CO)O_2^-$$

$$Au_2(CO)O_2^- + CO \xrightarrow{k_3} Au_2^- + 2CO_2$$



$k_1$, $k_2$: negative T-dependence !
→Barrierless reaction
(termolecular process less effective to stabilize the product at higher T)

$k_3$ has a positive T-dependence
→ Step 3 involves an activation barrier

## Calculations for the $Au_2COO_2^-$ intermediates

- Binding of $O_2$ and CO to $Au_2^-$ 1.3 eV and 0.9 eV, respectively
- Key intermediates: $AuCOO_2^-$ (C) or $AuCO_3^-$ (D)
- (C) can be formed by association of CO (gas) to $Au_2O_2^-$ by an ER mechanism without a barrier
- formation of (D) by ER mechanism involves a small barrier of 0.3 eV
- LH mechanisms (that involve CO migration on $Au_2$ part) are not favourable (large barriers)

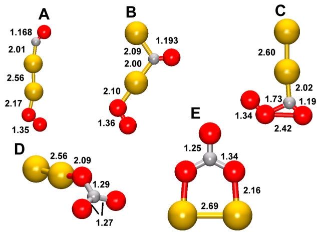
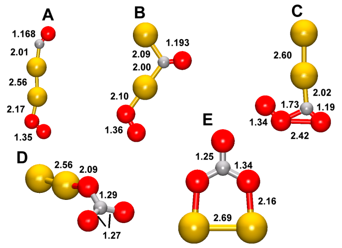


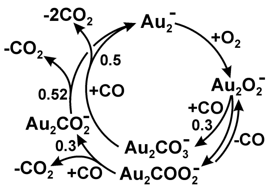
*Table 3.* Stability ($\Delta E$) Relative to the Structure Marked D (a Lower Value Corresponds to a Species of Higher Stability), Vertical Electron Detachment Energy (VDE), Binding Energy (to the Gold Dimer Anion) of CO (BE(CO), with $O_2$ Preadsorbed) and of $O_2$ (Be($O_2$), with CO Preadsorbed) for the Five Structures (A−E) of $Au_2CO_3^-$ Shown in Figure 6

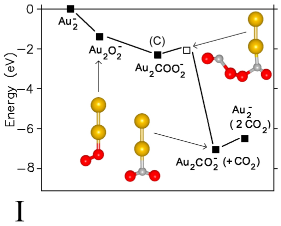
| structure | $\Delta E$ (eV) | VDE (eV) | BE(CO) (eV) | BE($O_2$) (eV) |
|---|---|---|---|---|
| A | 2.80 | 2.82 | 0.93 | 1.34 |
| B | 2.94 | 3.32 | 0.78 | 1.20 |
| C | 2.82 | 3.82 | 0.91 | 1.32 |
| D | 0 | 4.67 | 3.72 | 4.14 |
| E | 1.04 | 3.38 | 2.69 | 3.10 |

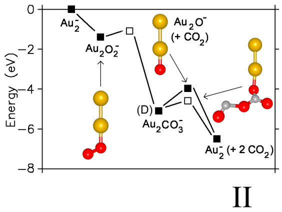
# Catalytic oxidation of CO by gas-phase $Au_2^-$ Proposed mechanisms

- Low-T activity (low barriers)
- $Au_2^-$ shares part of the negative charge with adsorbed $O_2$, stretching the O-O bond to about 1.35 Å (superoxo-state)
- Key intermediates: $AuCOO_2^-$ (C)
  or $AuCO_3^-$ (D)
- 2 scenarios I, II
- Eley-Rideal mechanisms only relevant
- LH mechanisms involve CO diffusion on gold and have too high barriers









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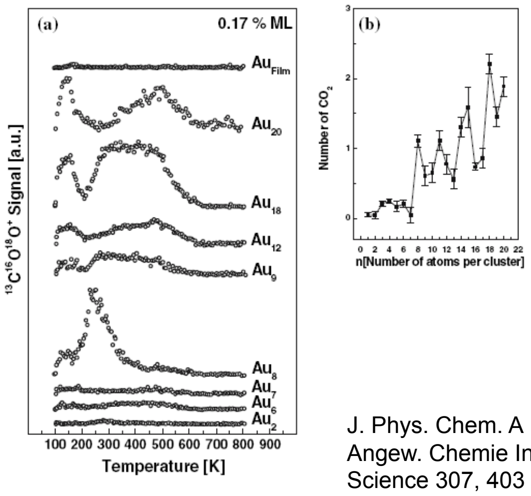
# Clusters on MgO

