Literature Seminar

Modern Alchemy ??

the Chemistry of
~ Cluster & Nanoparticle ~

2011. 06.07. (Tue)

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Introduction 1

Figure. Alchemist in medieval Europe
(a cover picture of Aldrich catalog 2010)

Alchemy

In a narrow sense, Alchemy is an ancient tradition the objective of which is turning base metals, such as lead or mercury, into noble metals, especially gold, by chemical reactions.
During it's trials, many chemicals have been found and many equipments developed.
These accomplishments are succeeded by today's chemistry.

Introduction 2

Modern Nucleosynthesis (Physics)

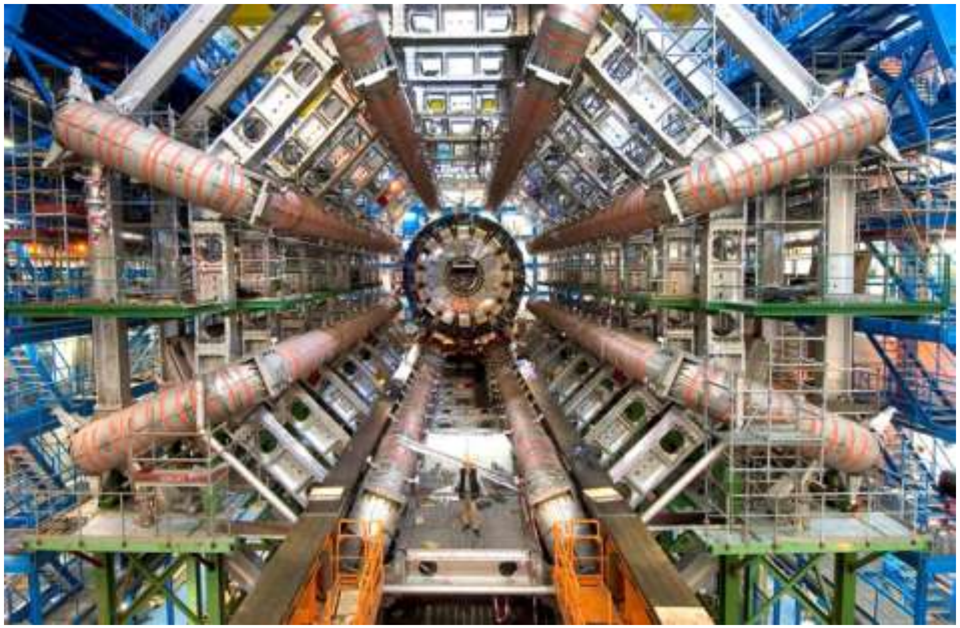


Figure. The Large Hadron Collider, the world's largest and highest-energy particle accelerator

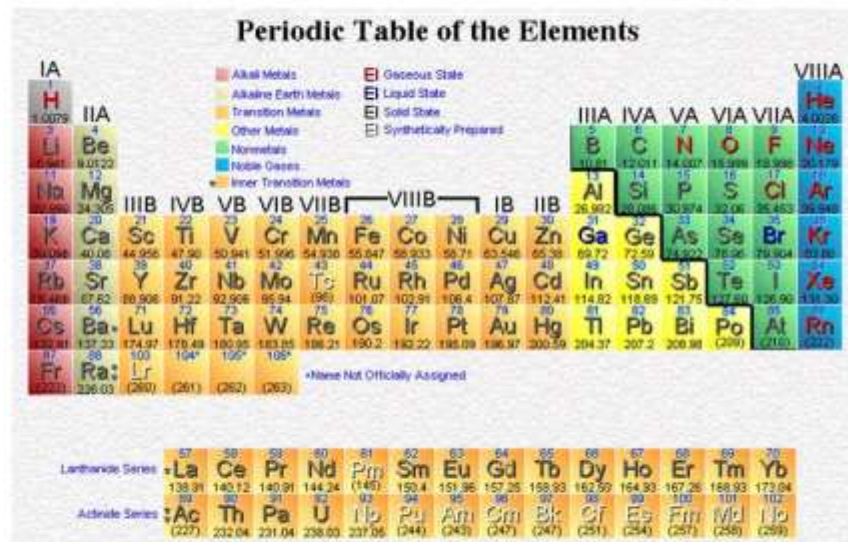
Today, atoms can be synthesized by accelerators.
In fact, you can synthesized gold from lead.
Lead accelerated up to 70% of the velocity of light collides with beryllium and then turns into gold.

