Reactivity of metal clusters

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What are clusters?

Aggregates of a countable number (2-10^n, n can be as high as 6 or 7) of particles (i.e atoms or molecules).

			Cluster						
		„micro"	*„small"*	*„large"*			*nano/micro crystals*		
Number of atoms	1	10	10^2	10^3	10^4	10^5	10^6	10^7	10^8
Surface atoms		10	10^2		10^3	10^4	10^5		
radius [nm]			1			10			10^2

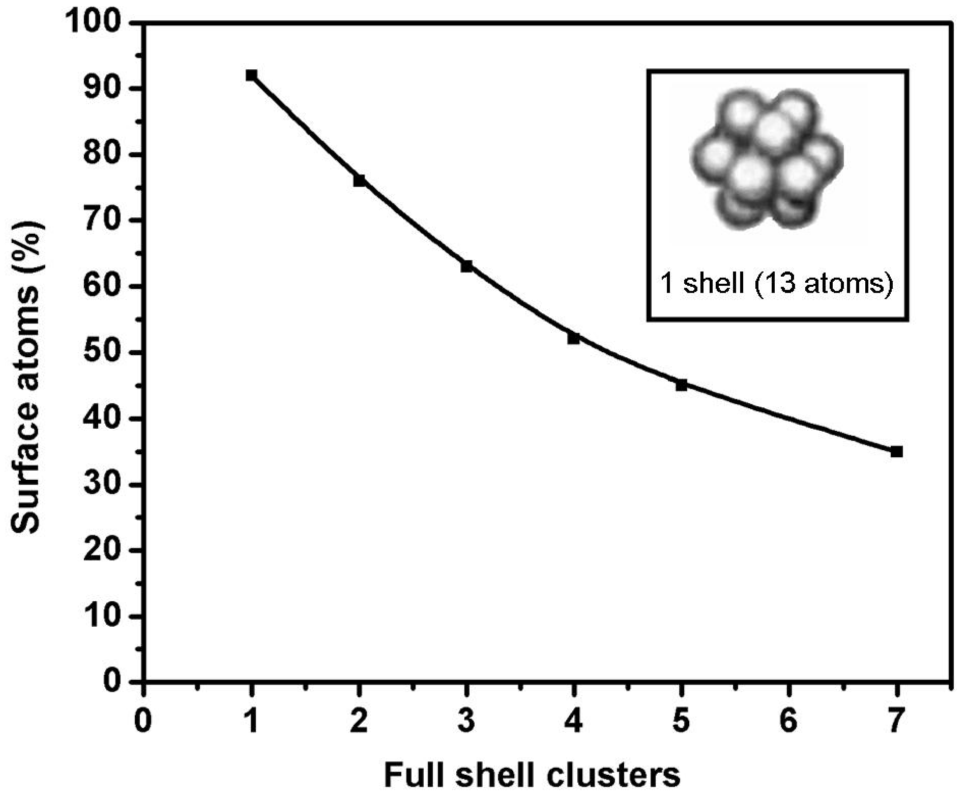
Why clusters are interesting?

- Own intrinsic properties
- Distinct from those of either discrete molecules or bulk matter
- How large must a cluster be before its properties resemble those of the bulk element?
- High ratio of surface to interior atoms in cluster

Questions?

- **To what extent do cluster properties resemble those of discrete molecules or infinite solids?**
- **Can tell us anything about the bonding or explain the properties?**
- **How cluster structure and properties varies with size?**
- **Can the evolution of band structure with increase in cluster size?**
- **Can phase transitions be observed and are they of same type found for bulk solids?**
- **What information of geometrical structures of the cluster is useful in understanding?**