Temperature programmed desorption spectra for $CO_2$ formation catalyzed by mass selected Au clusters on a thick MgO film
Heiz group 1999; theory: Häkkinen, Yoon, Landman



- Deposition of CO and $O_2$ on the $Au_N$/MgO at T< 100 K
- Cluster coverage low
- ramp-up of T, record $CO_2$ signal
- TPD cycles reproducable
- Highly size-dependent catalytic activity of $Au_N$ !
- $Au_8$ is the smallest active cluster

J. Phys. Chem. A 103, 9573 (1999)
Angew. Chemie Int. Ed 42, 1297 (2003)
Science 307, 403 (2005)

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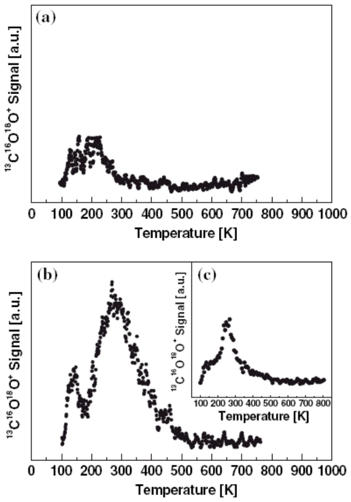
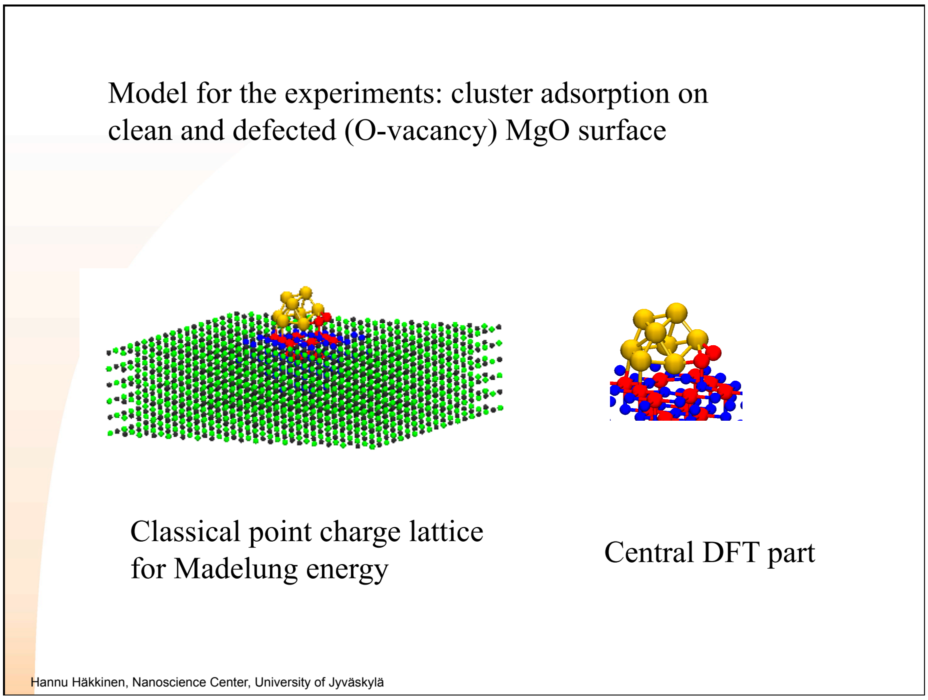
Defect-poor

