Aalto University
School of Chemical
Engineering

Chemistry of the Elements
Lecture 11
Ag, Au, Pd, Pt & Catalysis

2023-10-02

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Lecture 11 exercise set is available as a MyCourses Quiz

Contents

- Introduction
  - Terrestial abundance of Ag, Au, Pd, Pt

- Chemistry of **Ag** and **Au**
  - The importance of **relativistic effects** in heavy-element chemistry
  - Applications in **catalysis**

- Chemistry of **Pd** and **Pt**
  - Applications in **catalysis**

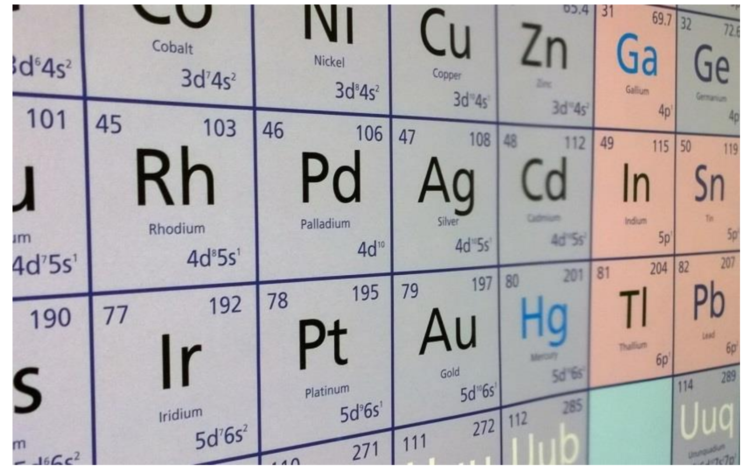
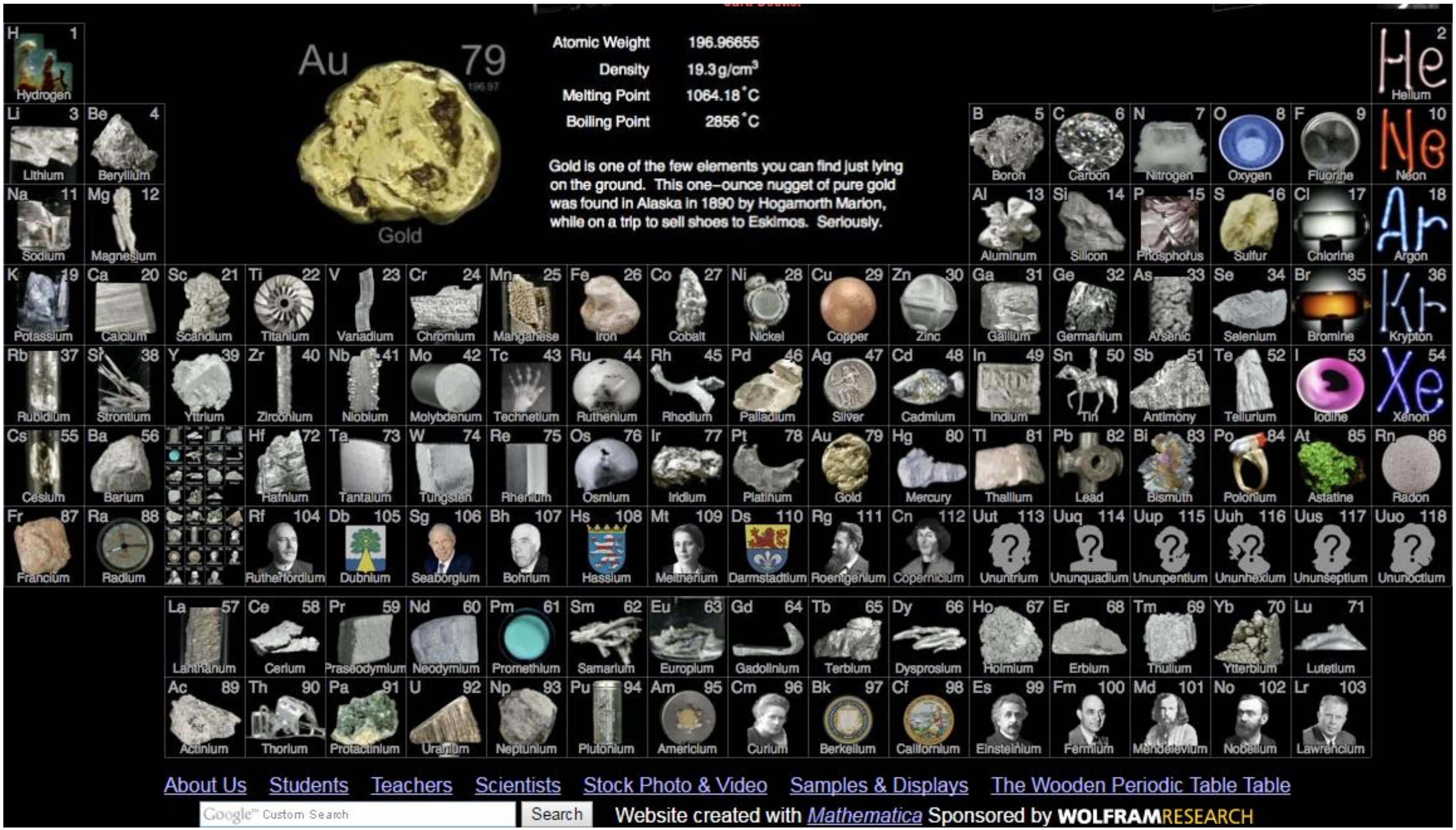


Figure: AJK

Figure: Shutterstock

Information on elements

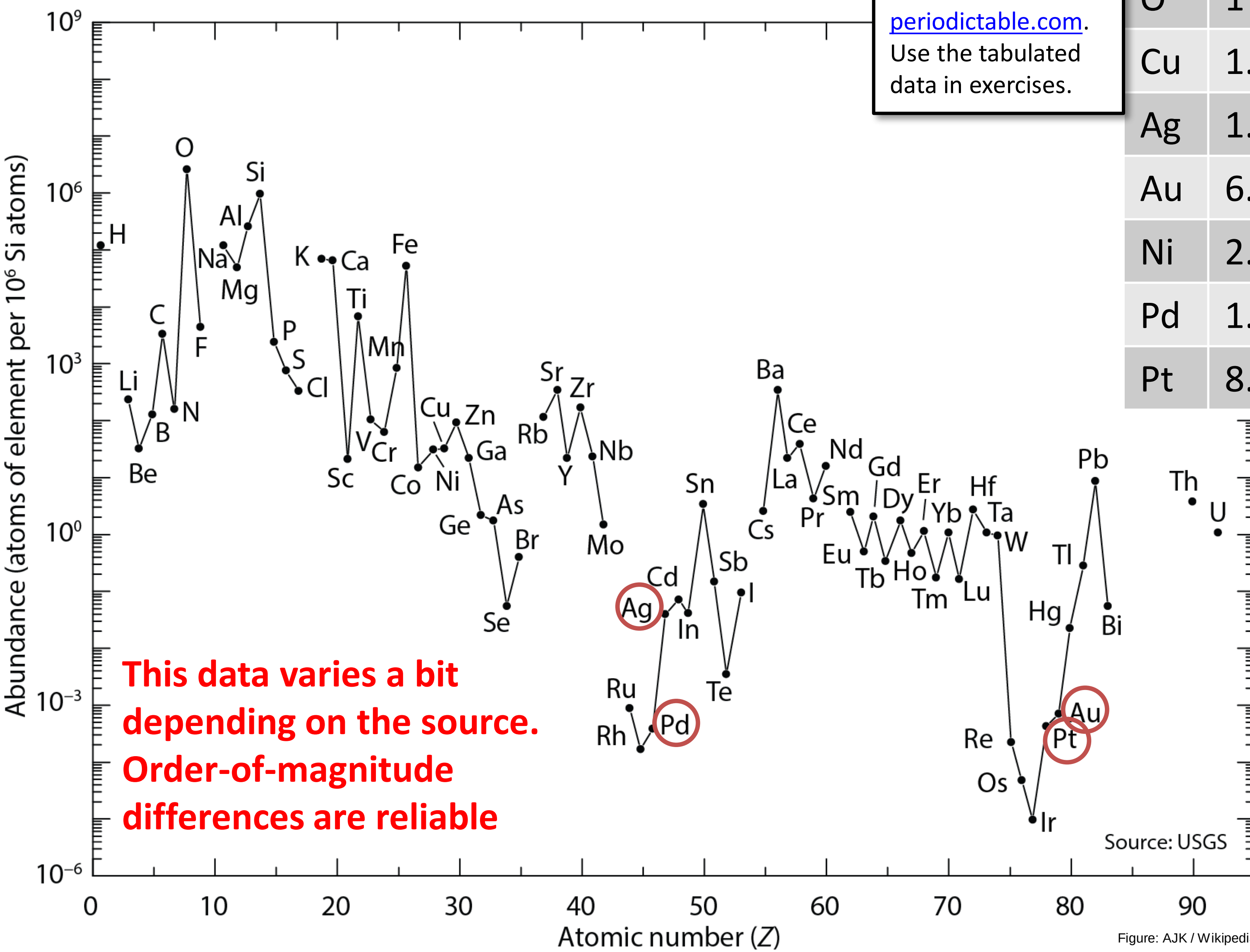
- An excellent resource on “applications” of elements: http://periodictable.com/
- Also includes excellent collection of technical data (by Wolfram Research)



Abundance in Earth's crust

Data in table from periodictable.com. Use the tabulated data in exercises.

	Relative abundance
O	1
Cu	1.5×10^{-4}
Ag	1.7×10^{-7}
Au	6.7×10^{-9}
Ni	2.0×10^{-4}
Pd	1.4×10^{-8}
Pt	8.0×10^{-8}



This data varies a bit depending on the source. Order-of-magnitude differences are reliable

Figure: AJK / Wikipedia

Ag, Au – metallic ground state

Property	Ag	Au
Atomic number	47	79
Electronic configuration	[Kr] $4d^{10}\ 5s^{1}$	[Xe] $4f^{14}\ 5d^{10}\ 6s^{1}$
Crystal structure	**Face-centered cubic** (FCC, *Fm*-3*m*)	

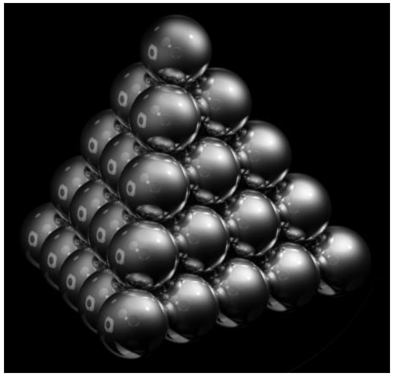


Figure: Wikipedia

74.05% of the total volume is occupied by spheres (maximum density possible in structures constructed of spheres of only one size)

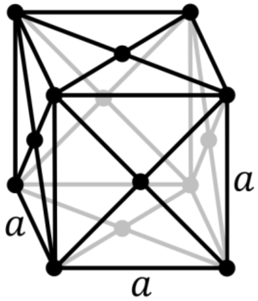
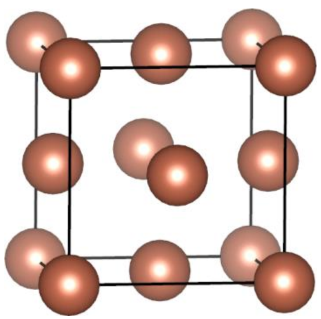