Variation of surface atom (%) with respect to number of clusters

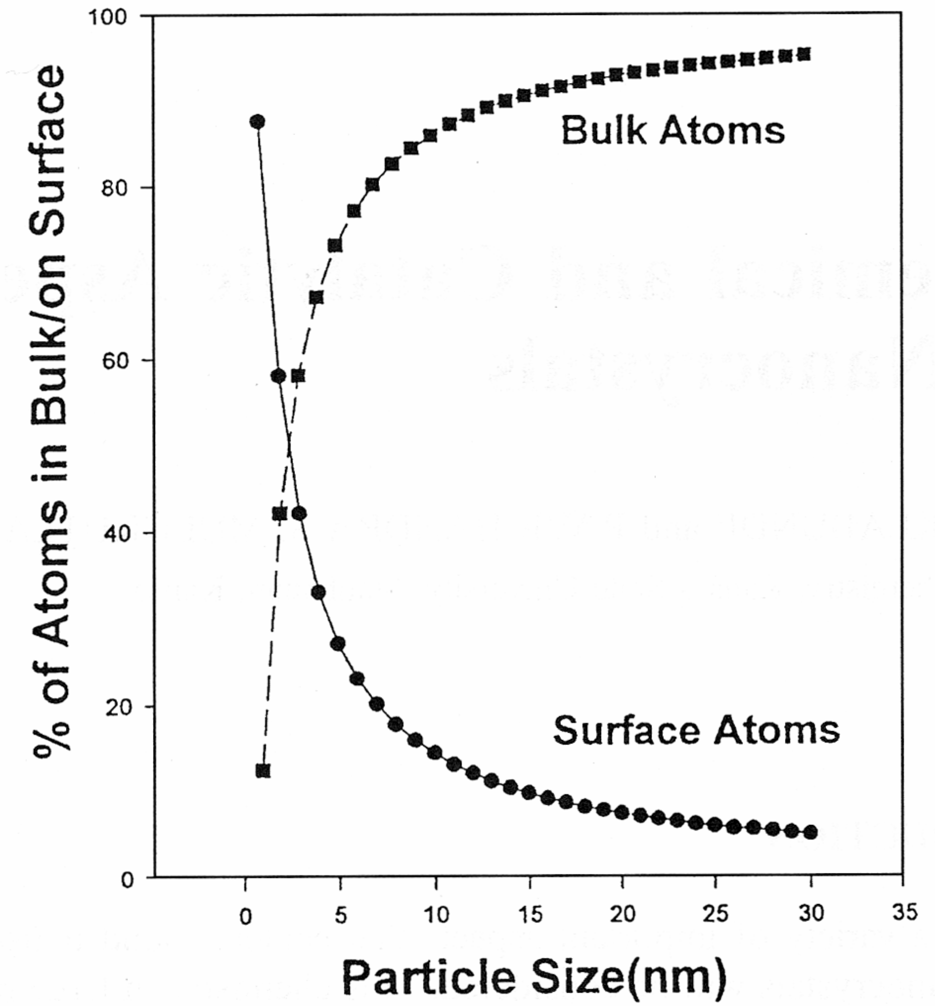


Reduction in the particle size results

- **Increase in surface to bulk atom ratio**
- **Increase in the surface area**

Surface to bulk ratio

Spherical iron clusters



• J. Phys. Chem. 1996, Vol. 100, p. 12142

Surface area dependence on particle size

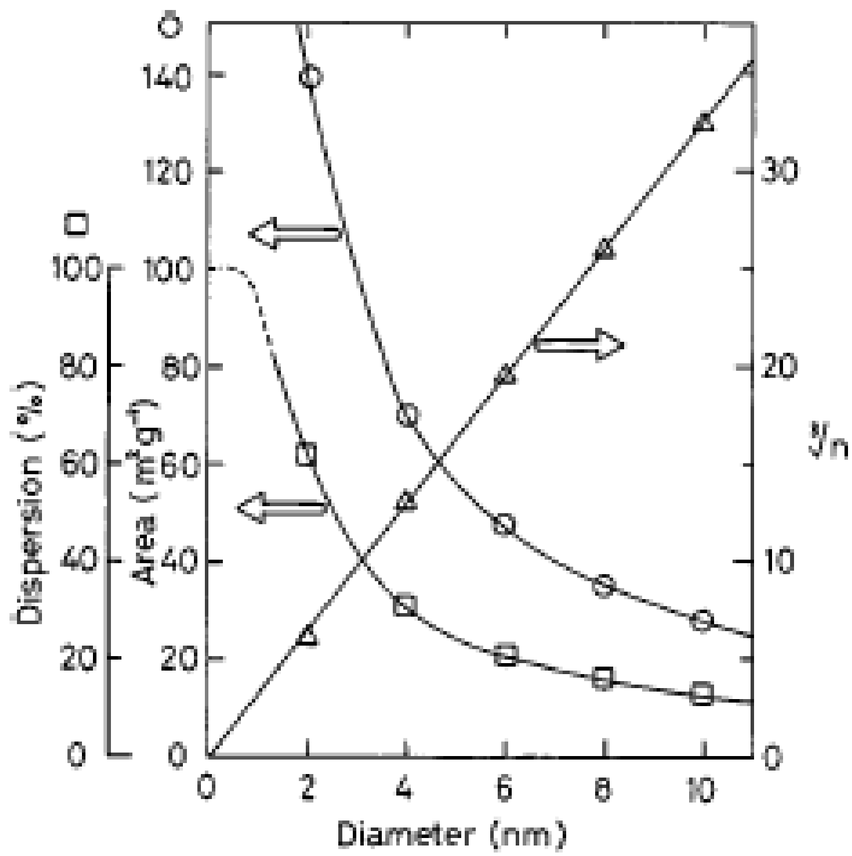
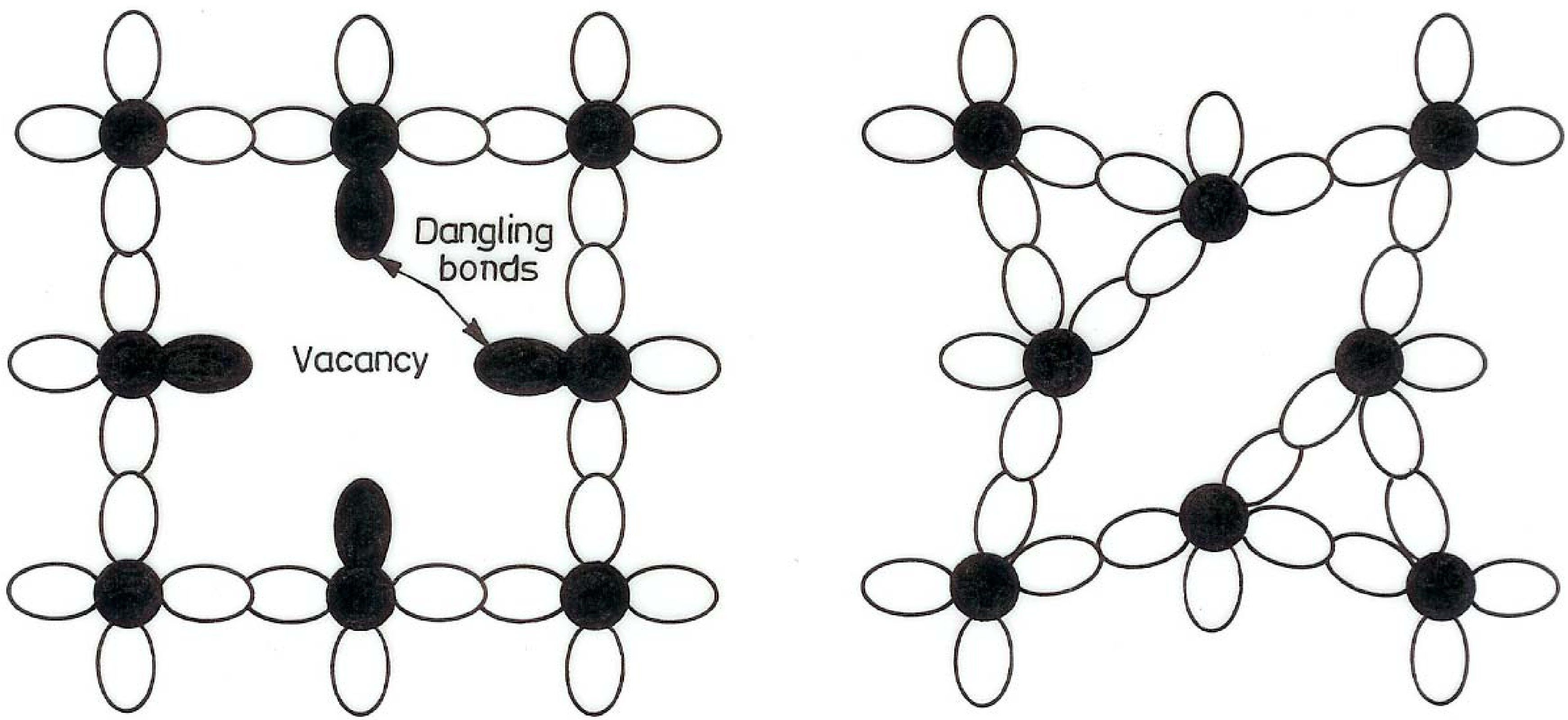


FIG. 2. Dependence of surface area (○), dispersion (□), and $\sqrt[3]{n}$ (n = number of atoms per particle) (△) on particle diameter for uniform spheres of gold.

What type of bonding?



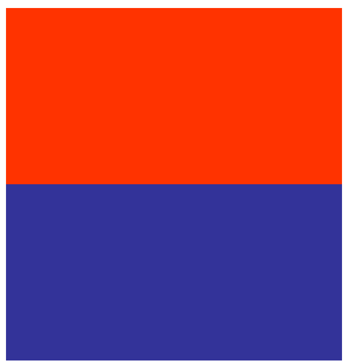
(a) an unrelaxed vacancy involving four dangling bonds and (b) a relaxed vacancy with no dangling bonds