Defect-rich



$Au_8$ active only on a “defect-rich” MgO support

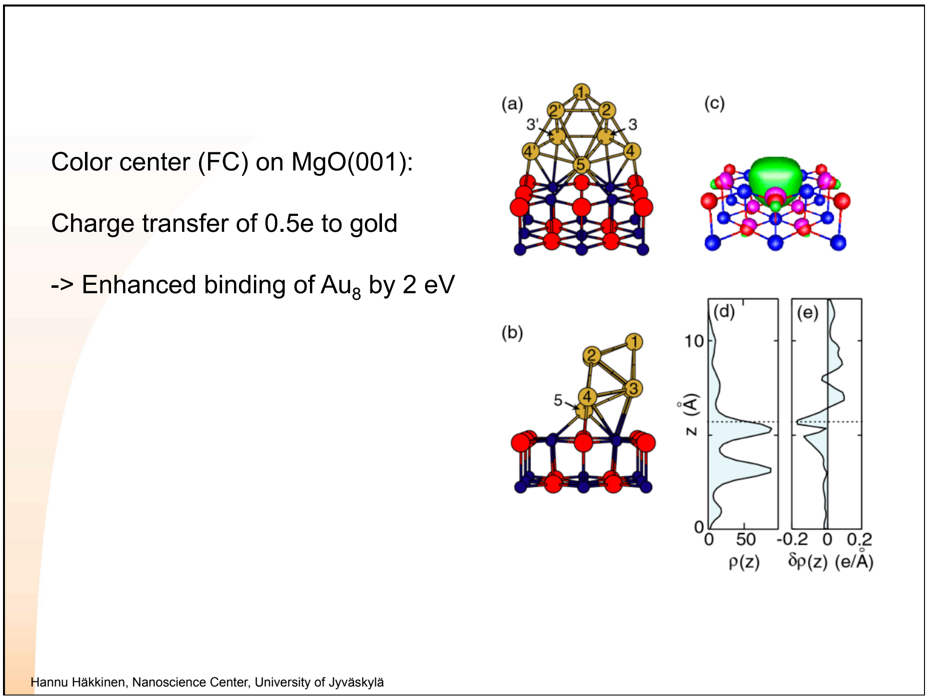
Earlier work (Heiz, Pacchioni) suggested point-like MgO surface defects



## Model for the experiments: cluster adsorption on clean and defected (O-vacancy) MgO surface

Classical point charge lattice for Madelung energy

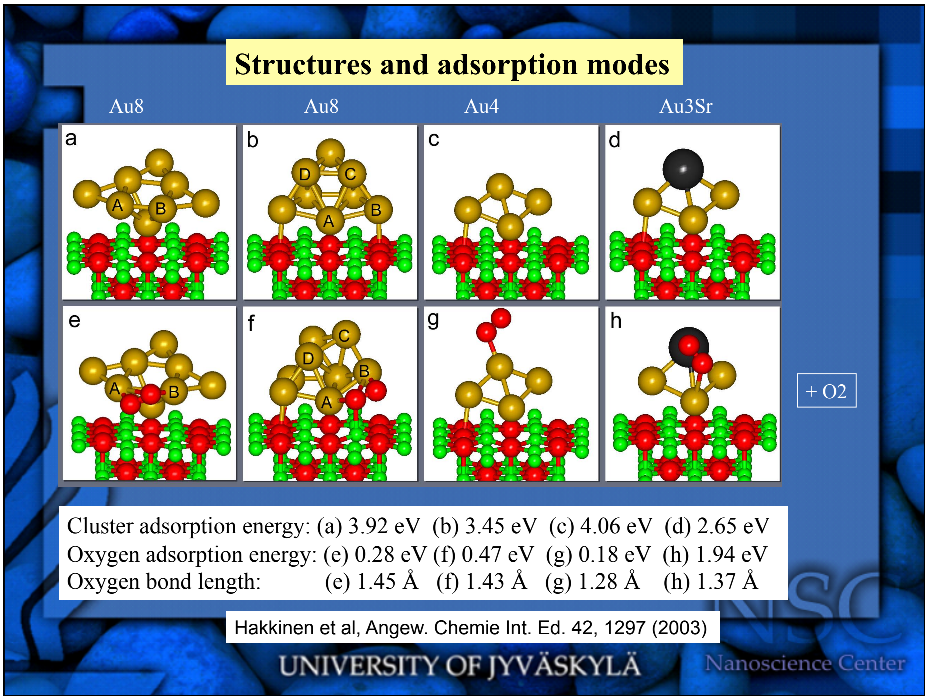
Central DFT part



Color center (FC) on MgO(001):