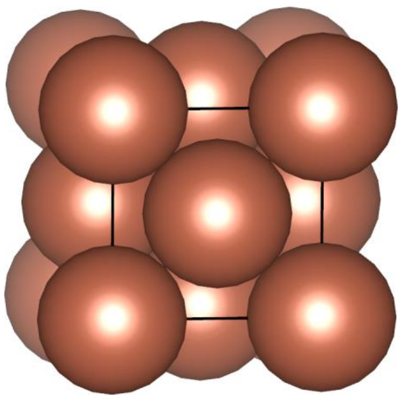
Figure: Wikipedia

FCC Bravais lattice

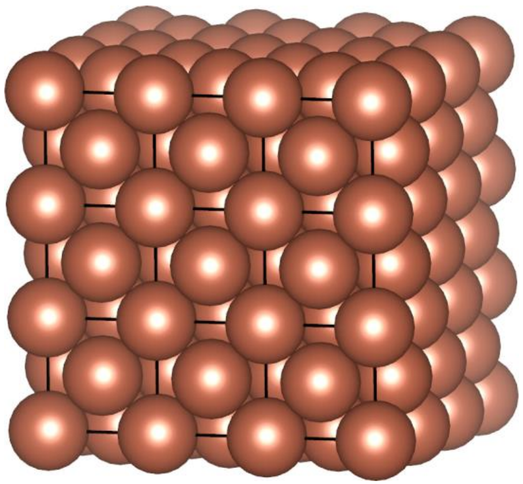


Figures: AJK

Cu/Ag/Au unit cell



Space-filling view



3x3x3 supercell

Can you spot the difference?

Figure: aptac-us.org

Figure: Shutterstock

Property	Ag	Au
Electronic configuration	[Kr] $\mathbf{4d^{10}\ 5s^{1}}$	[Xe] $4f^{14}$ $\mathbf{5d^{10}\ 6s^{1}}$
Crystal structure	FCC	FCC

Why does gold look so ... golden?

Relativistic effects in chemistry (1)

The two basic theories of modern physics are the theory of relativity and quantum mechanics. While the importance of the latter in chemistry was instantly recognized, it was not until the 1970s that the full relevance of relativistic effects in heavy-element chemistry was discovered.

P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

- Relativistic effects arise from the finite speed of light ($c \approx 137$ a.u., **a**tomic **u**nits)
- The relativistic mass increase for electrons with rest mass m_0 and speed v is

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

- The average radial velocity of **1s** electrons is roughly (Z = atomic numer)

$$<v> \approx Z \text{ (a.u.)}$$

- Example: for Hg (Z = 80), the speed of the **1s** electron is ca. 80 a.u.
- The relativistic mass increase leads to contraction of the effective Bohr radius (**1s**)

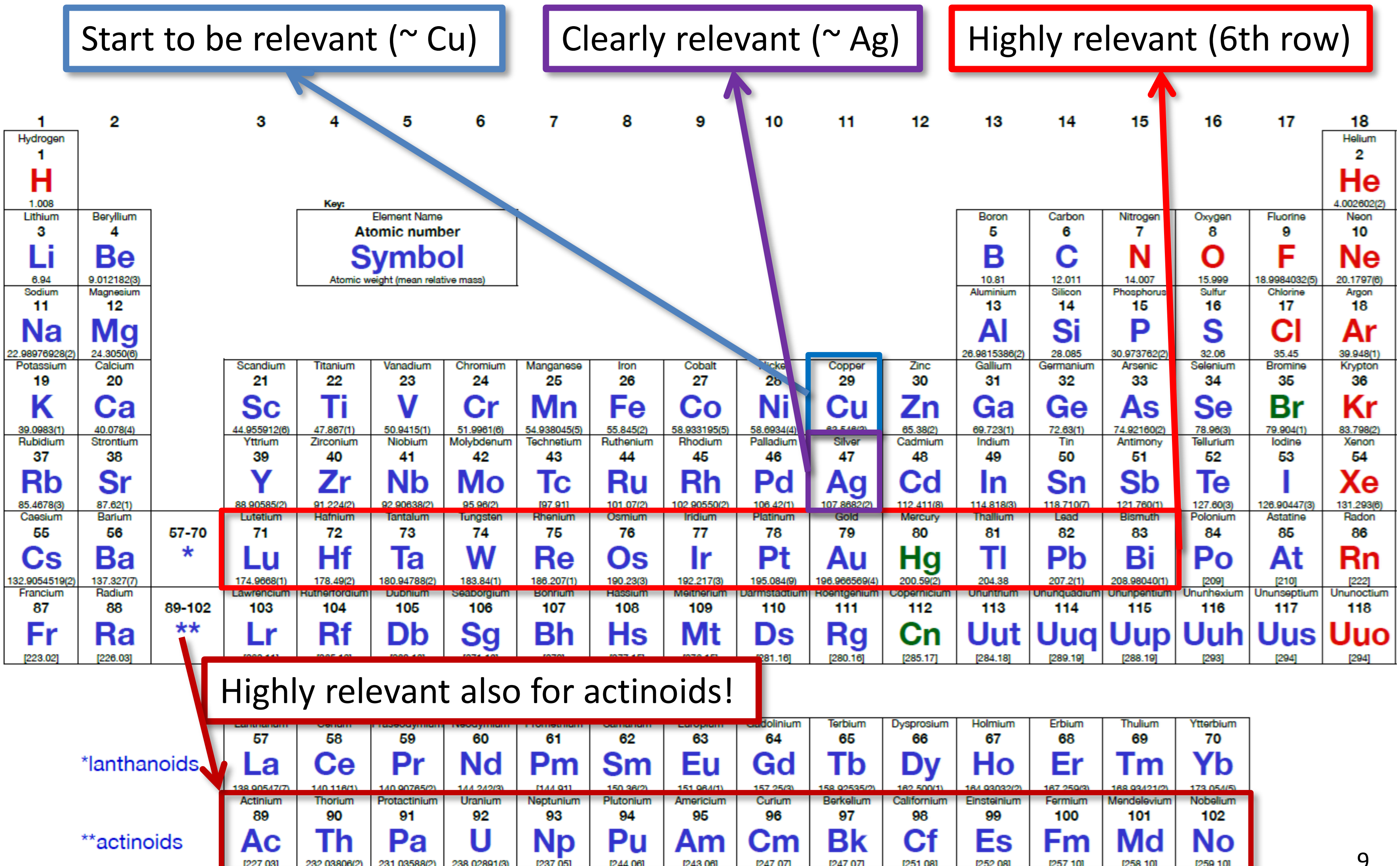
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{mZe^2}$$

- For Hg: v/c = 80 a.u. / 137 a.u. = 0.58. The radial shrinkage of 1s orbital a_0 is **23%** compared to hypothetical non-relativistic situation.

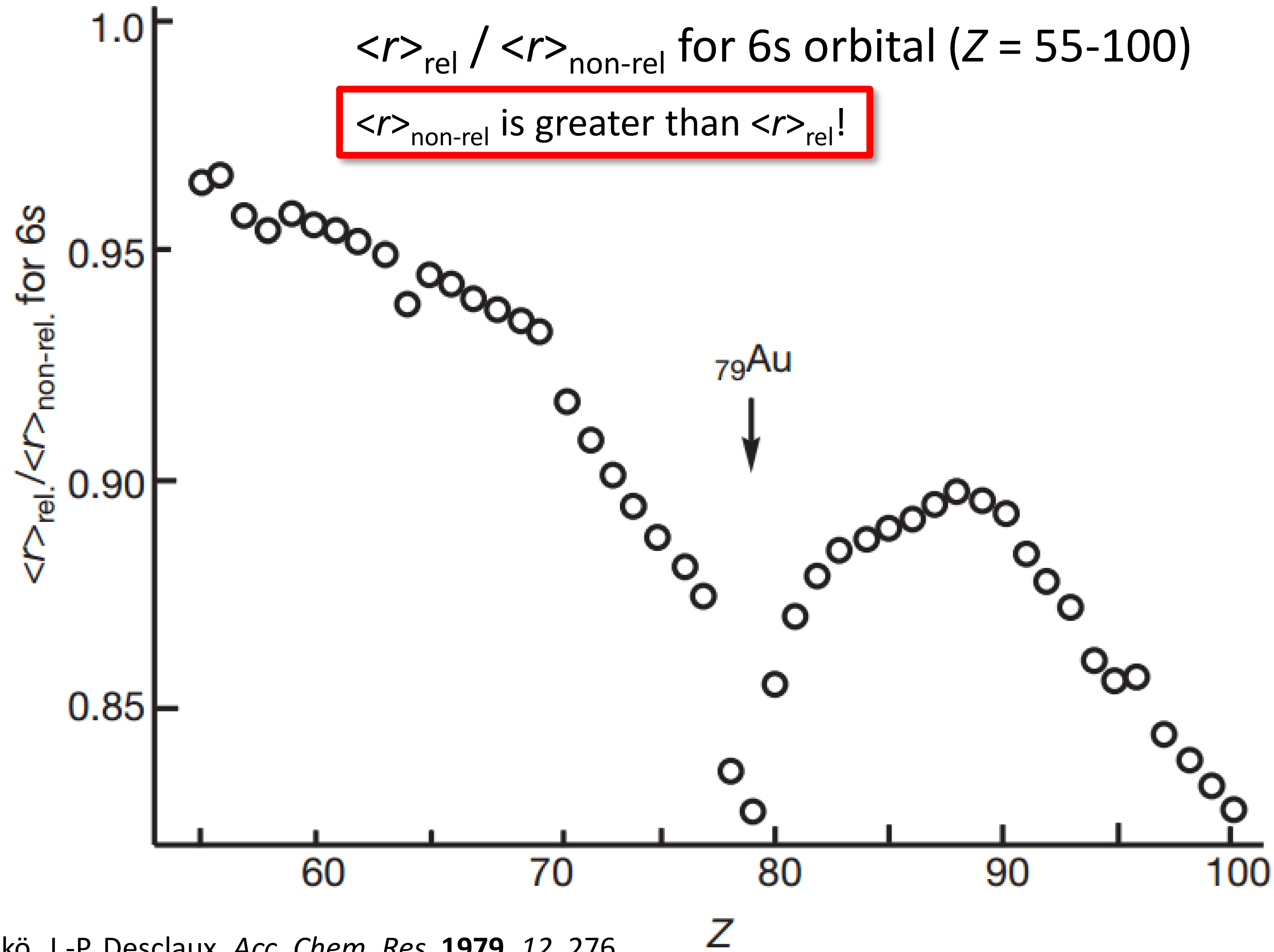
Relativistic effects on orbitals

- The semi-quantitative calculation on the previous slide showed that **1s** orbital of Hg contracts by ~23% due to relativistic mass increase
- The higher s shells are orthogonal to the 1s shell and must contract, too
  - The higher s shells, up to the valence shell, contract roughly as much as **1s** because their electron speeds near the nucleus are comparable and the contraction of the inner part of the wave function affects the outer part, too
- p-orbitals are also contracted due to relativity (and split into $p_{1/2}$ and $p_{3/2}$)
- d and f electrons never come close to the nucleus and they will be screened more strongly by the contracted s and p orbitals
- Bottom line:
  - s and p orbitals are **contracted and stabilized** due to relativity
  - d and f orbitals are **expanded and destabilized** due to relativity
- The relativistic effects for the valence orbitals increase as Z^2