But, even if you use the strongest lead - beam, you will spend a hundred trillion yen and a million year only to get 1g gold!!!

Today's topic

【1】 Super Atom

$$Al_{13} = Cl \ ?$$



【2】 Transition Metal Carbides

$$WC = Pt \ ??$$

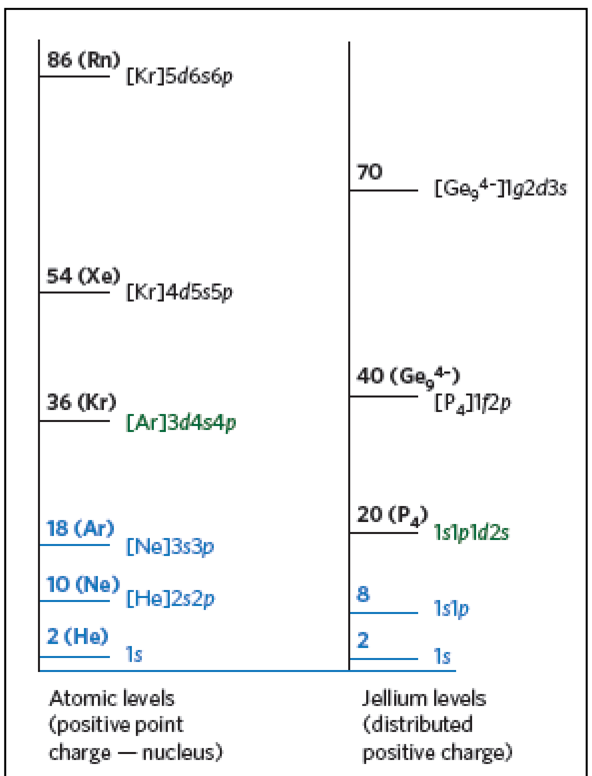
【3】 Bimetallic Nanoparticles

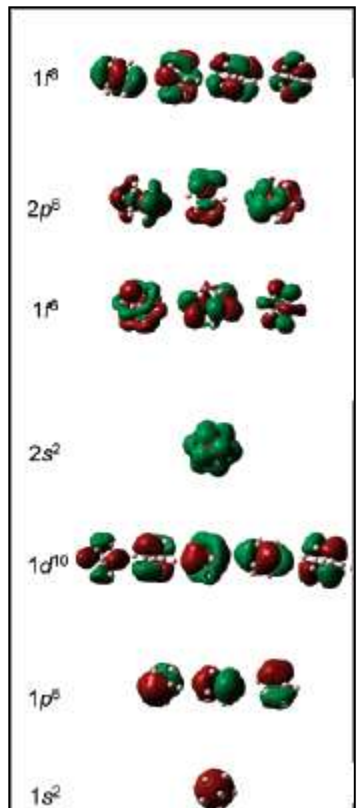
$$(Rh + Ag) \div 2 = Pd \ ???$$

What's Super Atom ? (1)

⊖
CN

The formation of strong bonds or closed electronic shells by groups of atoms can create species that react as if they were one atom.
Familiar examples include ions such as CN^-, which react as if it were halogens in so many cases that it is referred to as "pseudohalogens."