Charge transfer of 0.5e to gold

-> Enhanced binding of $Au_8$ by 2 eV



## Structures and adsorption modes

Cluster adsorption energy: (a) 3.92 eV (b) 3.45 eV (c) 4.06 eV (d) 2.65 eV
Oxygen adsorption energy: (e) 0.28 eV (f) 0.47 eV (g) 0.18 eV (h) 1.94 eV
Oxygen bond length: (e) 1.45 Å (f) 1.43 Å (g) 1.28 Å (h) 1.37 Å

Hakkinen et al, Angew. Chemie Int. Ed. 42, 1297 (2003)

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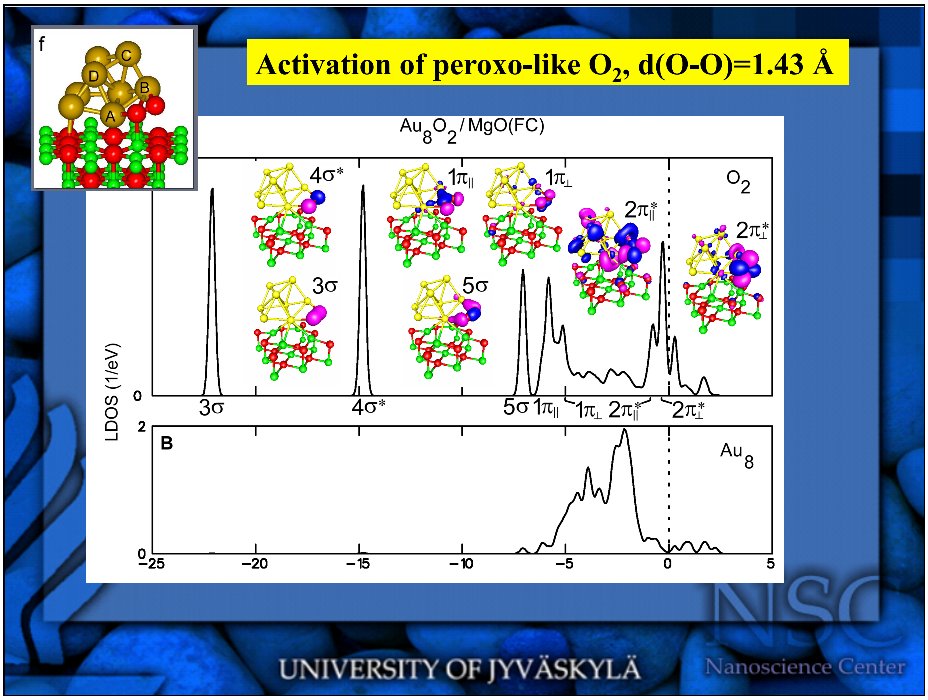