Relativity and periodic trends

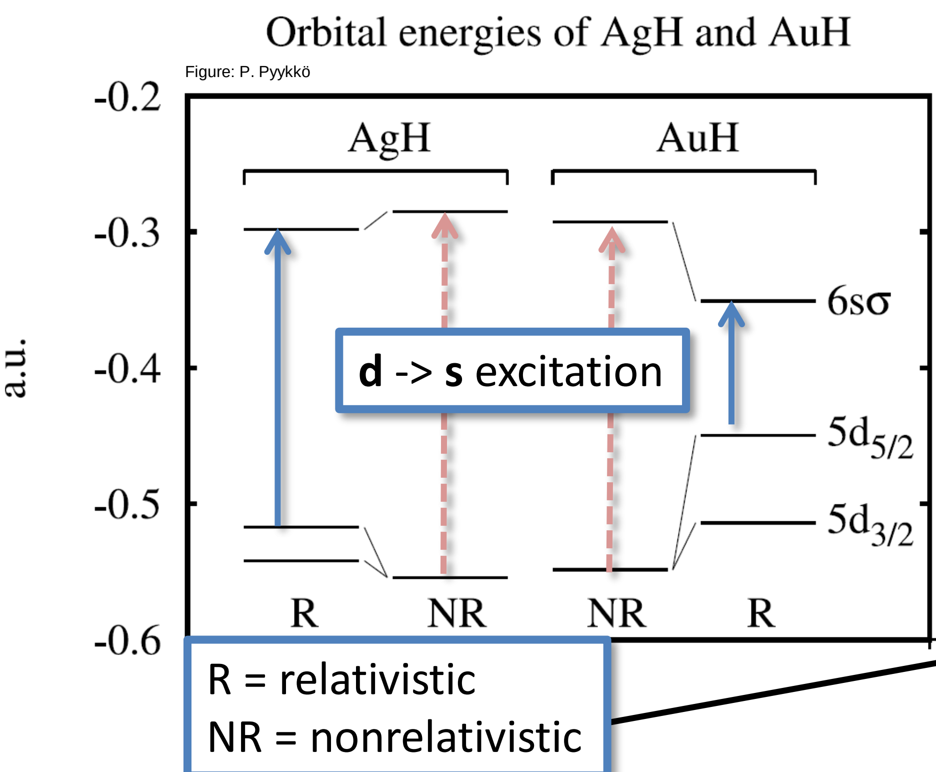


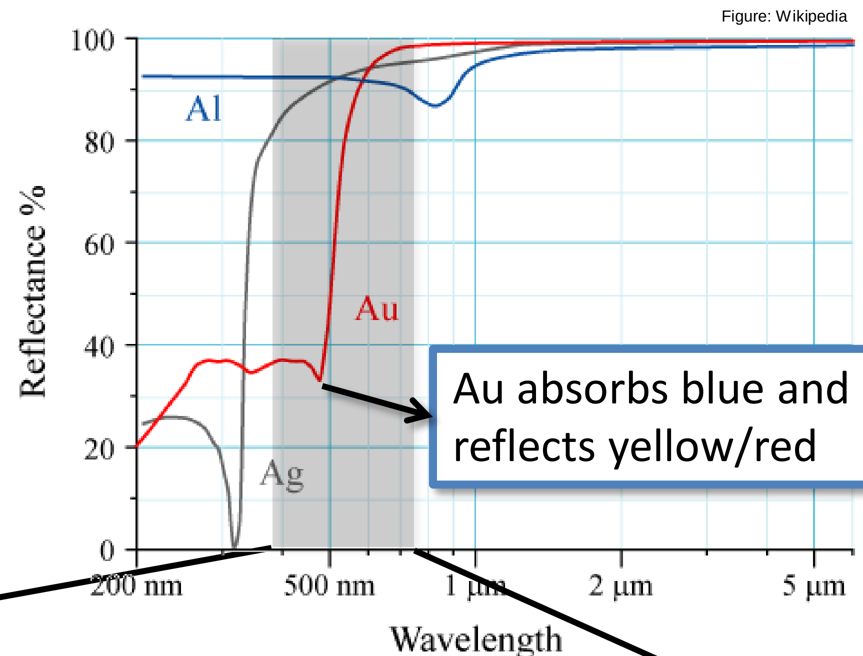
”Gold maximum” of relativistic effects



P. Pyykkö, J.-P. Desclaux, *Acc. Chem. Res.* **1979**, *12*, 276.

So, why is gold yellow?





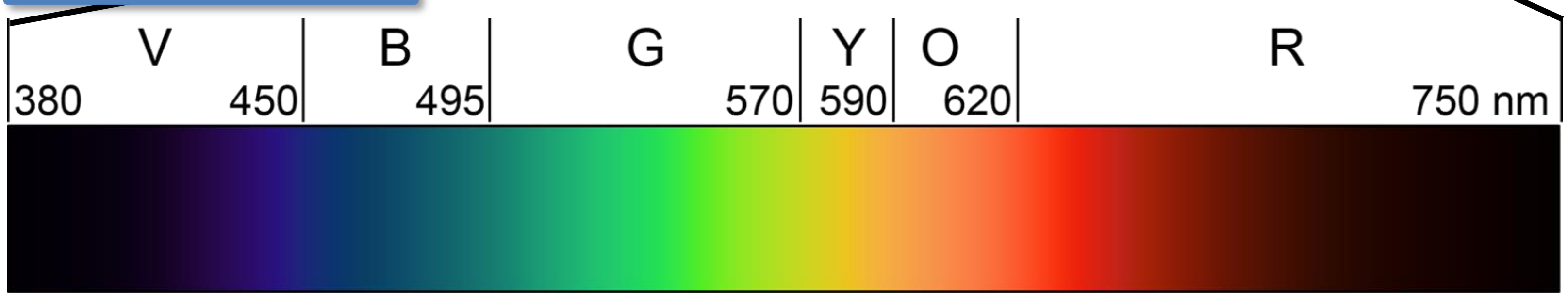


Figure: Wikipedia / AJK

Pauling Electronegativity trends

How much atom attracts electrons in a compound

V·T·E

Periodic table of electronegativity by Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group →
↓ Period

Period	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																		He
2	Li 0.98	Be 1.57												B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31												Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36		Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22		Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	La 1.1	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7[en 1]	Ra 0.9	Ac 1.1	**	Rf	Db	Sg											Ts	Og
				*	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
				**	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3[en 2]	

Halogens

Group 4

Group 11

d-metal with the highest electronegativity: **Au**

Figure: Wikipedia

Available online at www.sciencedirect.com

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Solid State Sciences 7 (2005) 1464–1474

Solid State Sciences

www.elsevier.com/locate/ssscie

Effects of relativistic motion of electrons on the chemistry of gold and platinum

Martin Jansen *

Max-Plank-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Received 24 March 2005; accepted 7 June 2005

Available online 25 October 2005

Dedicated to my esteemed colleague C.N.R. Rao on the occasion of his 70th birthday

Abstract

Experimental evidence proving the unique stabilization of the 6s orbital in platinum and gold is presented. The conclusions are drawn from the chemical reactivities, of both elements, as well as from structural and spectroscopic features of selected compounds. In particular, the opening of a band gap in transparent CsAu and Cs_2Pt, backed by band structure calculations, are regarded conclusive indications of Au^- and Pt^{2-} to exist as closed shell species in these compounds.

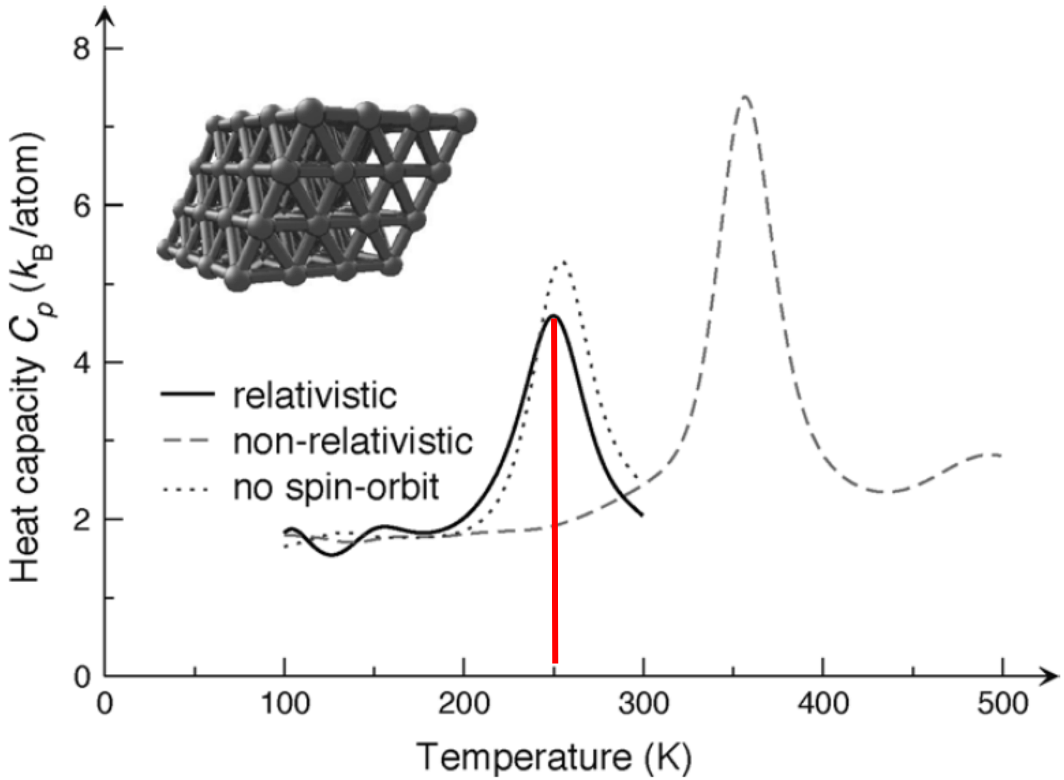
Keywords: Aurides; Platinides; Relativistic effects; Band structure calculation

CsAu is analogous to CsCl
-> "Gold as a halogen"

VIP Relativistic Effects Angew. Chem. Int. Ed. **2013**, *52*, 7583
DOI: 10.1002/anie.201302742

Evidence for Low-Temperature Melting of Mercury owing to Relativity**

Florent Calvo, Elke Pahl, Michael Wormit, and Peter Schwerdtfeger**



Melting point

	°C	K
Zn	420	693
Cd	321	594
Hg	-38.8	**234**

Source: periodictable.com / Wolfram Research

- Hg: [Xe] $4f^{14}$ $5d^{10}$ $6s^2$
- Closed shells only.
- 6s stabilized by relativistic effects.
- Metallic bonding energetically less favorable than in Zn, Cd

Figure 3. Heat capacity at constant zero pressure for the melting process of bulk mercury. The rhombohedral cell of the solid phase is shown as an inset.