Origin of the Properties

Bulk Metal

Unoccupied states

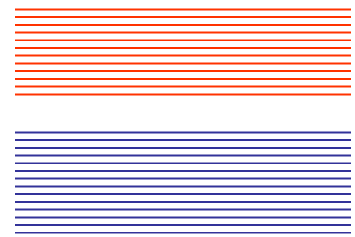
occupied states



Close lying bands

Decreasing the size…

cluster

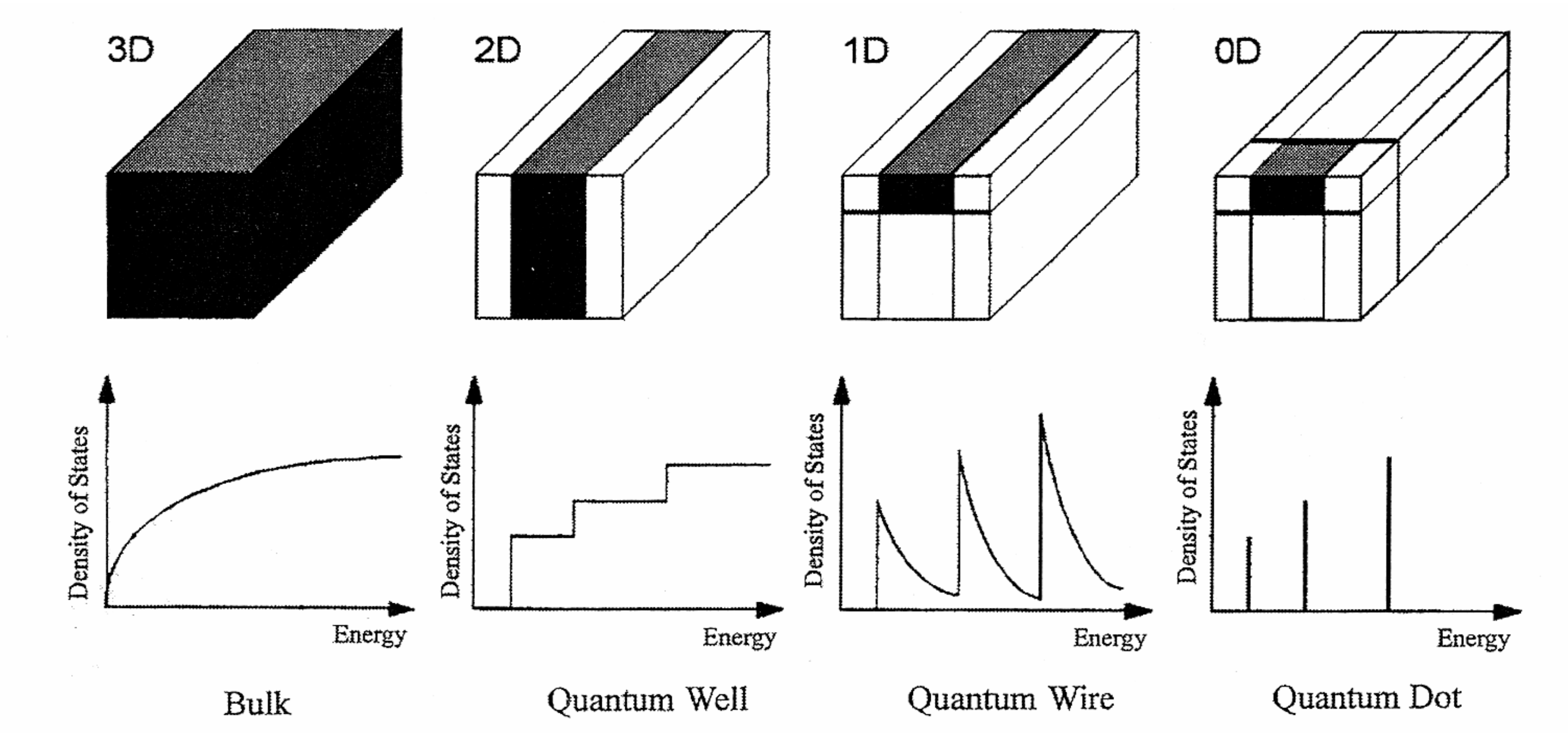


Separation between the valence and conduction bands

Unbound electrons have motion that is <u>not</u> confined

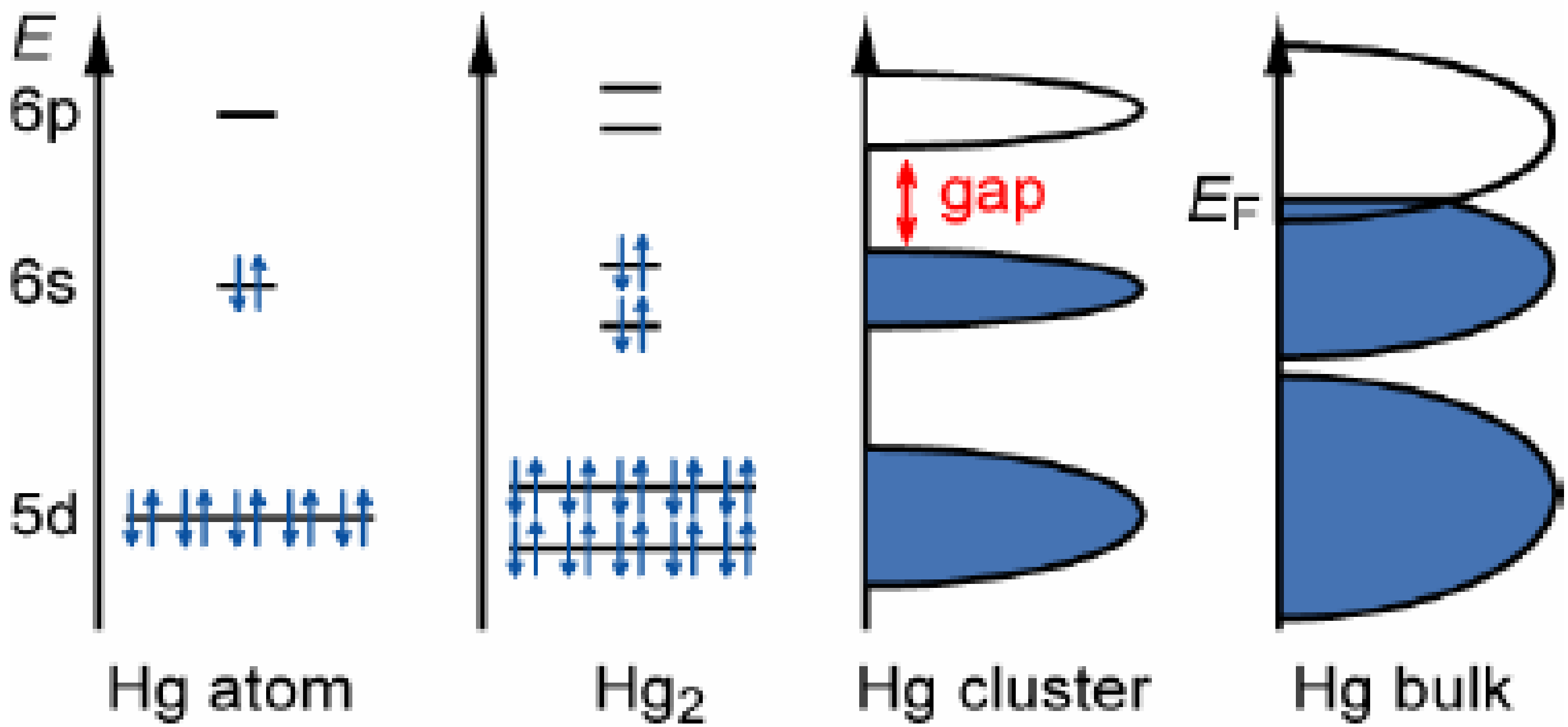
Electron motion becomes confined, and <u>quantization</u> sets in

Energy states with the shape and size



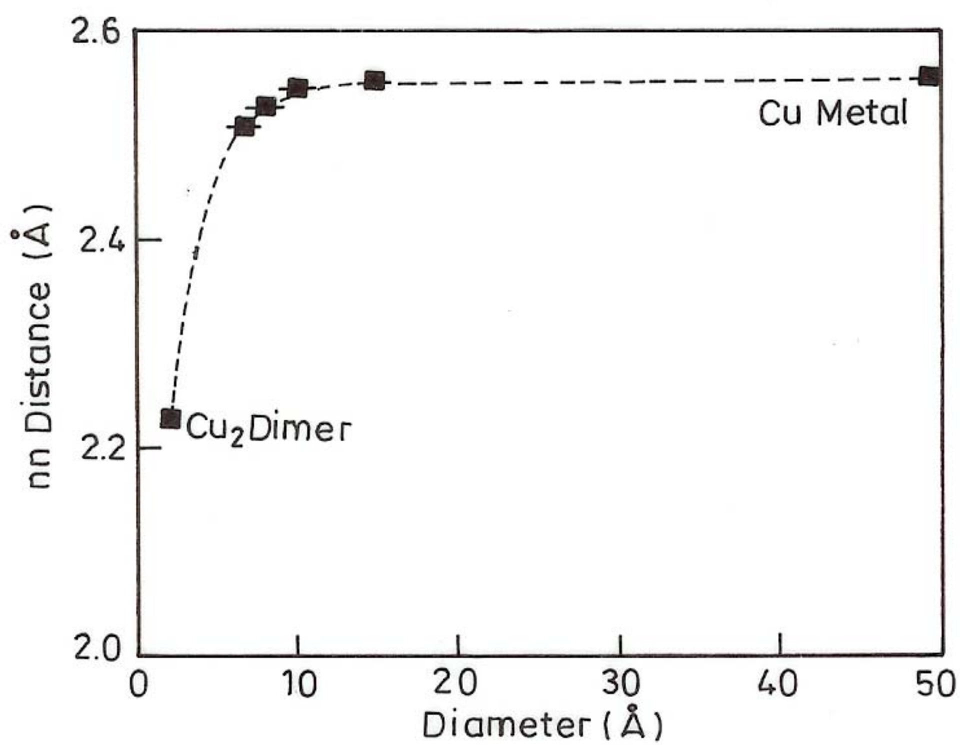
3 dimension to zero dimension, formation discrete energy levels occurs which results the atom like behaviour