## Activation of peroxo-like $O_2$, d(O-O)=1.43 Å

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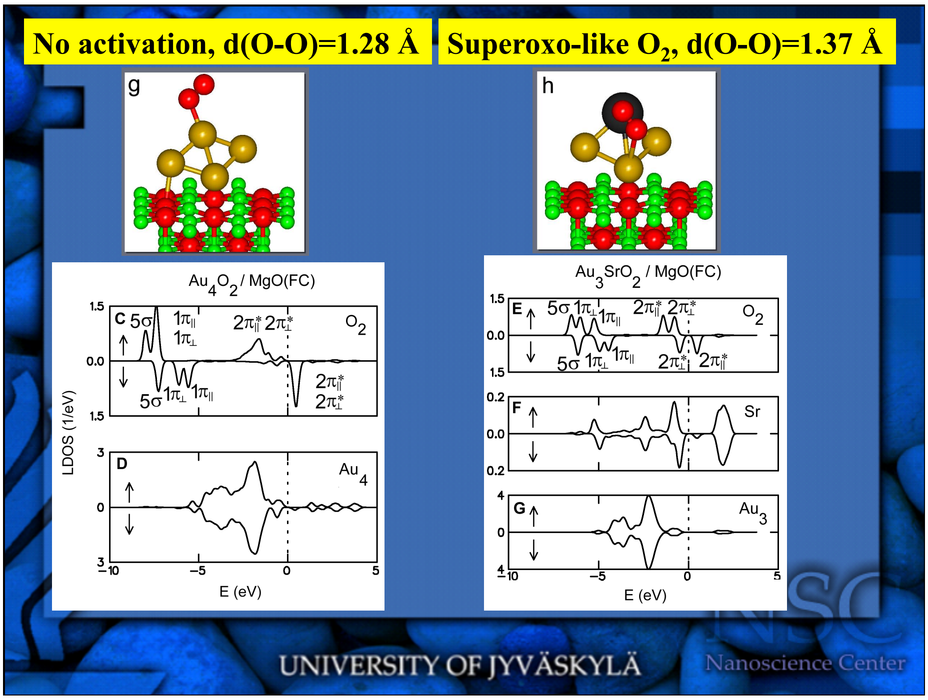
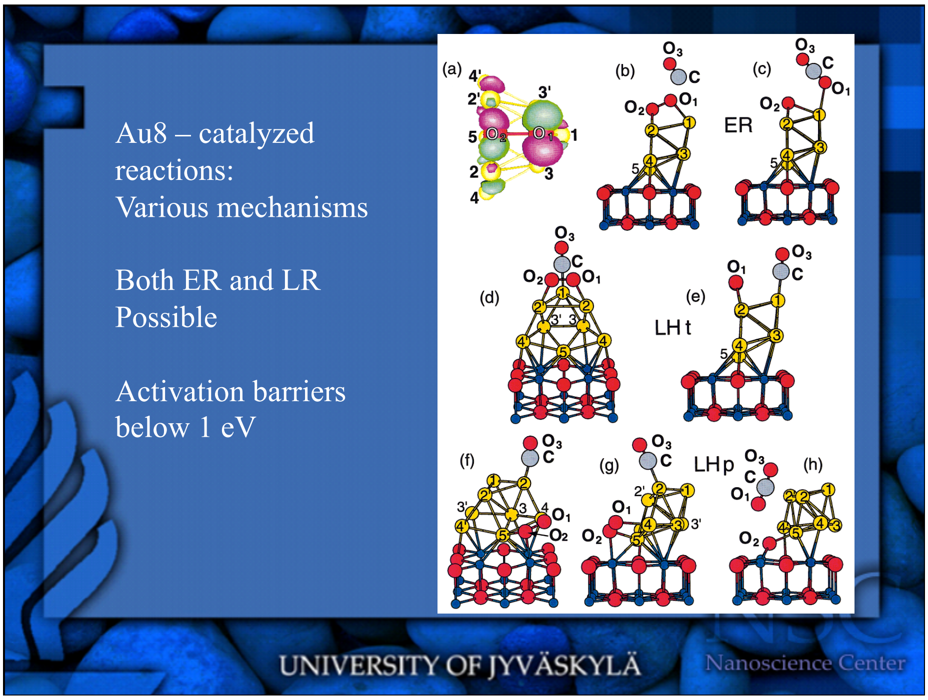


## No activation, d(O-O)=1.28 Å

## Superoxo-like $O_2$, d(O-O)=1.37 Å

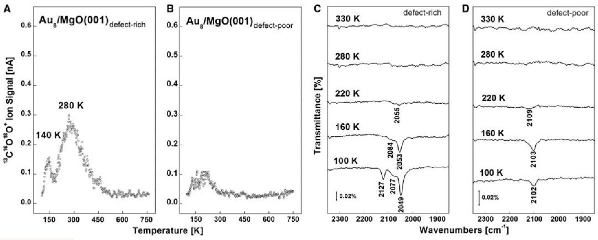


Au8 – catalyzed reactions:
Various mechanisms

Both ER and LR
Possible

Activation barriers
below 1 eV

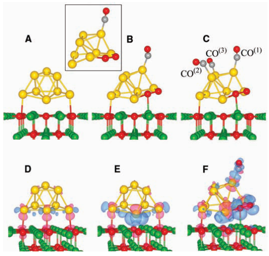
# The catalytically active $Au_8$ clusters are negatively charged !