PRL **106,** 018301 (2011) PHYSICAL REVIEW LETTERS week ending 7 JANUARY 2011

Relativity and the Lead-Acid Battery

Rajeev Ahuja,[1,*] Andreas Blomqvist,[1] Peter Larsson,[1] Pekka Pyykkö,[2,†] and Patryk Zaleski-Ejgierd[2,‡]

[1]*Division of Materials Theory, Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20, Uppsala, Sweden*

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(Received 30 August 2010; published 5 January 2011)

The energies of the solid reactants in the lead-acid battery are calculated *ab initio* using two different basis sets at nonrelativistic, scalar-relativistic, and fully relativistic levels, and using several exchange-correlation potentials. The average calculated standard voltage is 2.13 V, compared with the experimental value of 2.11 V. All calculations agree in that 1.7–1.8 V of this standard voltage arise from relativistic effects, mainly from PbO_2 but also from $PbSO_4$.

80%!

The Economist | World politics | Business & finance | Economics | Scien

Einstein and car batteries

A spark of genius

Without the magic of relativity, a car's starter motor would not turn

Jan 13th 2011 | From the print edition

Timekeeper

Like

Figure: The Economist

Oxidation states for Ag, Au

"Halogen"

Table 28.2 Oxidation states and stereochemistries of copper, silver and gold

Oxidation state	Coordination number	Stereochemistry	Cu	Ag/Au
-1 ($d^{10}s^2$)	?	?		$[Au(NH_3)_n]^-$ (liq NH_3)
0 ($d^{10}s^1$)	3	Planar	$[Cu(CO)_3]$ (10 K)	$[Ag(CO)_3]$ (10 K)
	4	—	$[(CO)_3CuCu(CO)_3]$ (30 K)	$[(CO)_3AgAg(CO)_3]$ (30 K)
$< +1$	8	See Fig. 28.10(a)		$[(Ph_3P)Au\{Au(PPh_3)\}_7]^{2+}$
	10	See Fig. 28.10(c)		$[Au_{11}I_3\{P(C_6H_4\text{-}4\text{-}F)_3\}_7]$
	12	Icosahedral		$[Au_{13}Cl_{12}(PMe_2Ph)_{10}]^{3+}$
1 (d^{10})	2	Linear	$[CuCl_2]^-$, Cu_2O	$[M(CN)_2]^-$
	3	Trigonal planar	$[Cu(CN)_3]^{2-}$	$[AgI(PEt_2Ar)_2]$, $[AuCl(PPh_3)_2]$
	4	Tetrahedral	$[Cu(py)_4]^+$	$[M(diars)_2]^+$, $[Au(PMePh_2)_4]^+$
		Square planar		$[Au\{\eta^2\text{-}Os_3(CO)_{10}H\}_2]^-$
	6	Octahedral		AgX (X = F, Cl, Br)
2 (d^9)	4	Tetrahedral	$Cs_2[CuCl_4]$[(a)]	
		Square planar	$[EtNH_3]_2[CuCl_4]$[(a)]	$[Ag(py)_4]^{2+}[Au\{S_2C_2(CN)_2\}_2]^{2-}$
	5	Trigonal bipyramidal	$[Cu(bipy)_2I]^+$	
		Square pyramidal	$[\{Cu(dmgH)_2\}_2]$[(b)]	
	6	Octahedral	$K_2Pb[Cu(NO_2)_6]$	
	7	Pentagonal bipyramidal	$[Cu(H_2O)_2(dps)]^{2+}$[(c)]	
	8	Dodecahedral (dist.)	$[Cu(O_2CMe)_4]^{2+}$	
3 (d^8)	4	Square planar	$[CuBr_2(S_2CNBu^t_2)]$	$[AgF_4]^-$, $[AuBr_4]^-$
	5	Square pyramidal	$[CuCl(PhCO_2)_2(py)_2]$[(d)]	$[Au(C_6H_4CH_2NMe_2\text{-}2)\text{-}(phen)(PPh_3)]^{2+}$
	6	Octahedral	$[CuF_6]^{3-}$	$[AgF_6]^{3-}$, $[AuI_2(diars)_2]^+$
4 (d^7)	6	?	$[CuF_6]^{2-}$	
5 (d^6)	6	Octahedral (?)		$[AuF_6]^-$

e.g. CsAu

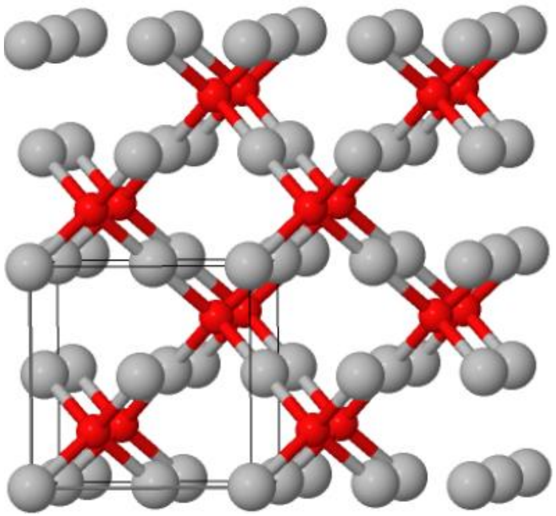
Most important for Ag, Au

Common for Au

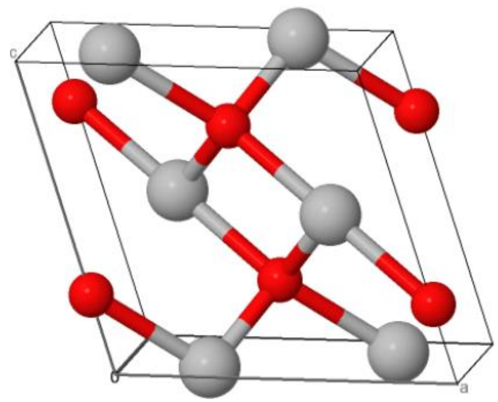
N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed. **1997**, Butterworth Heinemann.

Oxides of Ag and Au

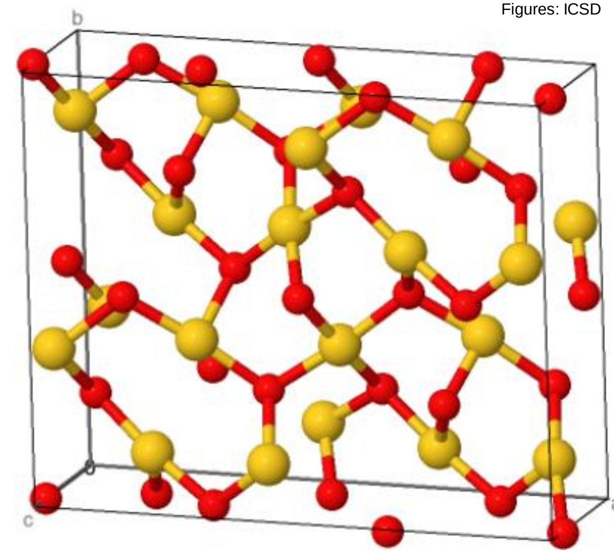
Figures: ICSD



Cubic Ag_2O
(analogous to Cu_2O)



Monoclinic AgO
(analogous to CuO)



Orthorhombic Au_2O_3
(thermally unstable, decomposes at 160°C)

Also for silver:
Ag_2O_3 with Ag(III)
Ag_3O_4 with Ag(II) and Ag(III)
Ag_3O with Ag(0) and Ag(I)

Applications of Au: Catalysis

Effect of a catalyst on an exothermic chemical reaction X + Y -> Z

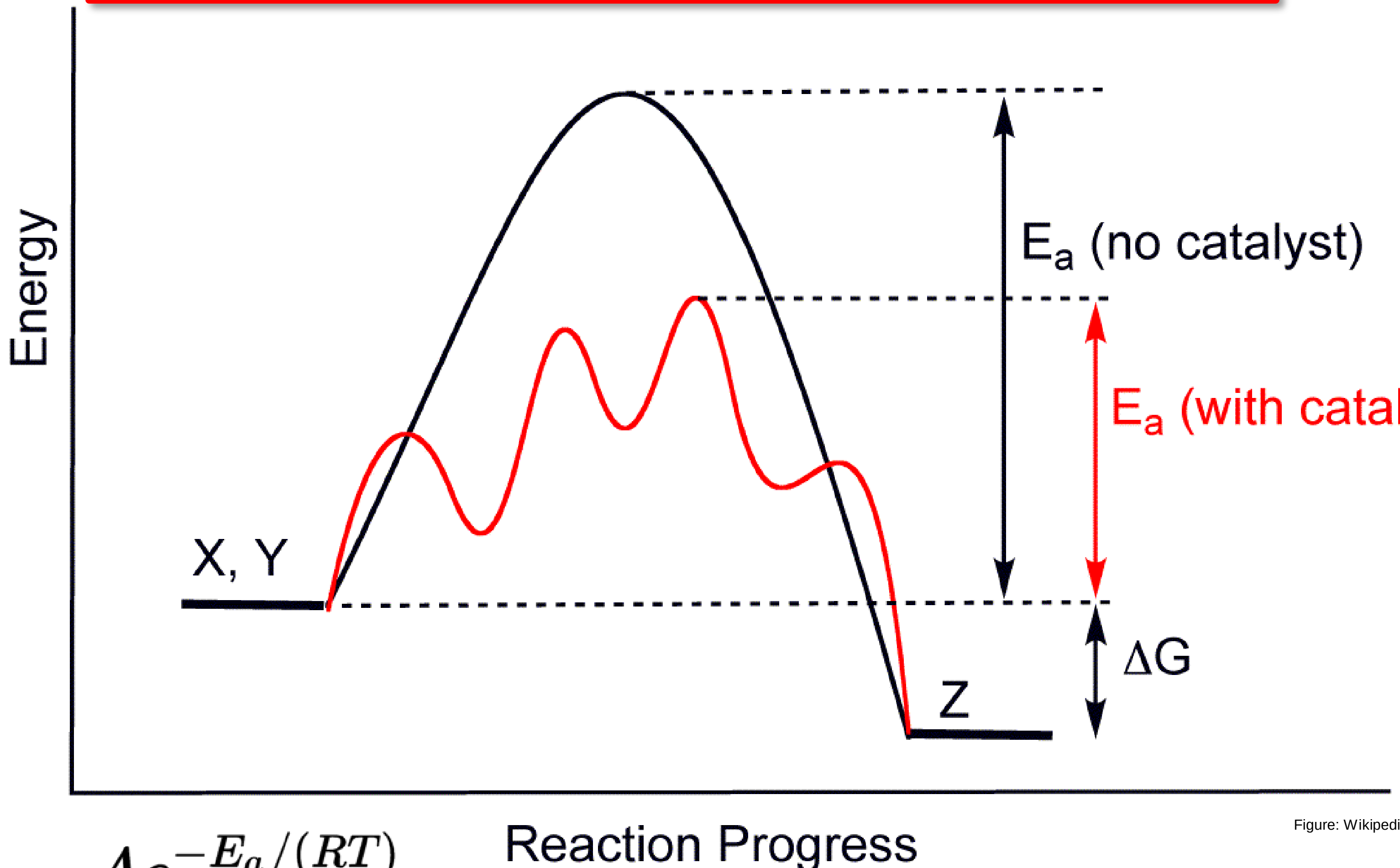


Figure: Wikipedia

$$k = Ae^{-E_a/(RT)}$$

Gold Catalysis

- Until recently, chemical inertness of bulk gold appeared to provide very limited opportunities to open up new and exciting chemistries
- However, gold, when sub-divided to the nanoscale (<< 100 nm), can be exceptionally active as a catalyst
- Nanoparticles of gold can help to **activate molecular oxygen under mild conditions** — at atmospheric pressure and temperatures of 60–80 C°
- Note that nanostructuring can also increase the activity of other metals, but for gold this is perhaps more interesting since the bulk form is so inert