The insulator to metal transition



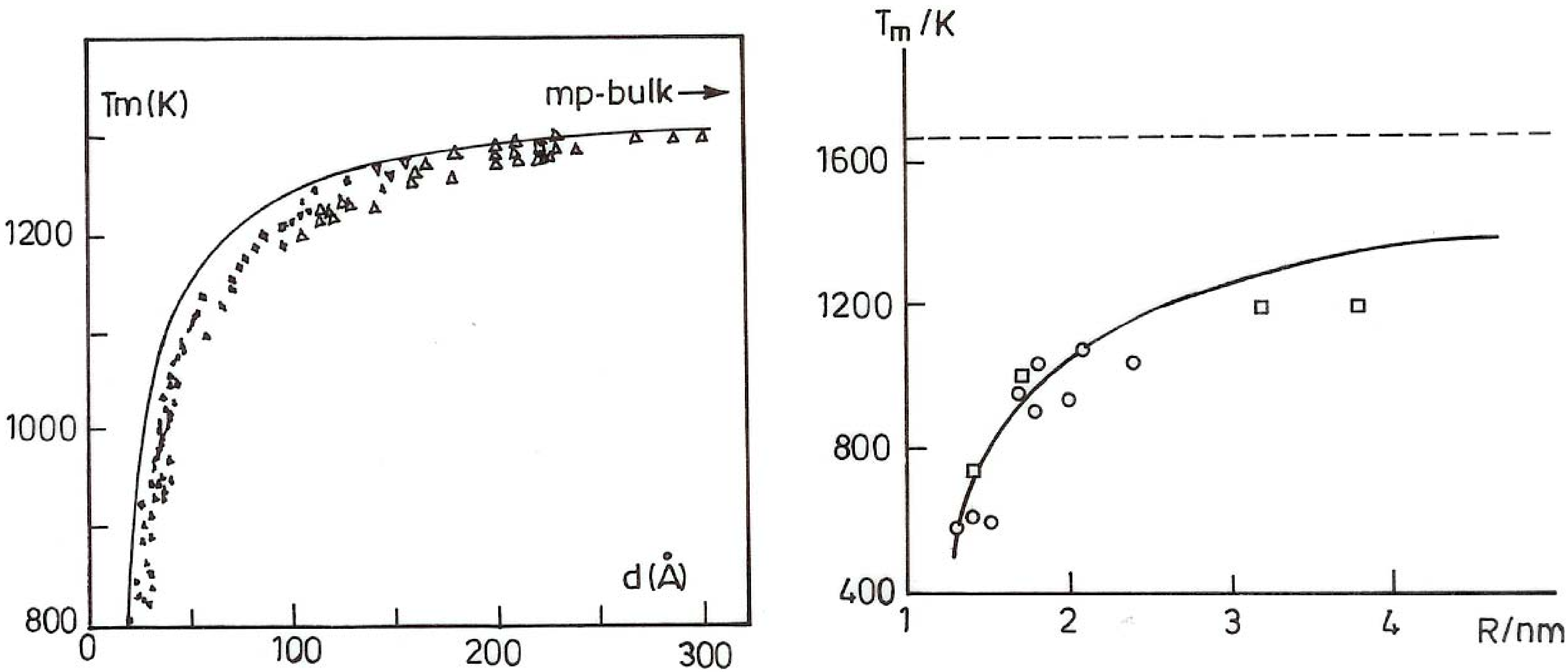
Hg = [Xe]$4f^{14}5d^{10}6s2$ ($6p^0$)

Physicochemical Properties



Variation in the interplanar distance with respect to particle size

Reduction in the particle size from bulk to cluster results in an increase in the proportion of surface energy and also alters the interparticle spacing



Variation in the melting point with respect to decreases in particle size (a) Aun Cluster (b) CdS

Effect on catalysis…………..

a) Redox potential or band gap or HOMO or LUMO gap

b) surface area (surface to volume ratio)

c) structure

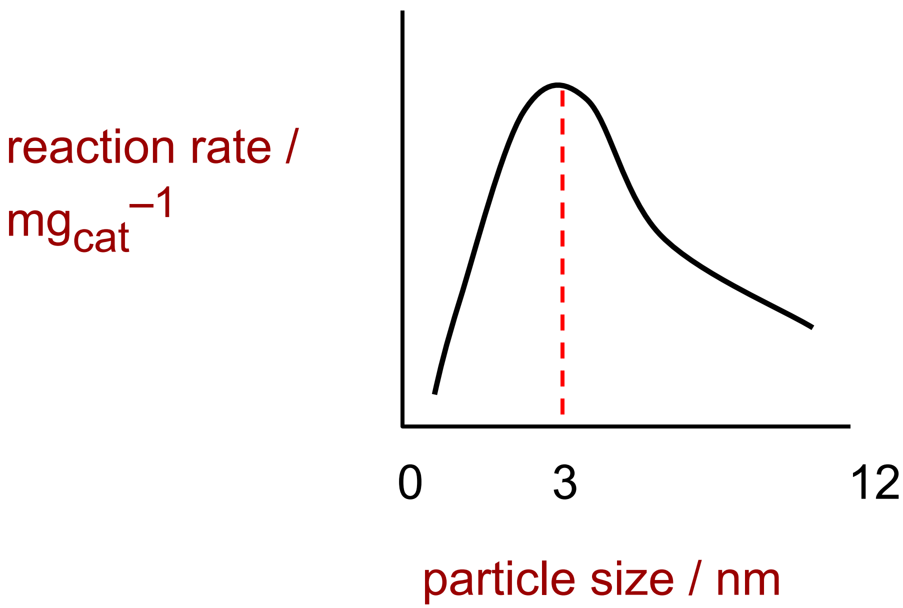
d) Morphology

e) Preferential orientation

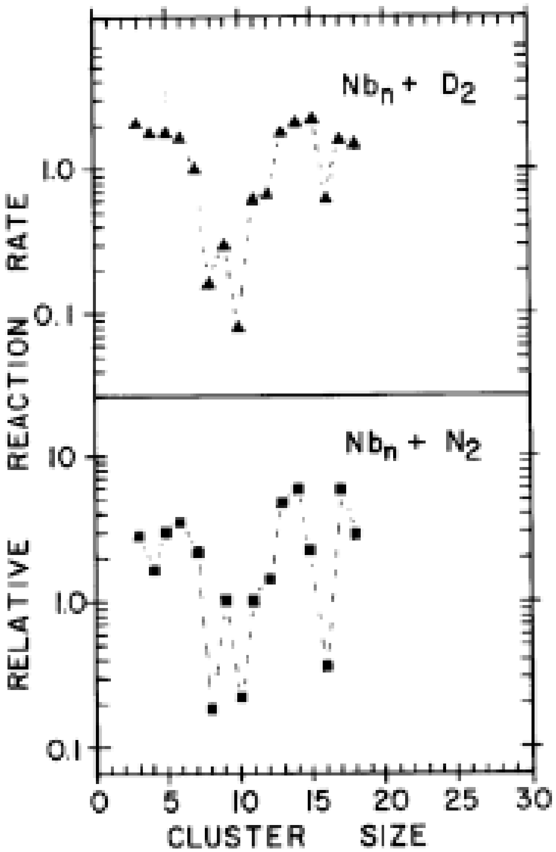
Catalyst Size Effects

Catalyst size effect for oxygen reduction

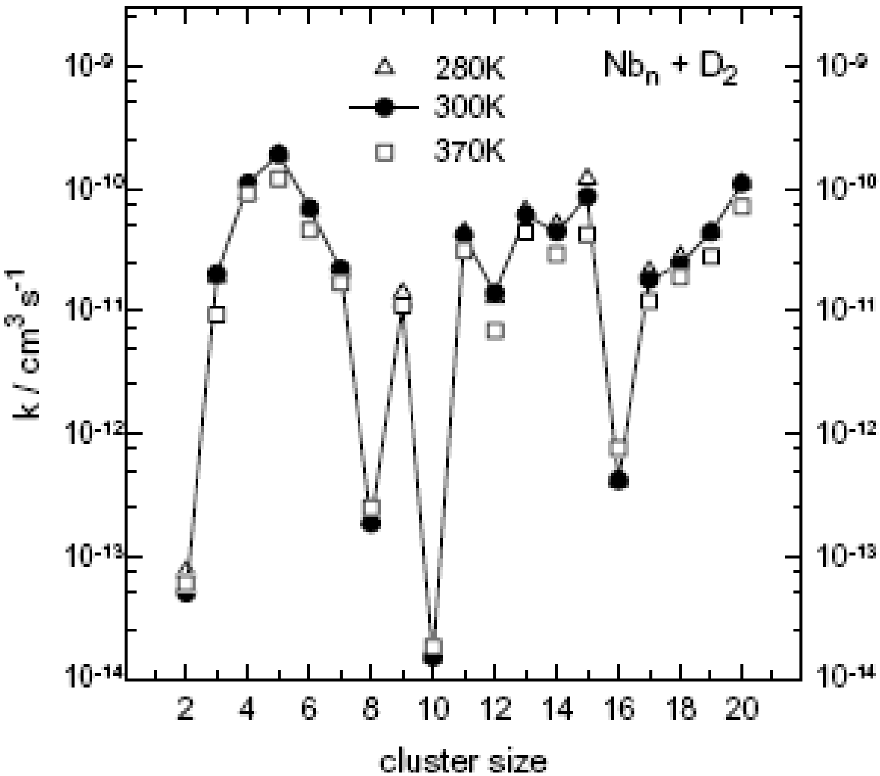
$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$$