## Charging Effects on Bonding and Catalyzed Oxidation of CO on $Au_8$ Clusters on MgO

Bokwon Yoon,[1] Hannu Häkkinen,[1]* Uzi Landman,[1]† Anke S. Wörz,[2] Jean-Marie Antonietti,[2] Stéphane Abbet,[2] Ken Judai,[2] Ueli Heiz[2]†

| | $S$ | $BE(O_2)$ (eV) | BE(CO) (eV) | $\Delta Q(Au_8/O_2/CO)$ ($e$) | $d$(CO) (Å) | $\nu$ ($^{13}CO$) ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| | | | | *F center* | | |
| A | 1 | 0.33 | 0.79 | 1.52 | 1.155 | 1937 |
| B | 0 | 0.47 | 0.65 | 1.58 | 1.156 | 1931 |
| | | | | *F-center–free* | | |
| C | 1 | 0.30 | 0.79 | 0.87 | 1.152 | 1965 |
| D | 0 | 0.15 | 0.91 | 1.01 | 1.150 | 1994 |



The calculated redshift (34 $cm^{-1}$) of the CO stretch on $Au_8$ on MgO and MgO(FC) agrees with the measured one for defect-free and defect-rich samples (25-53 $cm^{-1}$)

www.sciencemag.org SCIENCE VOL 307 21 JANUARY 2005

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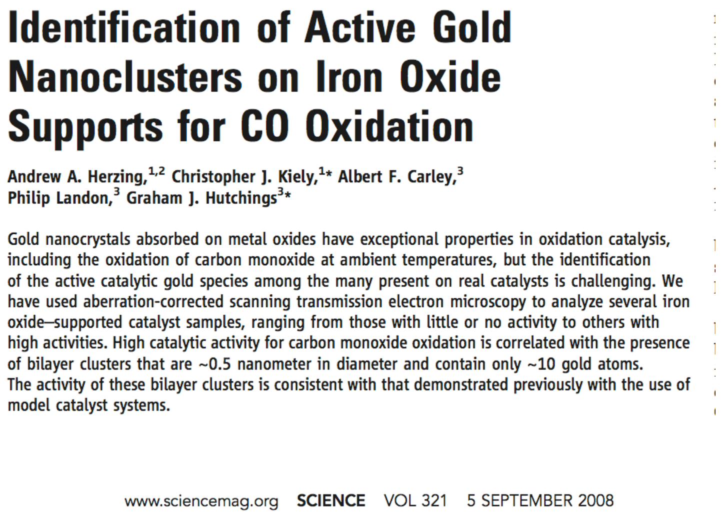
Conclusions
- strong binding to support needed
- negative charging of the cluster
- charge transfered to $O_2$ making
  it superoxo/peroxo -like
- no pre-dissociation of $O_2$ needed
  → low reaction barriers → low-T activity



# Identification of Active Gold Nanoclusters on Iron Oxide Supports for CO Oxidation

Andrew A. Herzing,[1,2] Christopher J. Kiely,[1]* Albert F. Carley,[3]
Philip Landon,[3] Graham J. Hutchings[3]*

Gold nanocrystals absorbed on metal oxides have exceptional properties in oxidation catalysis, including the oxidation of carbon monoxide at ambient temperatures, but the identification of the active catalytic gold species among the many present on real catalysts is challenging. We have used aberration-corrected scanning transmission electron microscopy to analyze several iron oxide–supported catalyst samples, ranging from those with little or no activity to others with high activities. High catalytic activity for carbon monoxide oxidation is correlated with the presence of bilayer clusters that are ~0.5 nanometer in diameter and contain only ~10 gold atoms. The activity of these bilayer clusters is consistent with that demonstrated previously with the use of model catalyst systems.

www.sciencemag.org SCIENCE VOL 321 5 SEPTEMBER 2008

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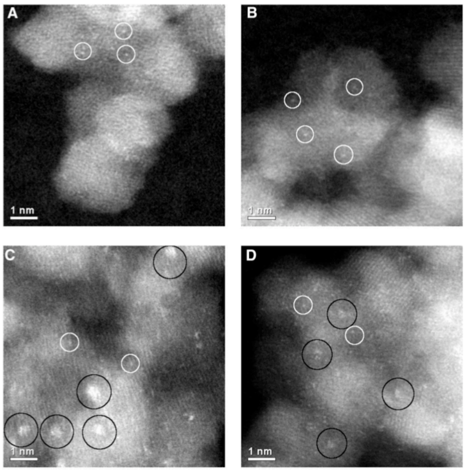

A,B inactive samples
Au atoms (white circles) and large particles

C,D active
About 10 atom clusters (dark circles)

www.sciencemag.org SCIENCE VOL 321 5 SEPTEMBER 2008

Ligand-protected Au clusters as CO oxidation catalysts?