NATURE|Vol 437|20 October 2005

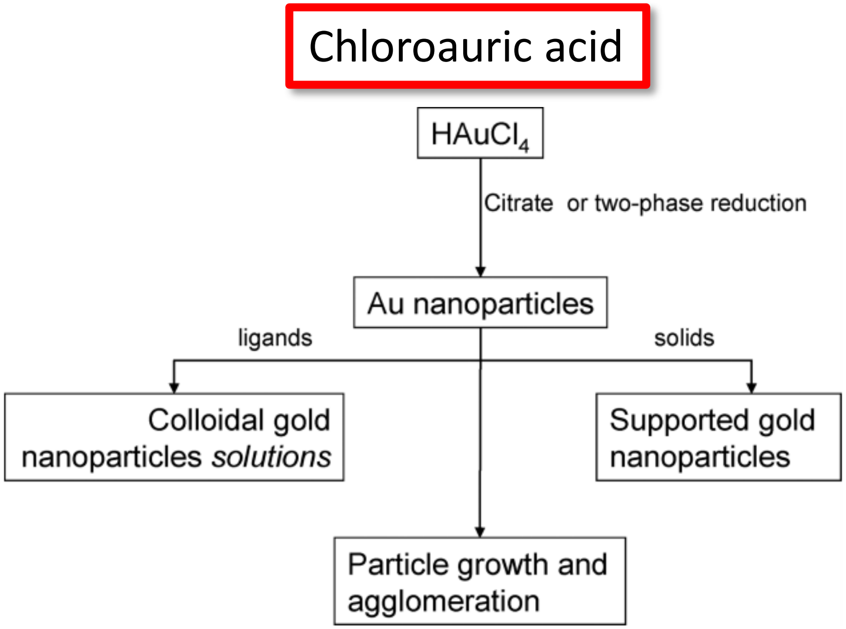
CATALYSIS

Gold rush

Masatake Haruta

The chemical industry would be transformed if selective oxidation of hydrocarbons could be achieved efficiently using cheap and clean oxygen from the air. Doing that with gold as a catalyst is a method gaining in allure.

Synthesis of gold nanoparticles



Scheme 2 Strategies to stabilize gold nanoparticles against agglomeration.

Chem. Soc. Rev., 2008, **37**, 2096–2126

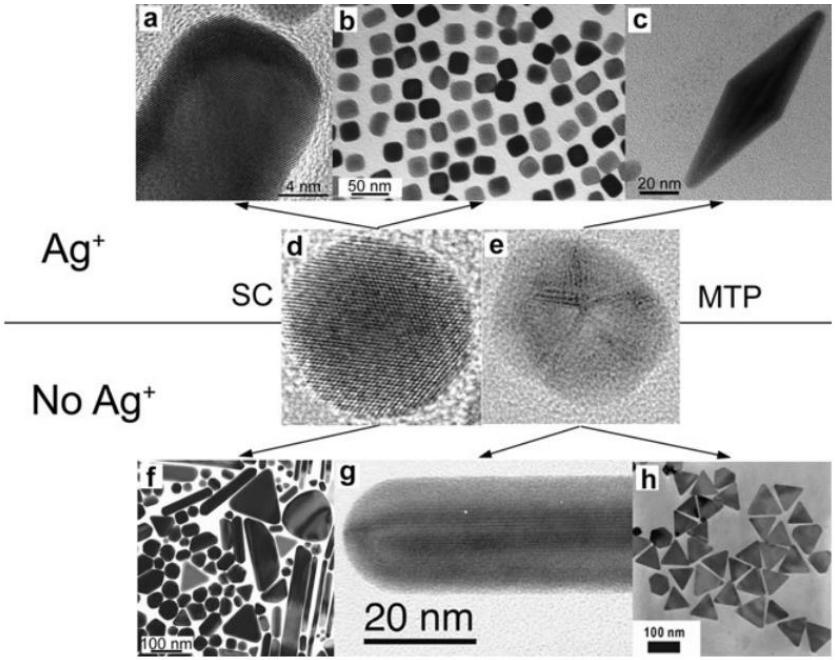


Fig. 1 Morphology dependence of gold nanoparticles grown from either single crystal (d) or multiply twinned (e) seeds, in the presence (a–c) and absence (f–h) of silver nitrate. Figures c and h reproduced with permission from ref. 10 and 18, respectively.

Chem. Soc. Rev., 2008, **37**, 1783–1791

Gold nanoparticles on TiO_2 support

Heterogenous catalysis: catalyst particles on a solid support

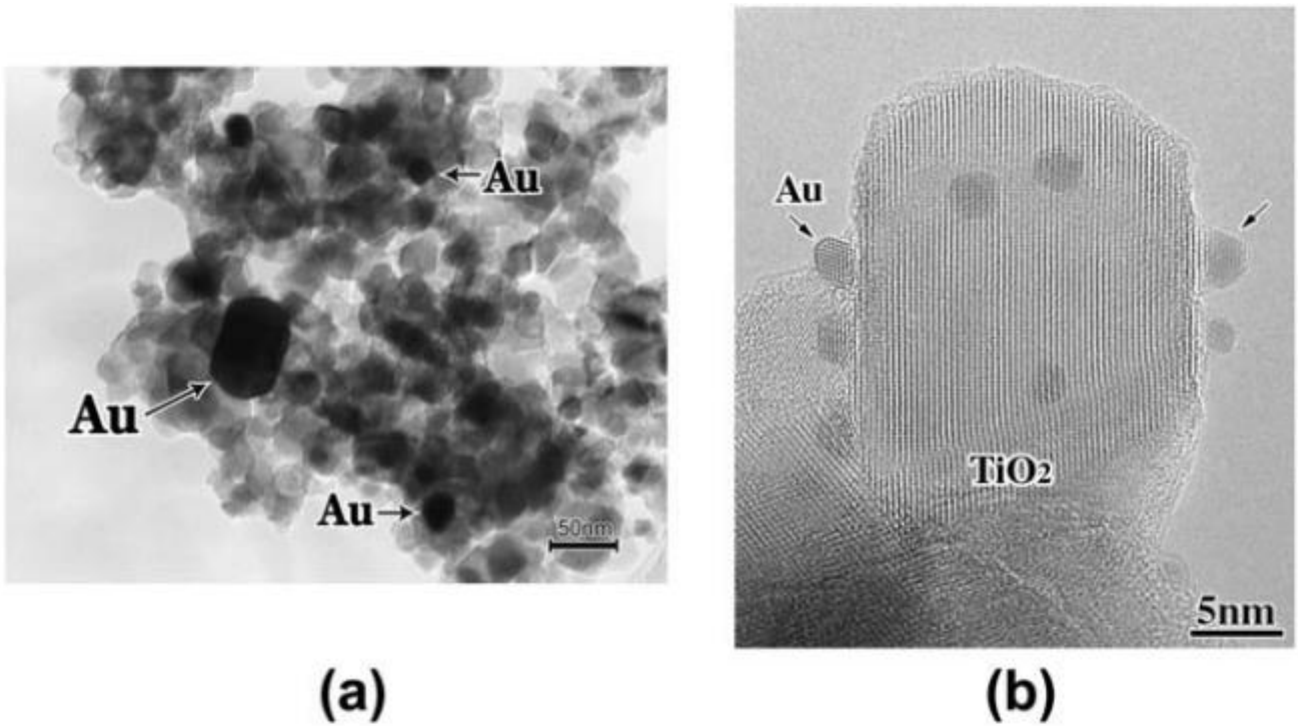
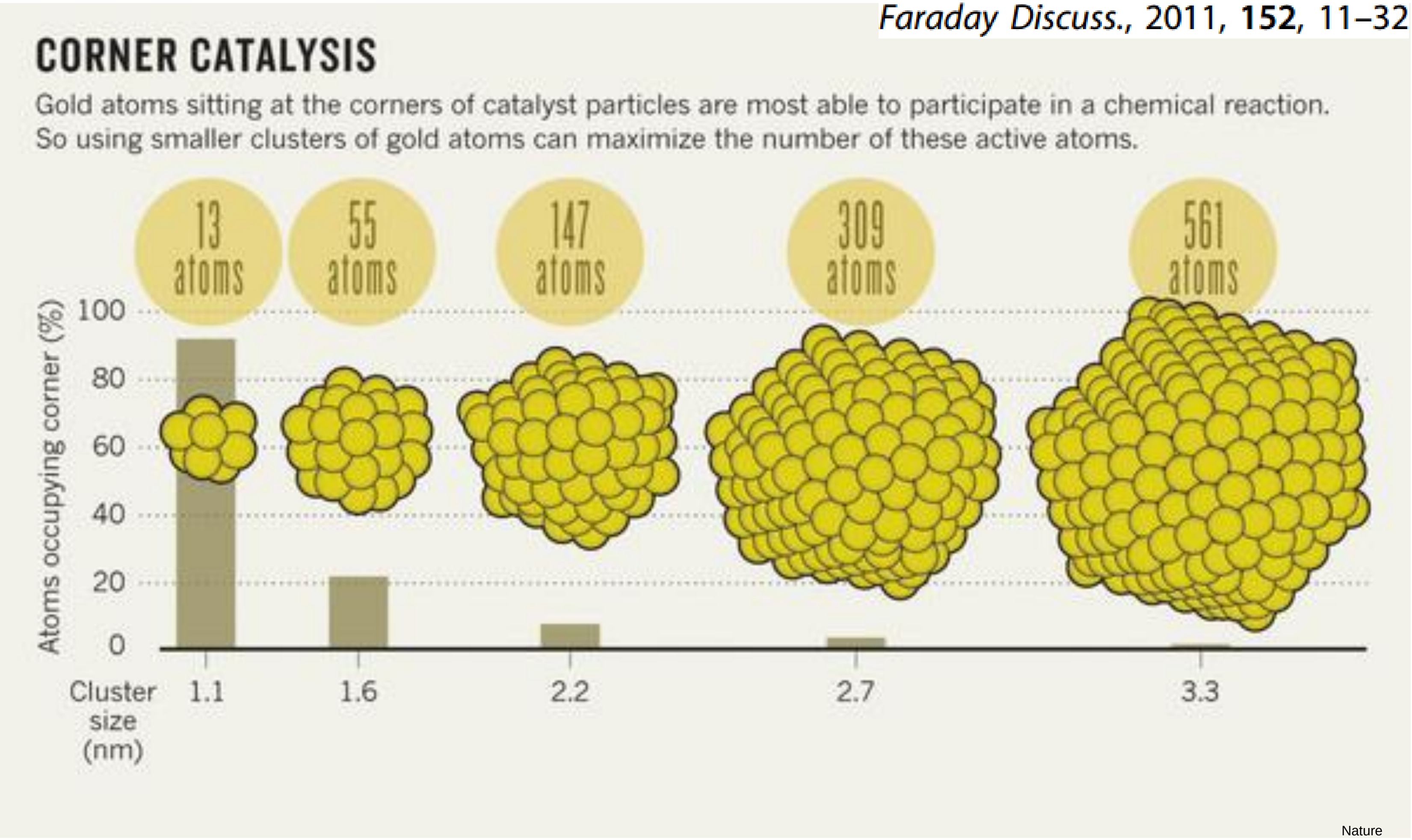


Fig. 15 TEM images of Au/TiO_2 prepared by (a) the impregnation method and (b) the deposition-precipitation methods followed by calcination in air at 673 K. Note that the support material is the same and Degussa TiO_2, p-25.