Pt/Carbon catalyst



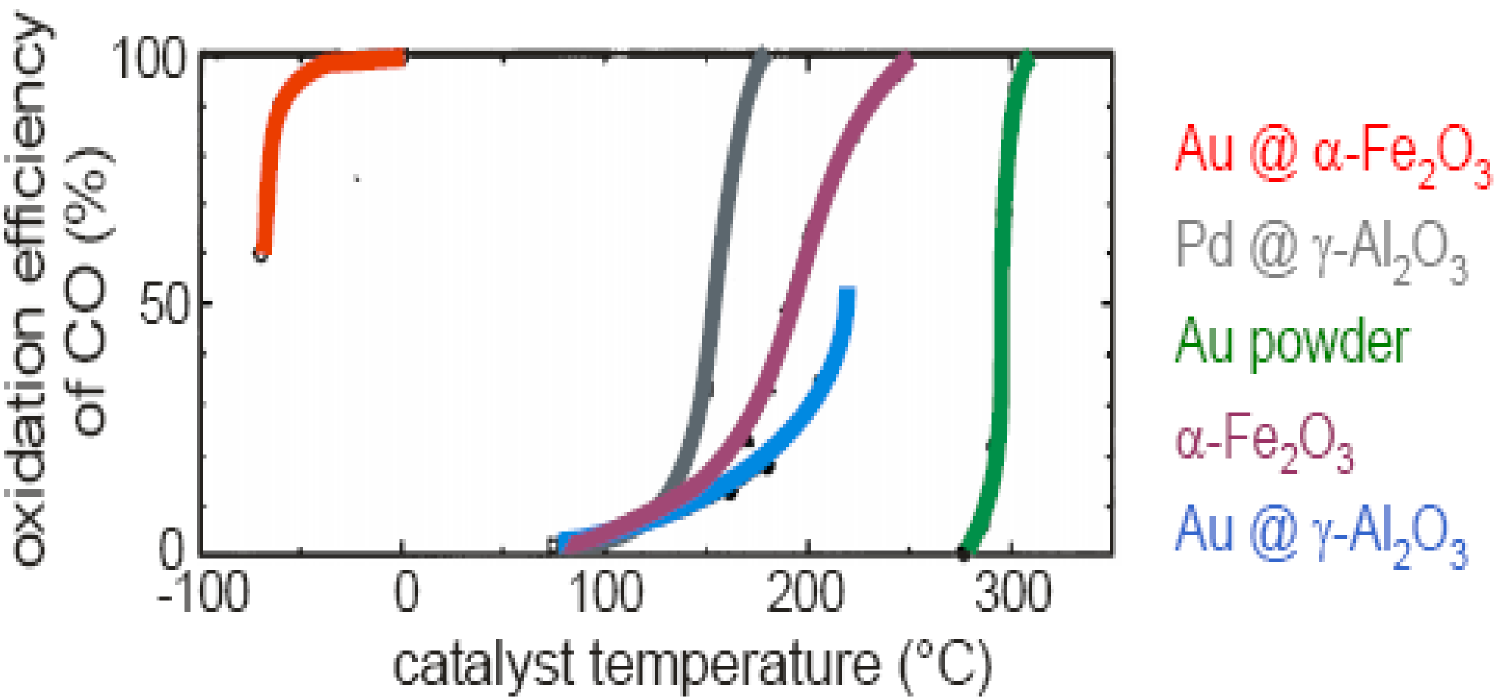
$Nb_n + D_2$
$Nb_n + N_2$
RELATIVE REACTION RATE
CLUSTER SIZE



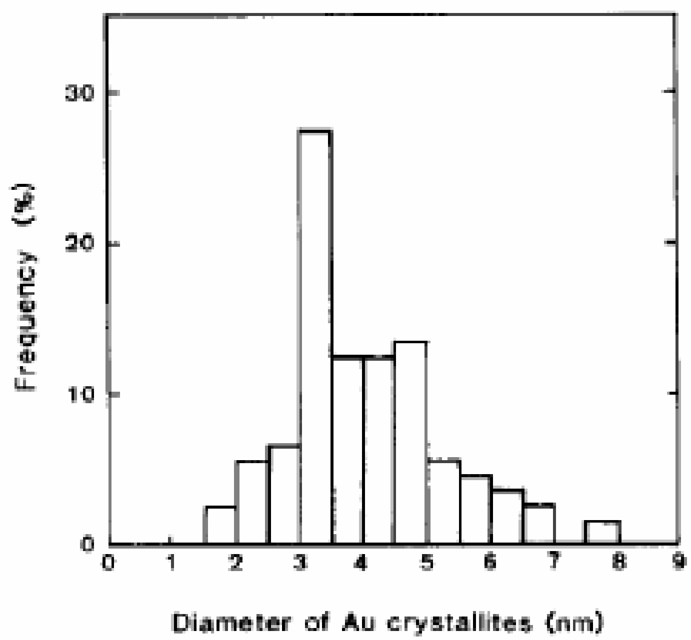
280K
300K
370K
$Nb_n + D_2$
$k / cm^3 s^{-1}$
cluster size

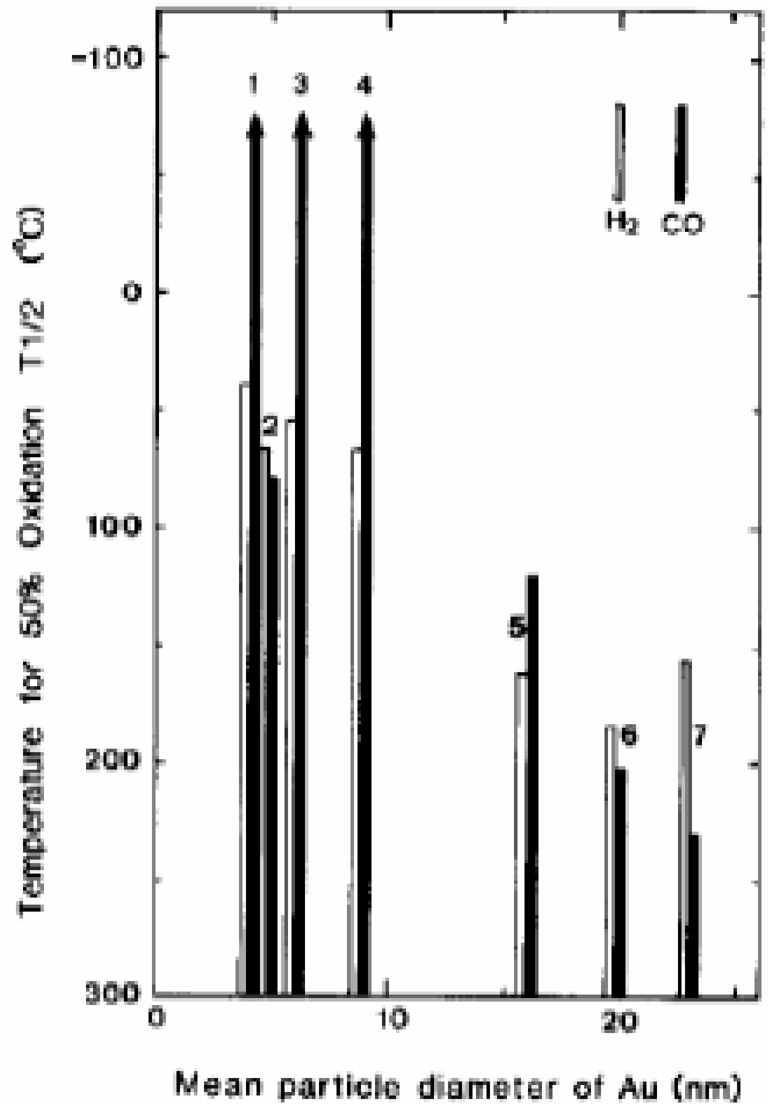
Physical Properties of Gold Compared to Those of Platinum and Mercury