Lopez-Acevedo et al,
Nature Chemistry 2, 329 (2010)

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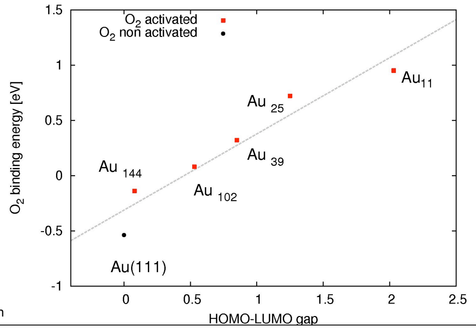
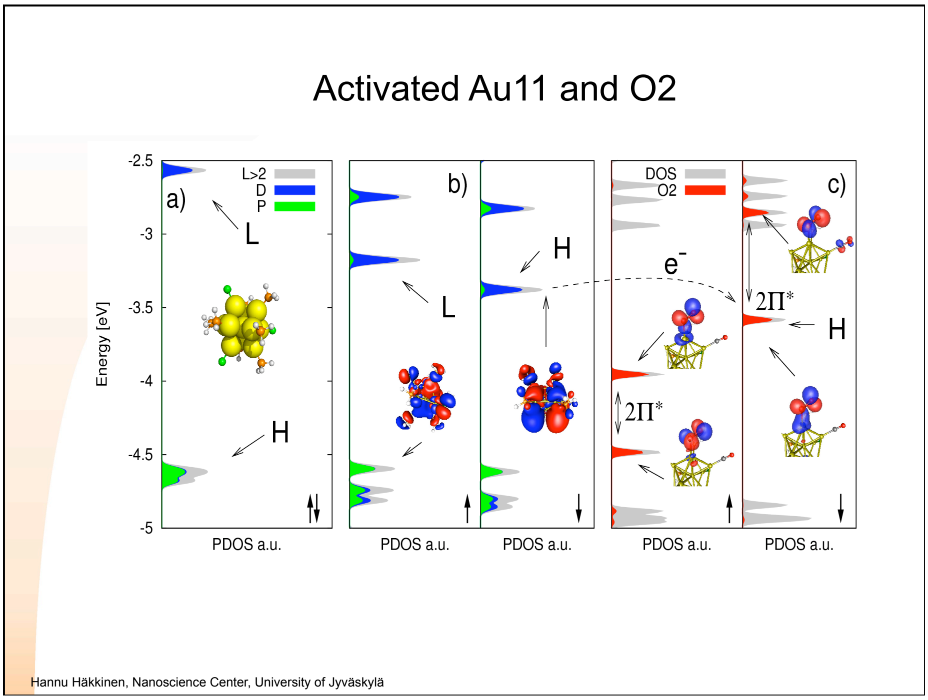
# ACTIVATION AND BINDING OF DIOXYGEN