Faraday Discuss., 2011, **152**, 11–32

Gold nanoparticles – size effect

Faraday Discuss., 2011, **152**, 11–32



Atomic and electronic structure of gold clusters: understanding flakes, cages and superatoms from simple concepts†

Hannu Häkkinen *Chem. Soc. Rev.*, 2008, **37**, 1847–1859 | 1847

Review on superatoms and magic numbers

Gold nanoparticles – size vs. shape

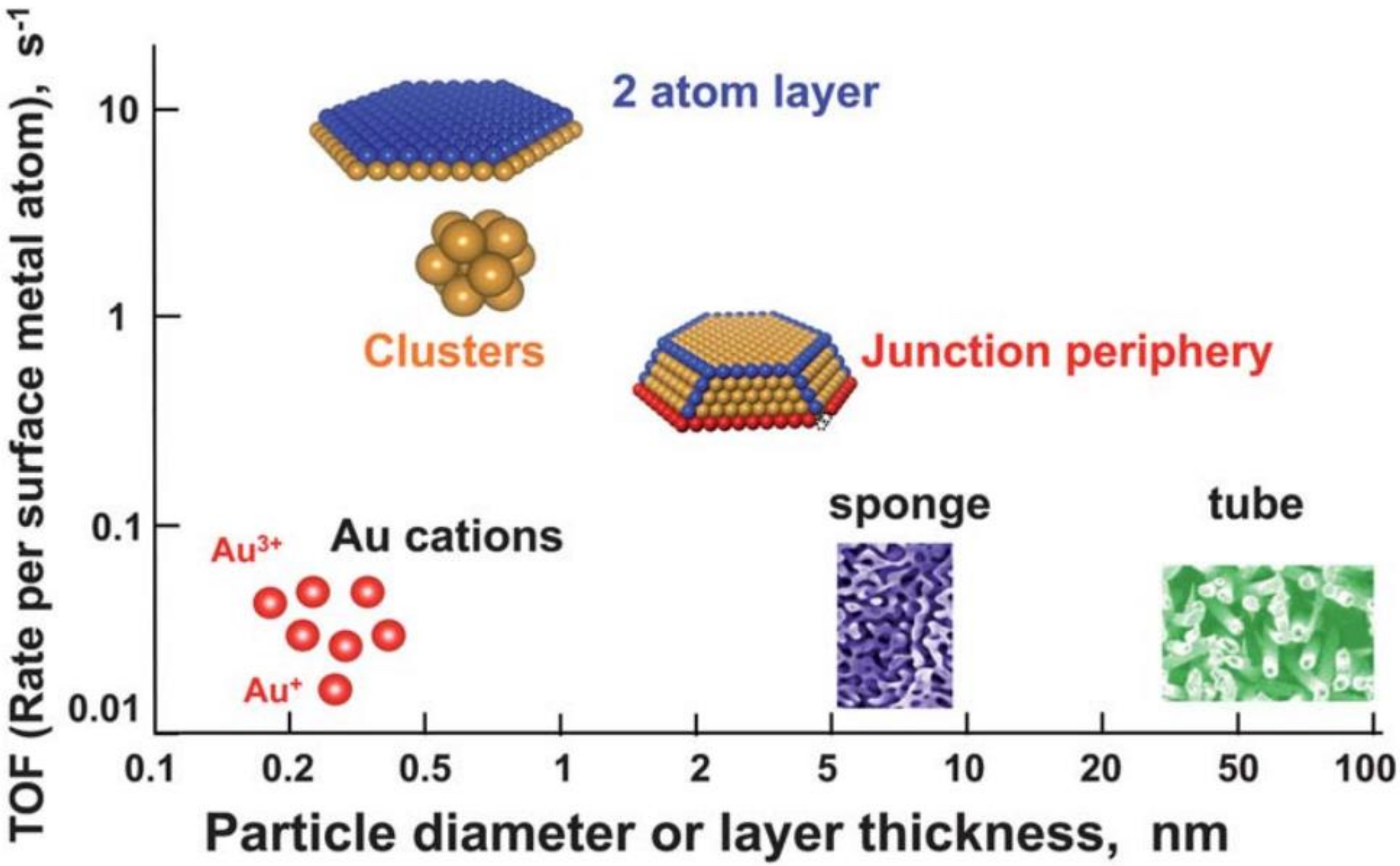
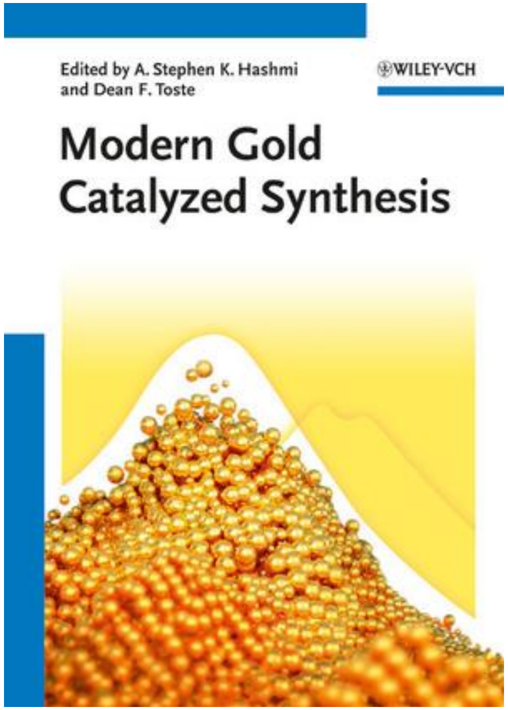


Fig. 4 Turn over frequency of CO oxidation at room temperature for various states of gold.

Faraday Discuss., 2011, **152**, 11–32

Examples of reactions catalyzed by Au nanoparticles

- **Selective oxidation of hydrocarbons**
  - Partial oxidation of methane to methanol–formaldehyde, and petrol derivatives to oxygenates
  - Great interest from the point of view of industrial organic chemistry
- **Low temperature CO oxidation**
- Acetylene hydrochlorination
- Addition of nucleophiles to acetylenes
- Selective hydrogenation of N–O bonds
- Alcohol oxidation to acids and aldehydes
- Direct formation of hydrogen peroxide



Pd, Pt – metallic ground state

Property	Pd	Pt
Atomic number	46	78
Electronic configuration	[Kr] $4d^{10}$	[Xe] $4f^{14}$ $5d^{9}$ $6s^{1}$
Crystal structure	Face-centered cubic (FCC, *Fm*-3*m*)	

74.05% of the total volume is occupied by spheres (maximum density possible in structures constructed of spheres of only one size)

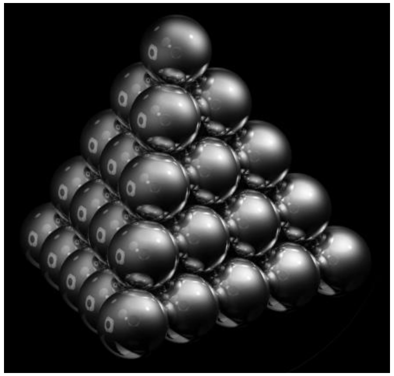
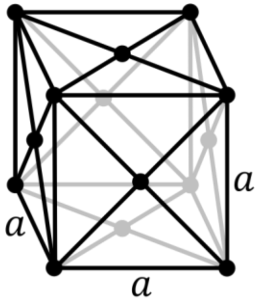
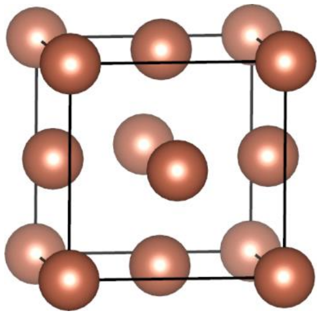


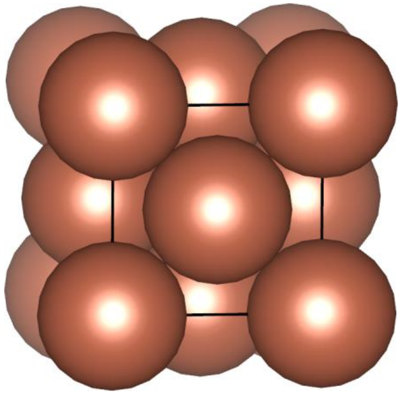
Figure: Wikipedia



Wikipedia

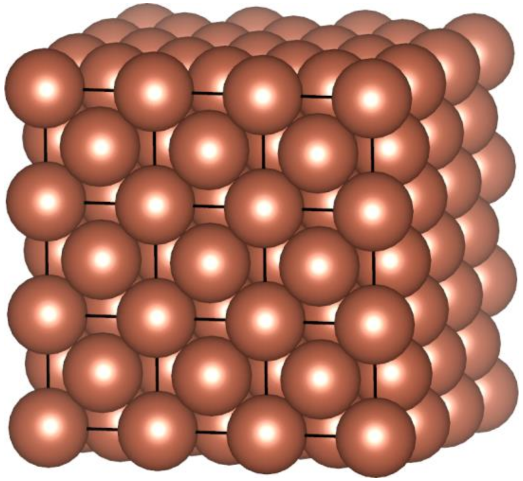
FCC Bravais lattice





Figures: AJK

Ni/Pd/Pt unit cell



3x3x3 supercell

Oxidation states for Pd, Pt

Missing from here: -2 for Pt (e.g. Cs_2Pt)!

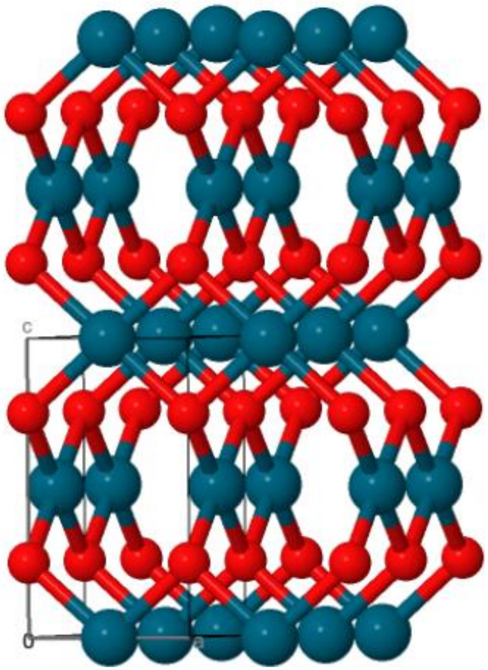
Table 27.2 Oxidation states and stereochemistries of compounds of nickel, palladium and platinum