Property	Pt	Au	Hg
Atomic number	78	79	80
Atomic mass	195.08	196.9665	200.59
Electronic configuration	[Xe]$4f^{14}5d^{9}6s^{1}$	[Xe]$4f^{14}5d^{10}6s^{1}$	[Xe]$4f^{14}5d^{10}6s^{2}$
Structure	fcc	fcc	A10
Lattice constant (nm)	0.392	0.408	0.299
Metallic radius (nm)[a]	0.1385	0.14420	0.151
Density (g cm^{-3})	21.41	19.32	13.53
Melting temp. (K)	2042	1337	234.1
Boiling temp. (K)	4443	3081	630
Sublimation enthalpy (kJ mol^{-1})	469 ± 25	343 ± 11	59.1 ± 0.4
First ionization energy (kJ mol^{-1})	866	890	1007



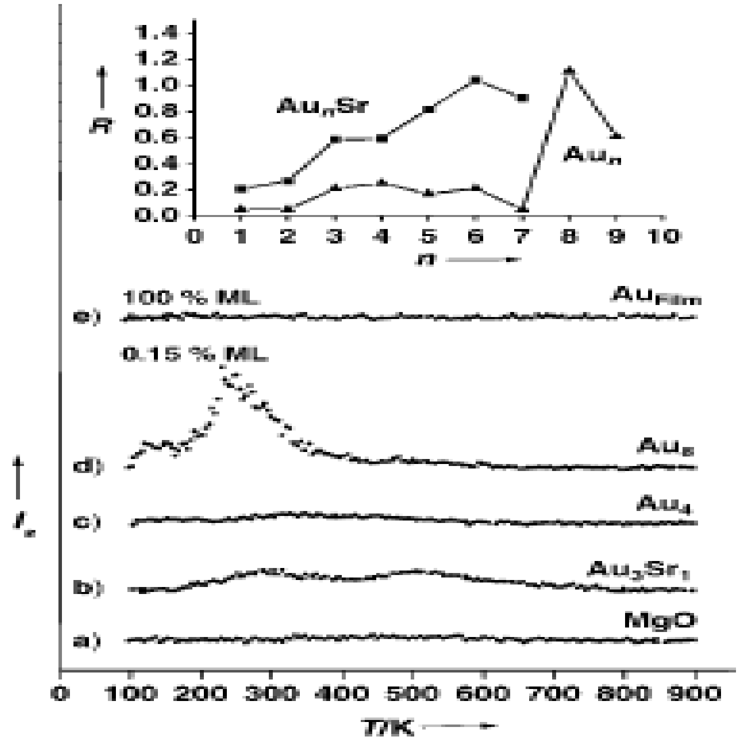
Gold nano-particles @ α-Fe_2O_3, Co_3O_4, and NiO prepared by co-precipitation
Catalytic oxidation of H_2 and CO with air as oxidant


Frequency (%)
30
20
10
0
0 1 2 3 4 5 6 7 8 9
Diameter of Au crystallites (nm)


-100
0
100
200
300
Temperature for 50% Oxidation T1/2 (°C)
1
3
4
2
5
6
7
H2 CO
0
10
20
Mean particle diameter of Au (nm)