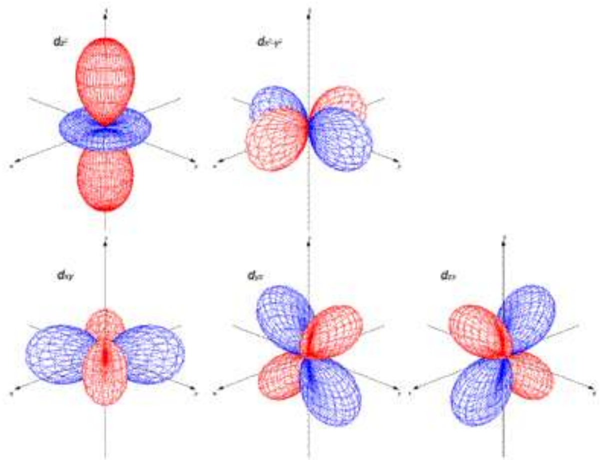


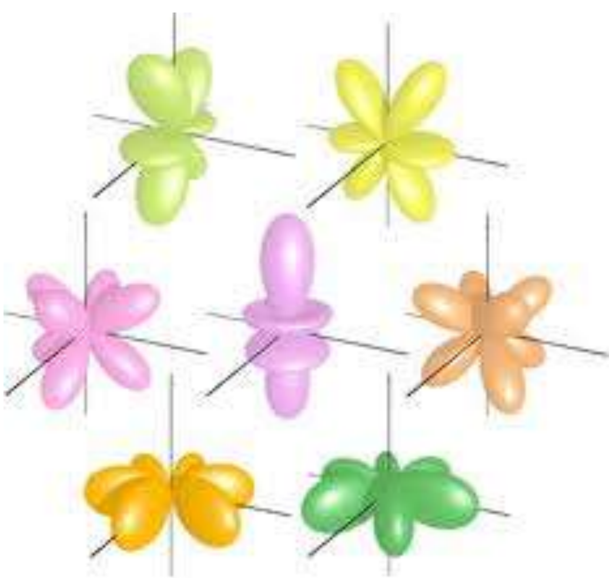
C60

Figure | (left) A comparison of the energy levels (shells) for an atom and for a jellium sphere. (right) Molecular orbital (MO) diagram for Al_{13}^-

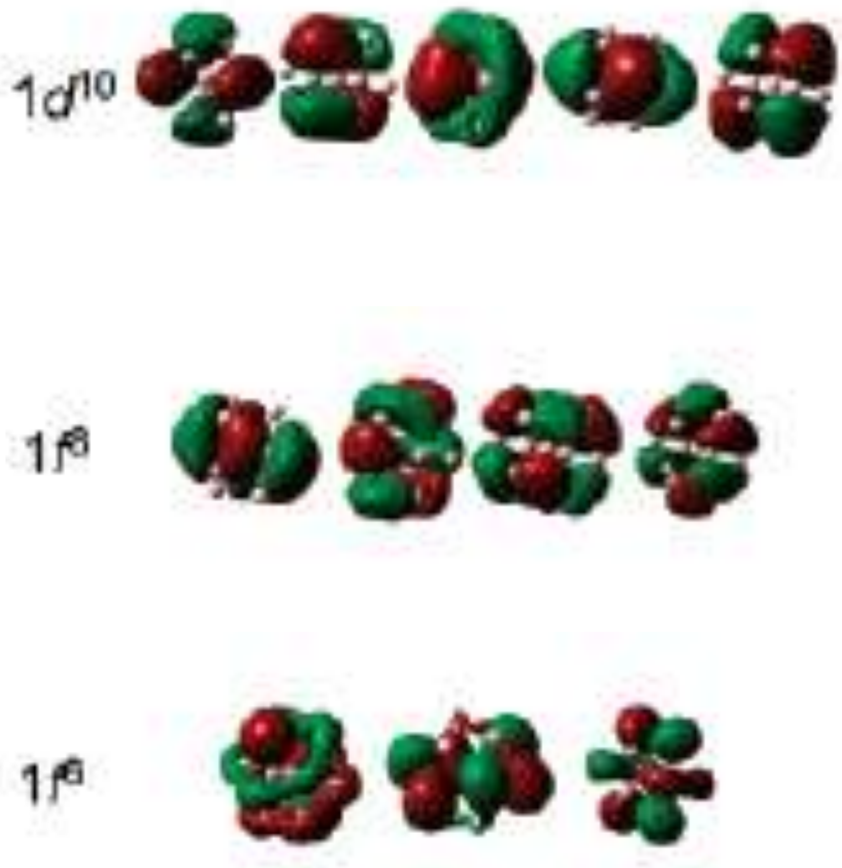
What's Super Atom ? (2)