Oxidation state	Coordination number	Stereochemistry	Ni	Pd/Pt
−1	4	?	$[Ni_2(CO)_6]^{2-}$	
0 (d^{10})	3	Planar	$[Ni\{P(OC_6H_4\text{-}2\text{-}Me)_3\}_3]$	$[M(PPh_3)_3]$
	4	Tetrahedral	$[Ni(CO)_4]$	$[M(PF_3)_4]$
1 (d^9)	4	Tetrahedral	$[NiBr(PPh_3)_3]$	
	3	Trigonal planar	$[Ni(NPh_2)_3]^-$	
2 (d^8)	4	Tetrahedral	$[NiCl_4]^{2-}$	
Most important for Pd, Pt		Square planar	$[Ni(CN)_4]^{2-}$	$[MCl_4]^{2-}$
	5	Trigonal bipyramidal	$[Ni(PPhMe_2)_3(CN)_2]$	$[M(qas)I]^{+}$[(a)]
		Square pyramidal	$[Ni(CN)_5]^{3-}$	$[Pd(tpas)Cl]^{+}$[(b)]
	6	Octahedral	$[Ni(H_2O)_6]^{2+}$	$[Pd(diars)_2I_2]$
		Trigonal prismatic	NiAs	
	7	Pentagonal bipyramidal	$[Ni(dapbH)_2(H_2O)_2]^{2+}$[(c)]	
3 (d^7)	4	Square planar	—	$[Pt(C_6Cl_5)_4]^-$
Common for Pt	5	Trigonal bipyramidal	$[NiBr_3(PEt_3)_2]$	
	6	Octahedral	$[NiF_6]^{3-}$	$[PdF_6]^{3-}$
4 (d^6)	6	Octahedral	$[NiF_6]^{2-}$	$[MCl_6]^{2-}$
	8	"Piano-stool"	—	$[Pt(\eta^5\text{-}C_5H_5)Me_3]$
5 (d^5)	6	Octahedral	—	$[PtF_6]^-$
6 (d^4)	6	Octahedral	—	PtF_6

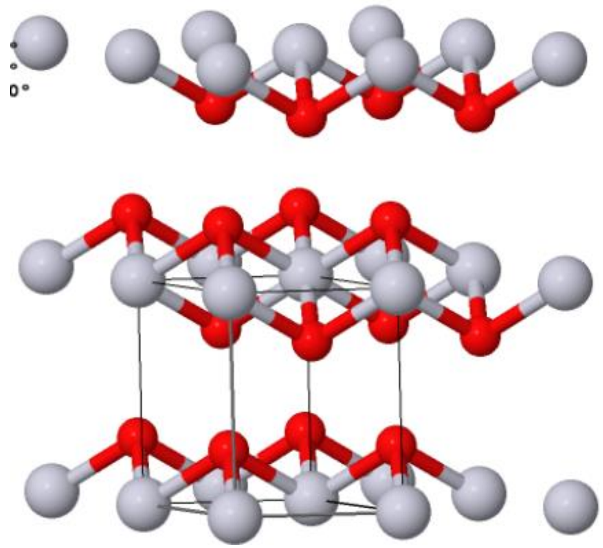
N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed. **1997**, Butterworth Heinemann.

Oxides of Pd and Pt

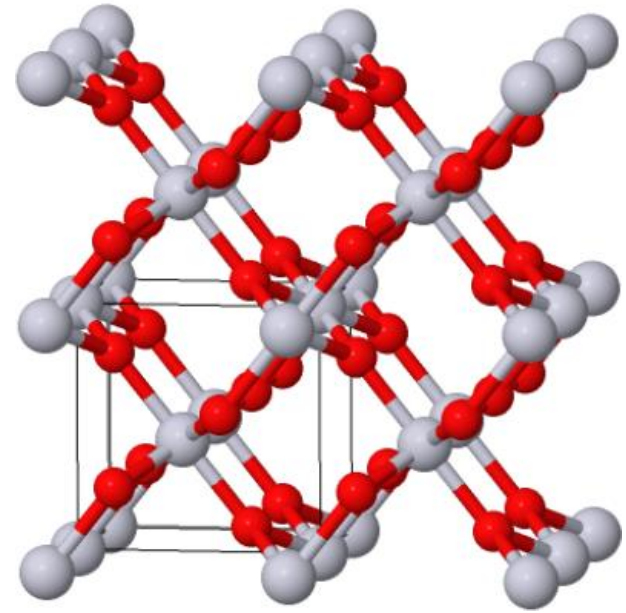
ICSD



PdO



PtO_2 ($T < 800$ °C)



PtO_2 ($T > 800$ °C)

Also for platinum:
PtO with Pt(II)
Pt_3O_4 with Pt(II) and Pt(IV)

Pd and Pt in catalytic applications

A.J. Medford et al. / Journal of Catalysis 328 (2015) 36–42

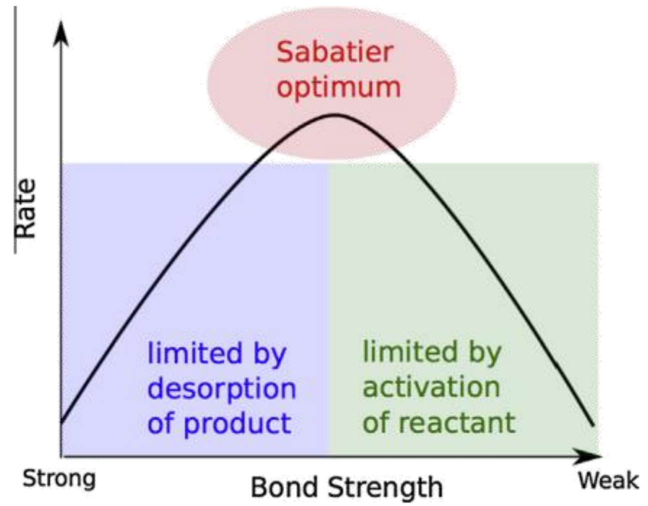
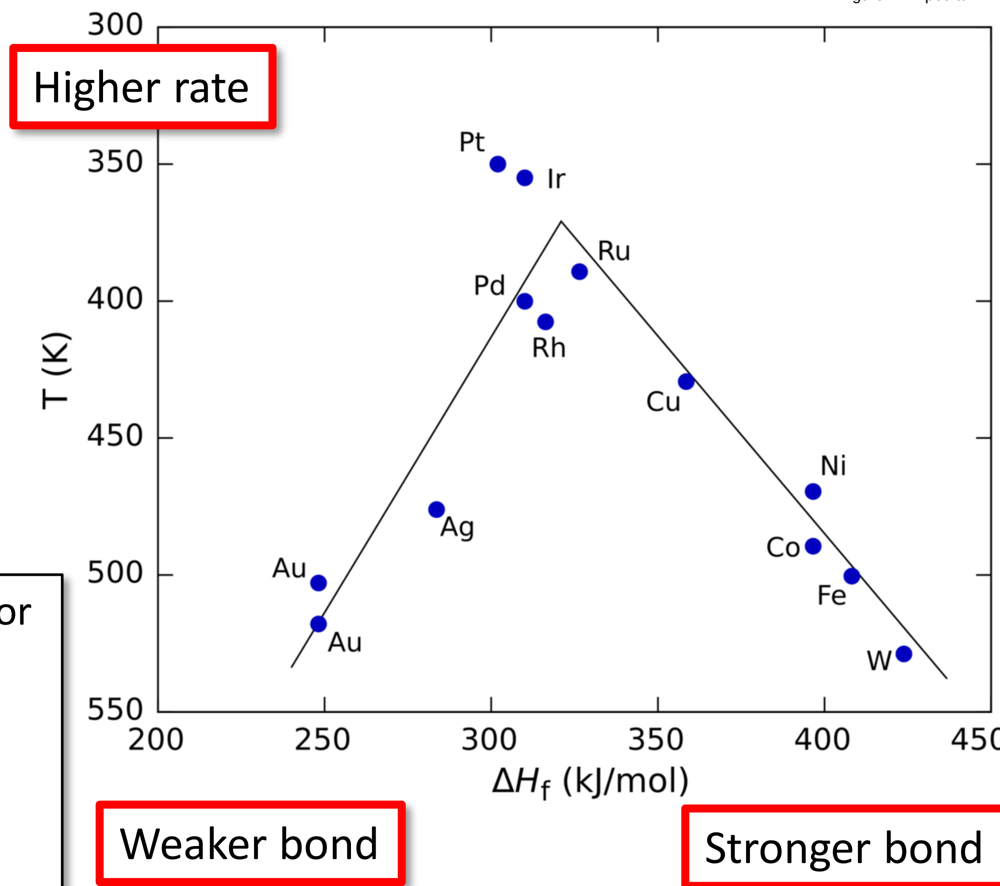


Fig. 1. Schematic representation of the qualitative Sabatier principle.

- **Sabatier principle** is a qualitative guideline for heterogeneous catalysis.
- The best catalysts should bind atoms and molecules with an **intermediate strength**
  - Not too weakly in order to be able to activate the reactants
  - Not too strongly to be able to desorb the products.
- This leads to a volcano- type relationship between activity and bond strength

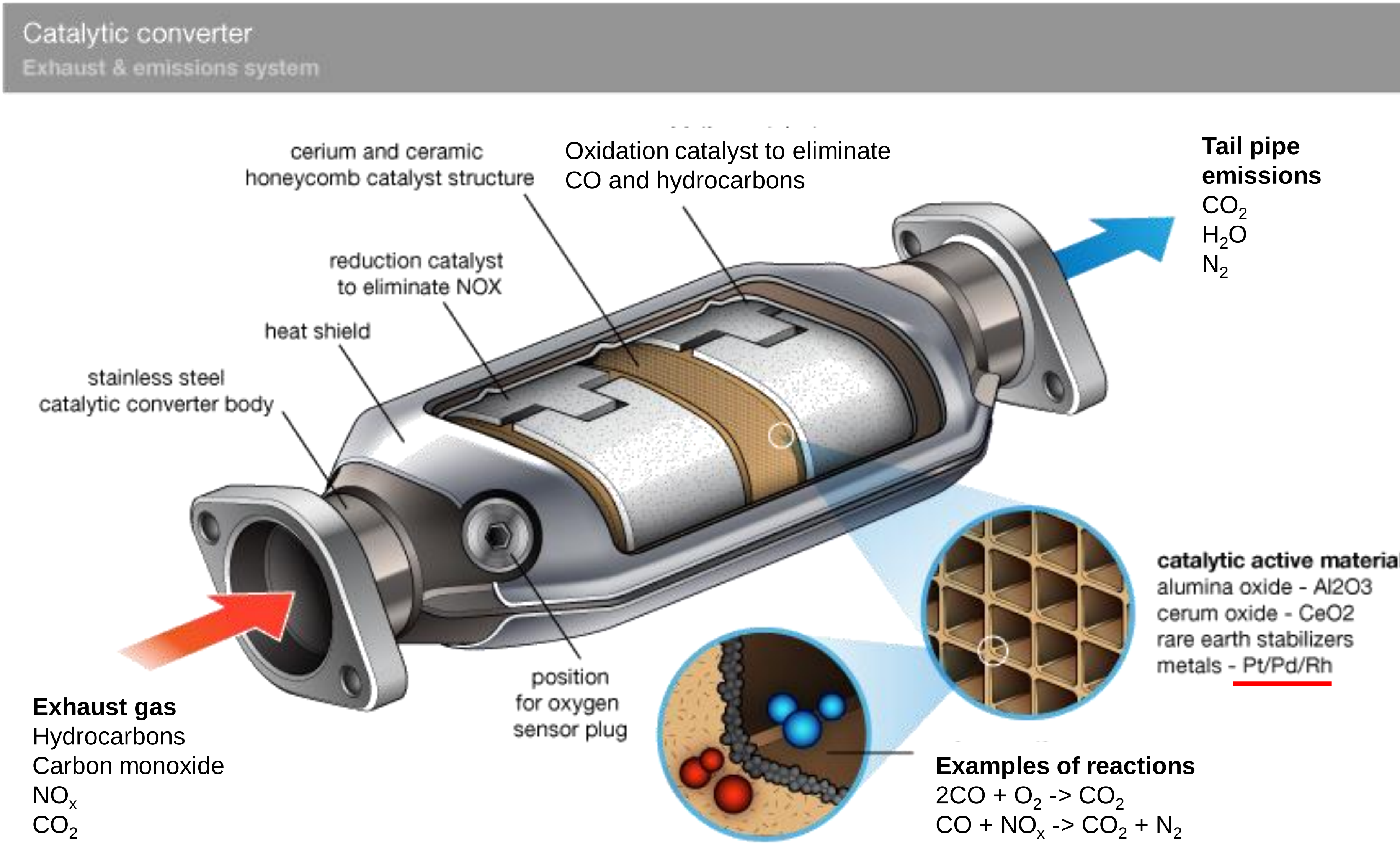
Figure: Wikipedia



Volcano plot for the decomposition of formic acid on transition metals

Pd and Pt in catalytic converters

Figure: pakwheels.com



Oxidation catalyst to eliminate CO and hydrocarbons

Tail pipe emissions
CO_2
H_2O
N_2

Exhaust gas
Hydrocarbons
Carbon monoxide
NO_x
CO_2

Examples of reactions
$2CO + O_2$ -> CO_2
$CO + NO_x$ -> $CO_2 + N_2$

Pd-catalyzed coupling reactions (Nobel Prize in Chemistry 2010)