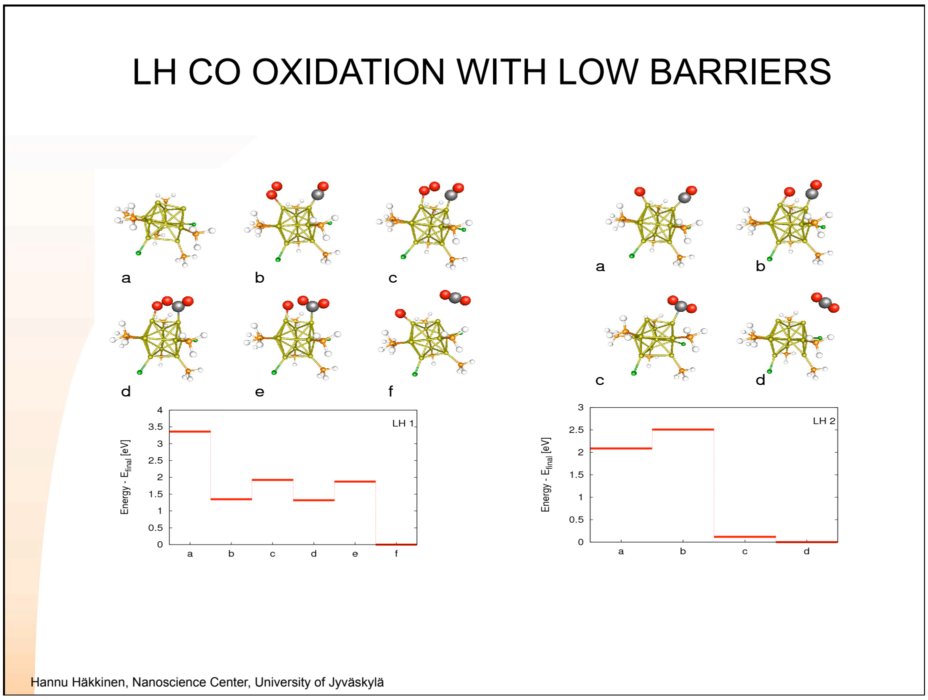
| Fully protected cluster | D (nm) | $D_C$ (nm) | $N_e$ | HL gap (eV) | Ligand removed | $N_e$* | BE($O_2$) (eV) | d(Au-O) (Å) | d(O-O) (Å) |
|---|---|---|---|---|---|---|---|---|---|
| $Au_{11}(PH_3)_7Cl_3$ | 1.2 | 0.6 | 8 | 2.03 | Cl | 9 | 0.95 | 2.17 | 1.31 |
| $Au_{25}(SR)_{18}^{-1}$ | 1.6 | 0.6 | 8 | 1.25 | $Au_2(SR)_3$ | 9 | 0.72 | 2.24 | 1.31 |
| $Au_{39}(PH_3)_{14}Cl_6^{-1}$ | 1.8 | 1.2 | 34 | 0.85 | Cl | 35 | 0.3 | 2.2 | 1.3 |
| $Au_{102}(SR)_{44}$ | 2.2 | 1.2 | 58 | 0.53 | $Au(SR)_2$ | 59 | 0.08 | 2.19 | 1.30 |
| $Au_{144}(SR)_{60}$ | 2.4 | 1.4 | 84 | 0.08 | $Au(SR)_2$ | 85 | -0.15 | 2.22 | 1.29 |
| Au(111) surface |  |  |  | 0 |  |  | -0.54 | 2.26 | 1.24 |





## Activated Au11 and O2

Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

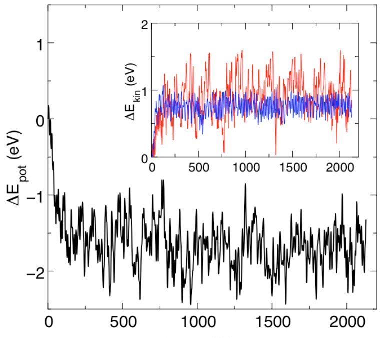


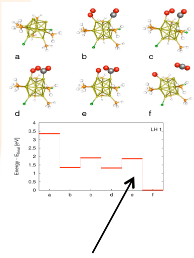
## LH CO OXIDATION WITH LOW BARRIERS

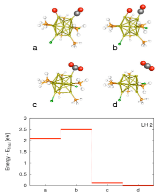
Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

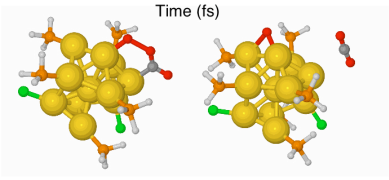
# Dynamic effects

- $CO_2$ takes out 50% of reaction heat
- Au11 does not decompose









**t = 0 fs** **t = 121 fs**

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- Ligand-stabilization of small, catalytically active gold clusters could be a route to prepare oxidation catalysts
- The activity is correlated with the quantized electronic structure (HOMO-LUMO gap)
- Suitable chemistry known, stabilization with supports an important issue
- The electronic structure of ≈100 Au atom particle already ”too close” to bulk Au → inert towards $O_2$ !