Atomic orbital



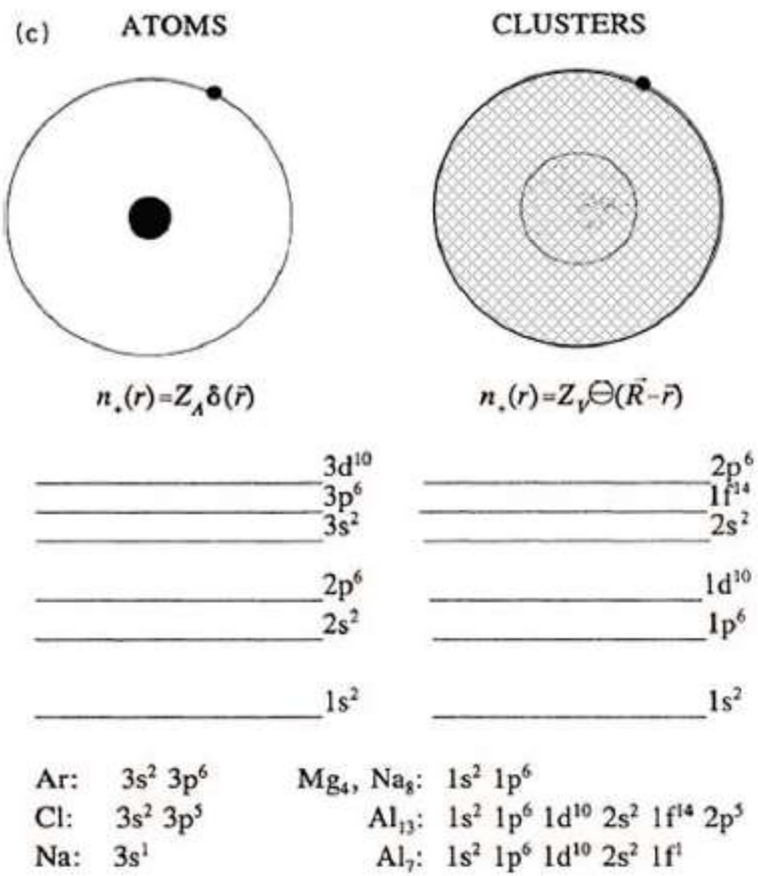


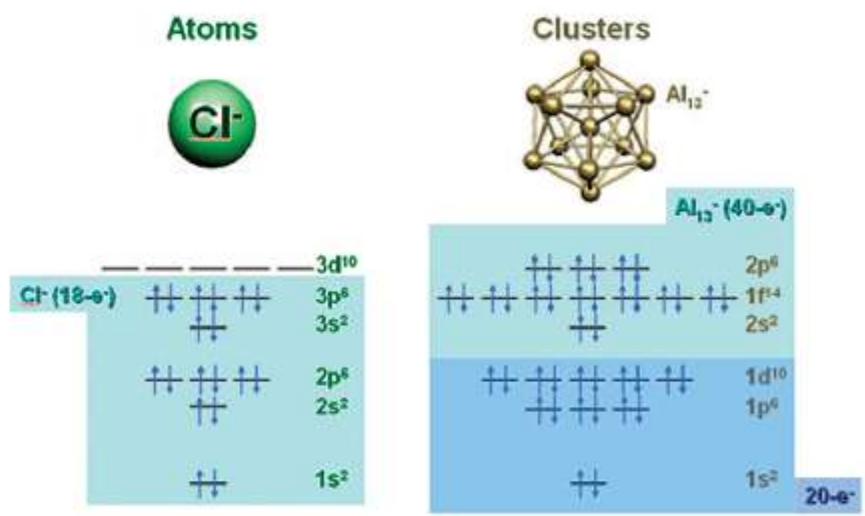
Jellium orbital



What’s Super Atom ? (3)

The superatom suggestion is that free electrons in the cluster occupy a new set of orbitals that are defined by the entire group of atoms rather than by each individual atom separately.