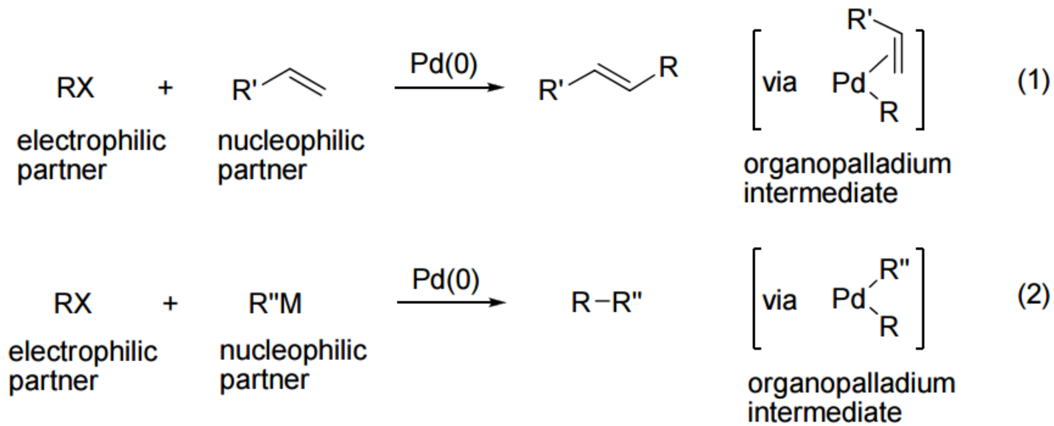


Figure: Nobel committee

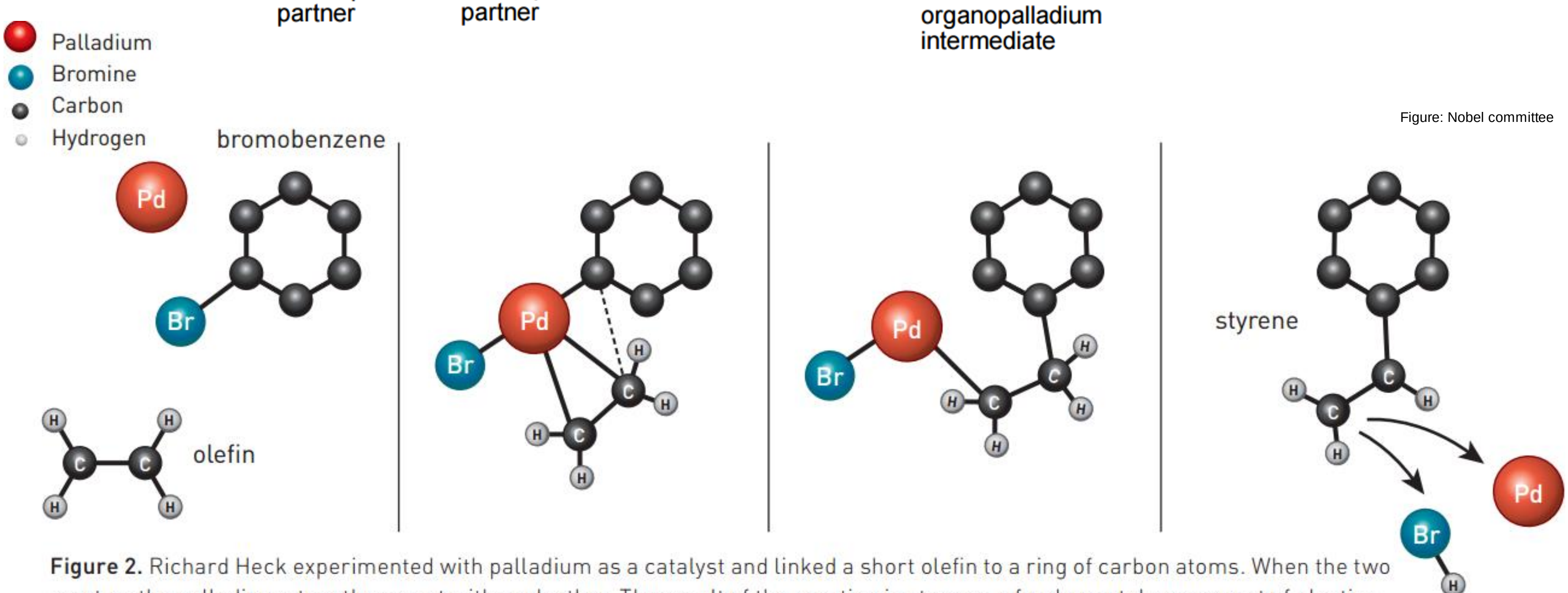


Figure 2. Richard Heck experimented with palladium as a catalyst and linked a short olefin to a ring of carbon atoms. When the two meet on the palladium atom they react with each other. The result of the reaction is styrene, a fundamental component of plastics.

Pt catalysts in organic synthesis

- Often the so-called Adams's catalyst is used instead of platinum metal
  - Platinum(IV) oxide hydrate, PtO_2•H2O
  - More consistent behavior in comparison to Pt metal
- During the (catalyzed) reaction, platinum metal is then formed (actual catalyst)
  - The platinum metal is possibly formed as nanoclusters
- Valuable catalyst for
  - Hydrogenation
  - Hydrogenolysis
  - Dehydrogenation
  - Oxidation reactions

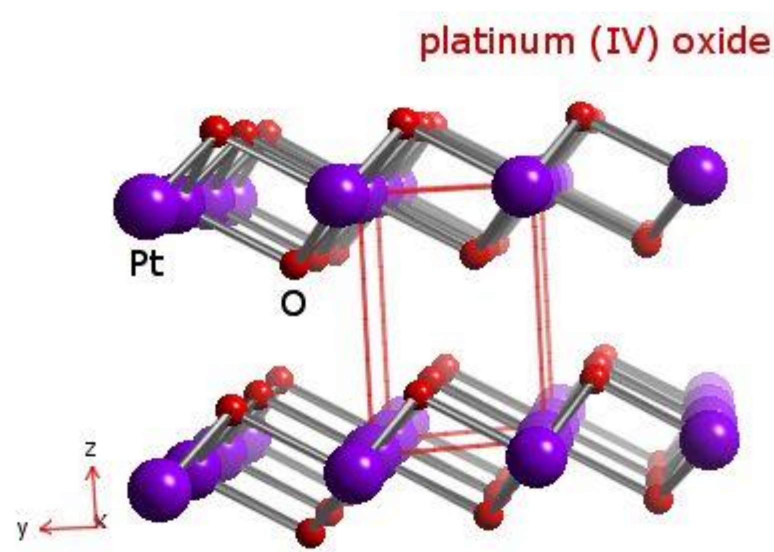


Figure: Webelements

Pt catalysts in fuel cells

- Proton-Exchange-Membrane (PEM) hydrogen fuel cells can be used for converting chemical energy to electricity
- Operating temperatures < 100°C
- Net reaction: $H_2 + ½O_2 \rightarrow H_2O$
- Both anode and cathode reaction need a catalyst
- Pt is currently the most important catalyst
- Pt might be too expensive to enable widespread applications of such fuel cells
  - CO poisoning is also an issue
- Plenty of ongoing research on improved carrier materials for Pt (e.g. nanostructured carbon)

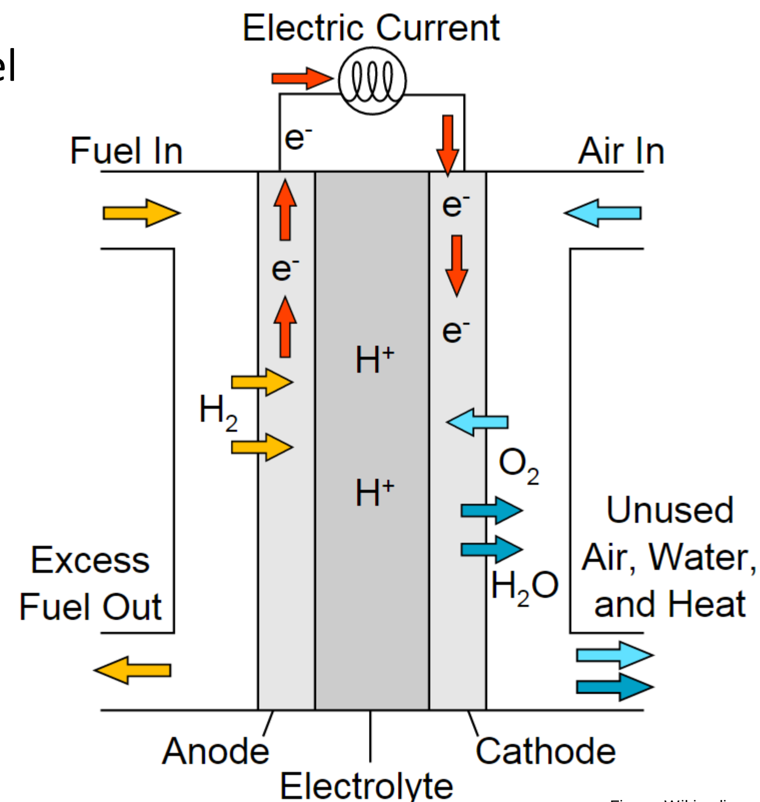


Figure: Wikipedia

ACS Catalysis

Recent work on the related *hydrogen evolution reaction* in Aalto

Electrochemical Activation of Single-Walled Carbon Nanotubes with Pseudo-Atomic-Scale Platinum for the Hydrogen Evolution Reaction

ACS Catal. **2017**, *7*, 3121−3130

Mohammad Tavakkoli,[*,†] Nico Holmberg,[†] Rasmus Kronberg,[†] Hua Jiang,[‡] Jani Sainio,[‡] Esko I. Kauppinen,[‡] Tanja Kallio,[†] and Kari Laasonen[*,†]