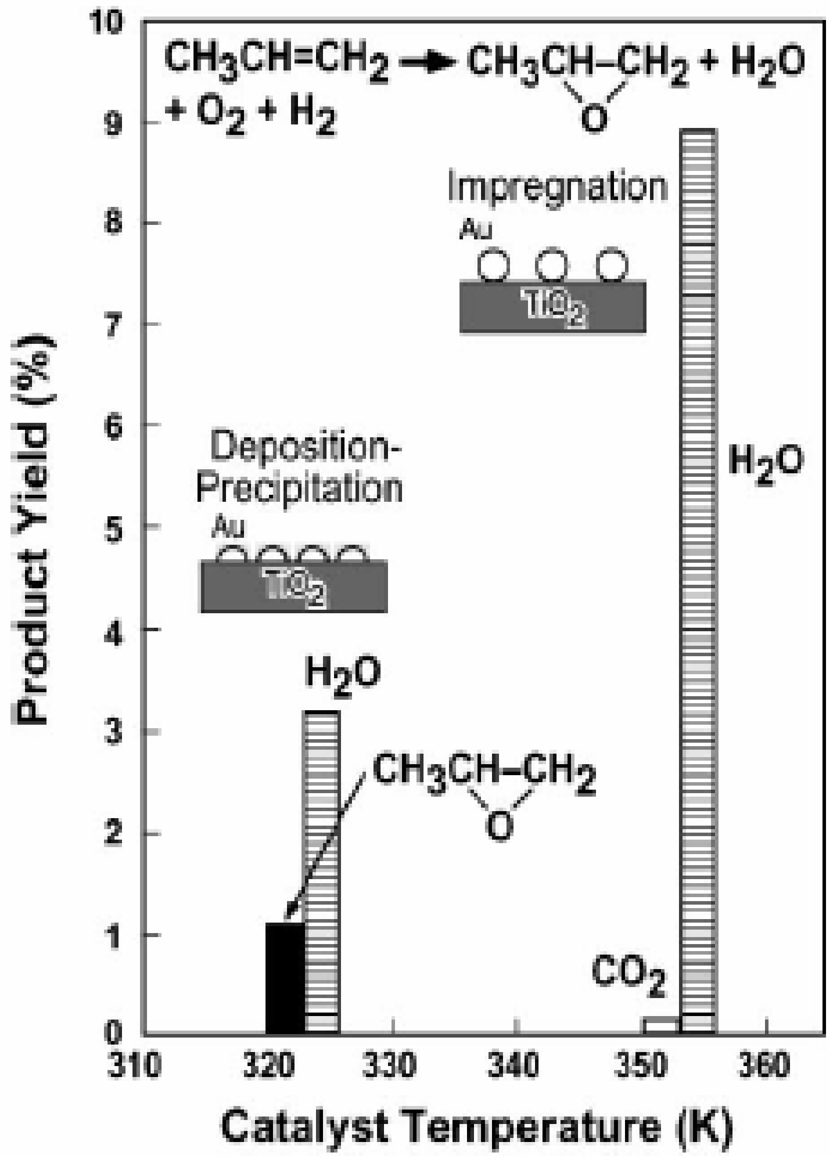
Au cluster and catalysis

TPR profile

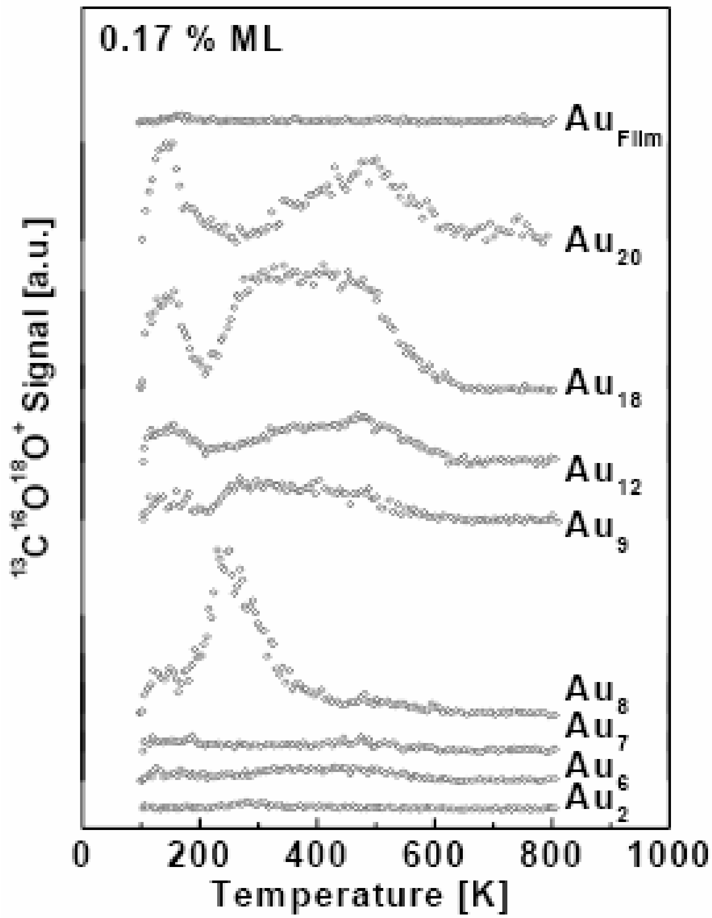


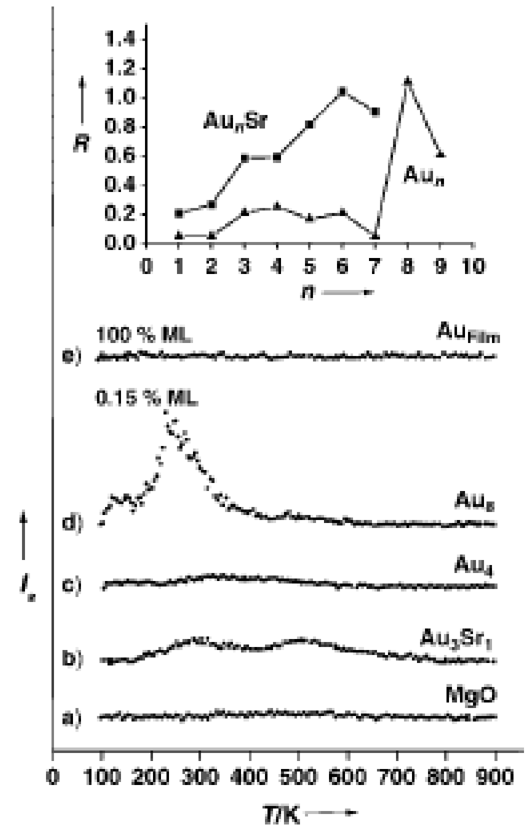
a) MgO(100) film,b) Au3Sr/MgO, c) Au4/MgO, d)Au8/MgO(FC), and e) multilayer Au film grown on MgO(100). The Au4/MgO(FC), pure MgO film

Landman *et al*., Angew. Chem. Int. Ed. 2003, 42, No. 11



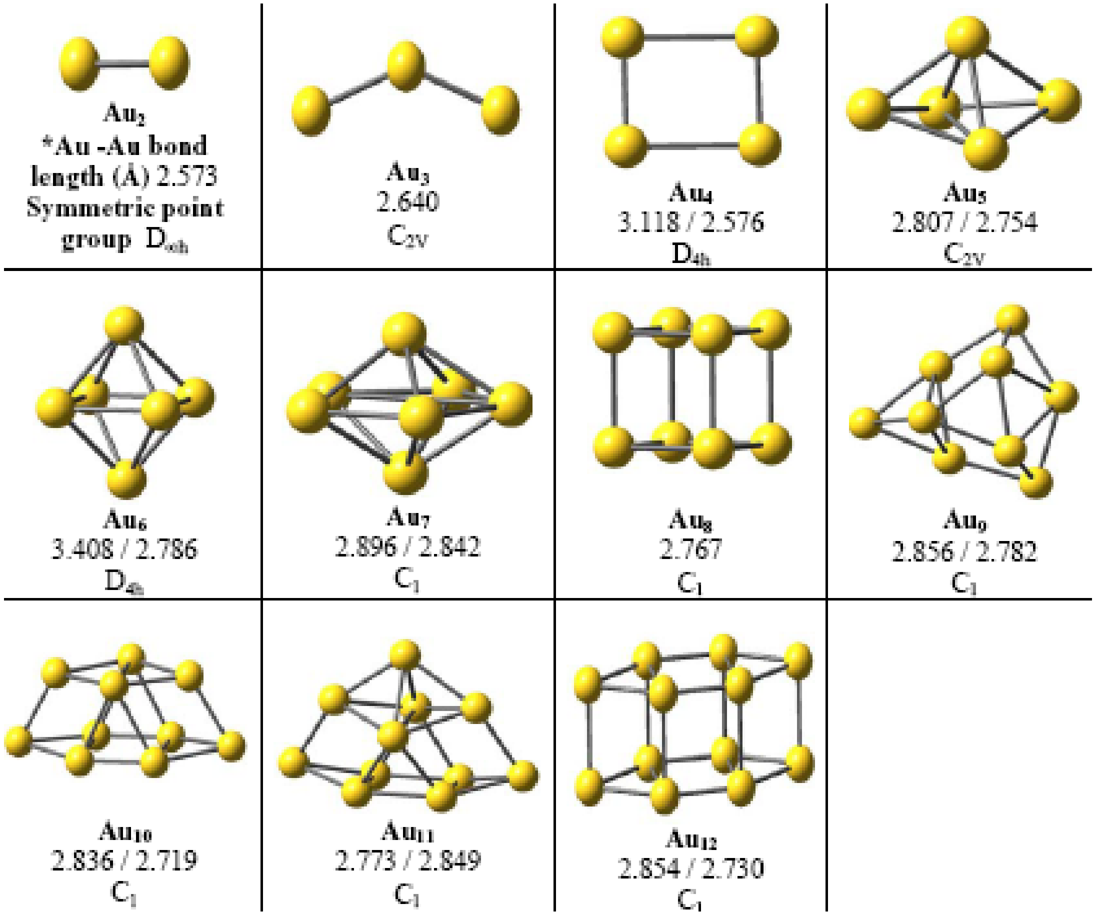
CH3CH=CH2 + O2 + H2 → CH3CH–CH2 (O) + H2O
Impregnation
Au
TiO2
Deposition-Precipitation
Au
TiO2
H2O
CH3CH–CH2 (O)
CO2
H2O
Product Yield (%)
Catalyst Temperature (K)
0
1
2
3
4
5
6
7
8
9
10
310
320
330
340
350
360





- **Aun (n<8) inert**
- **Au8 smallest gold catalyst**
- **Au3Sr smallest doped cluster**
- **MgO and Au film inert**

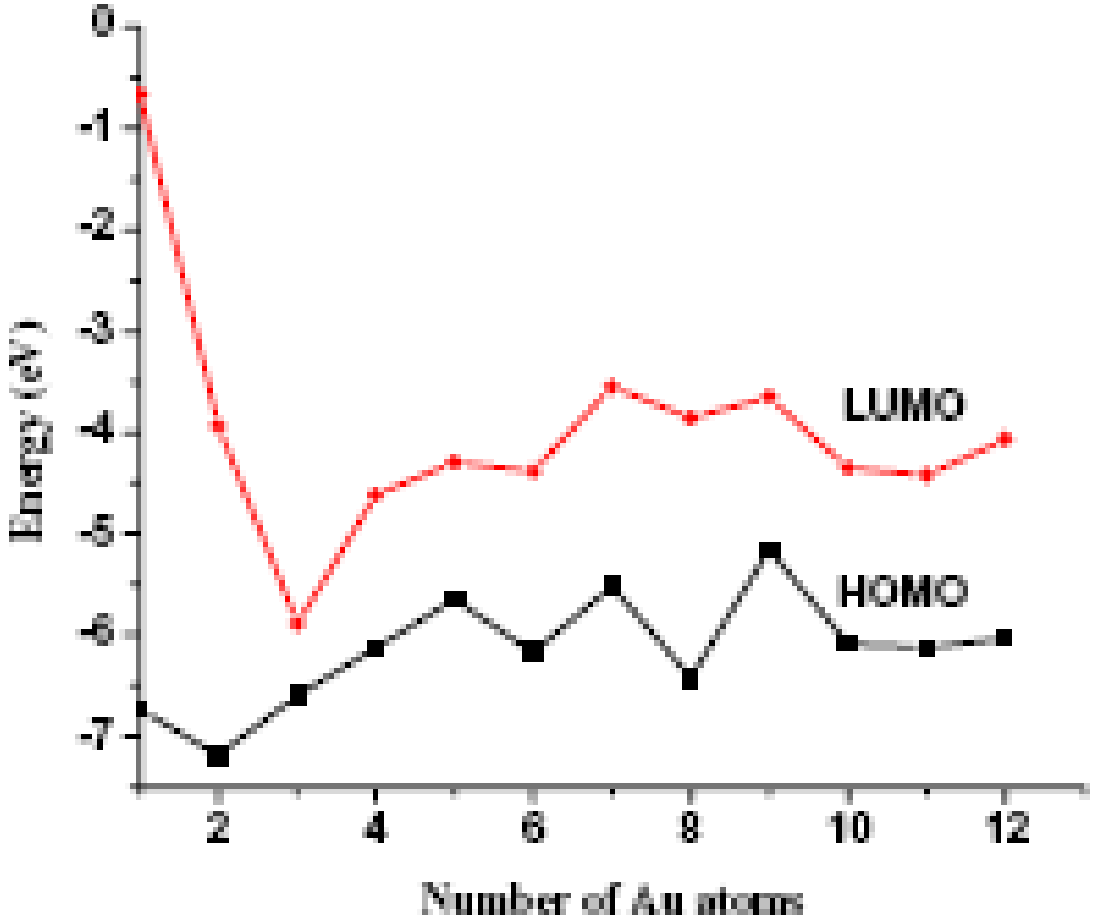
The geometrical parameters of various gold clusters



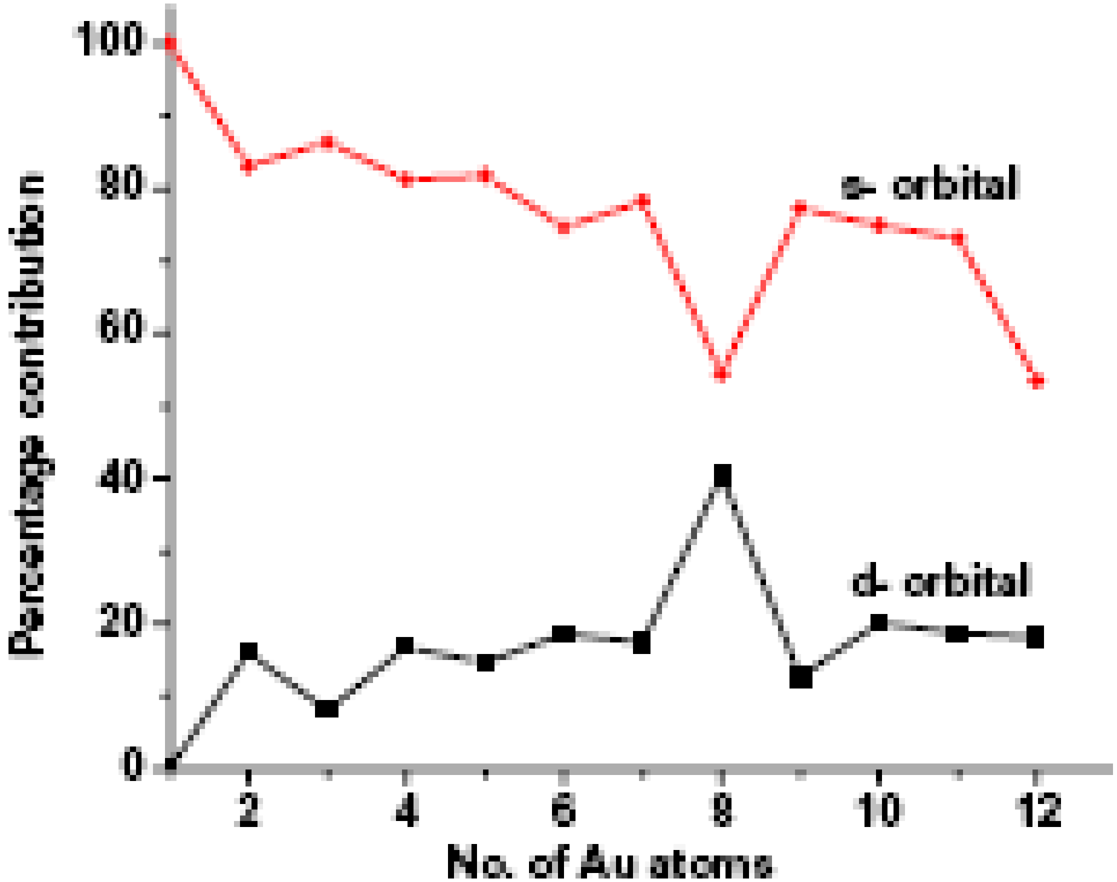
Cluster	Total energy (eV)	Stabilization energy* (eV)
Au	-3685.32	-
Au_2	-7372.50	-0.93
Au_3	-11058.70	-0.92
Au_4	-14745.19	-0.98
Au_5	-18432.03	-1.09
Au_6	-22119.02	-1.19
Au_7	-25806.59	-1.34
Au_8	-29493.40	-1.36
Au_9	-33180.88	-1.45
Au_{10}	-36868.19	-1.50
Au_{11}	-40555.20	-1.52
Au_{12}	-44241.83	-1.50

* Stabilization energy = [total energy of the cluster] – [No. of atoms] [energy of atom] / [total No. of atoms]

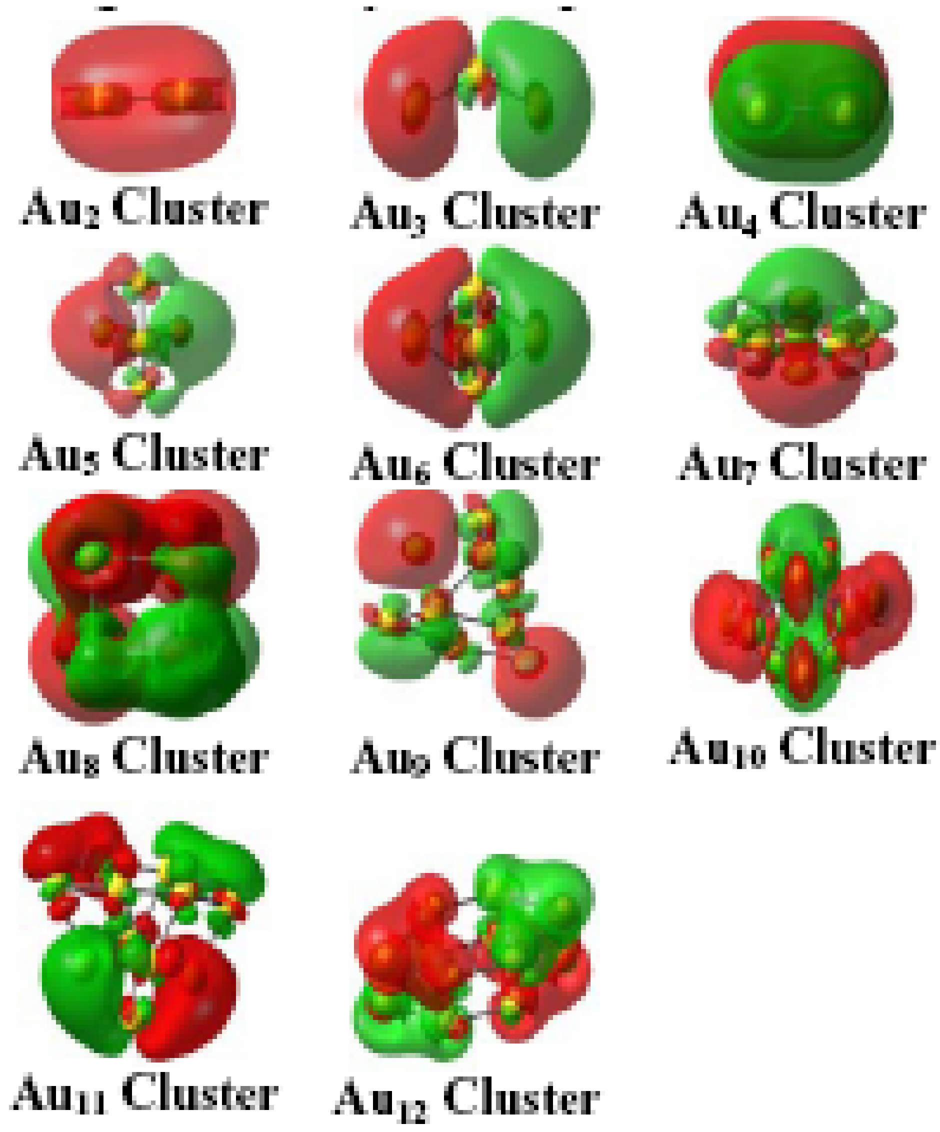
HOMO – LUMO energy levels of various gold clusters



The percentage of s and d- orbital contributions



HOMO level frontier orbital contour of various gold clusters



In case of gold, a particular sized nanoparticles posses spatially oriented, symmetry allowed orbitals and the corresponding eigen values are appropriate for interaction with the incoming adsorbate molecules that undergo surface transformations.

For other sized nanoparticles the frontier wave functions have predominant '*s*' character and hence there is no spatial orientation or Eigen values matching and hence these other nanoparticles are not reactive enough.

Due to these spatially oriented Eigen functions, these gold clusters interacted with support and the reactant system exhibits altered activity.

Thank you