Discovery of Super Atom

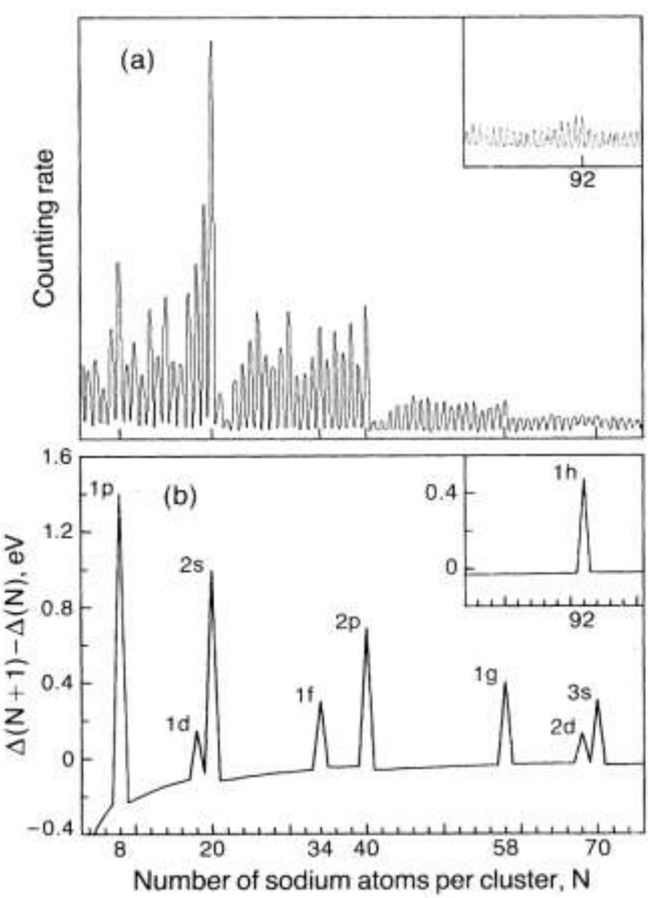


Figure | Sodium cluster

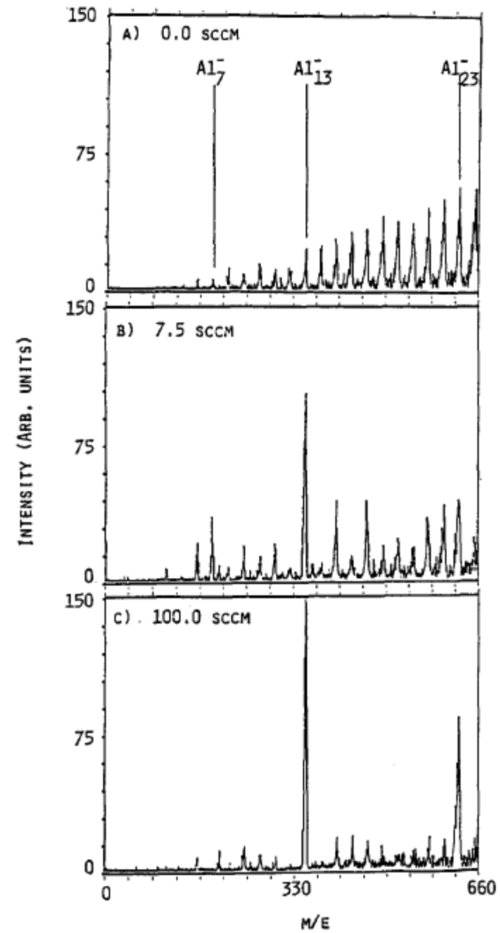


Figure | Aluminum cluster

Knight, W. D. *et al., Phys. Rev. Lett.* **1984**, *52*, 2141.
Castleman, A. W. *et al., J. Chem. Phys.* **1989**, *91*, 2753.

Equipment

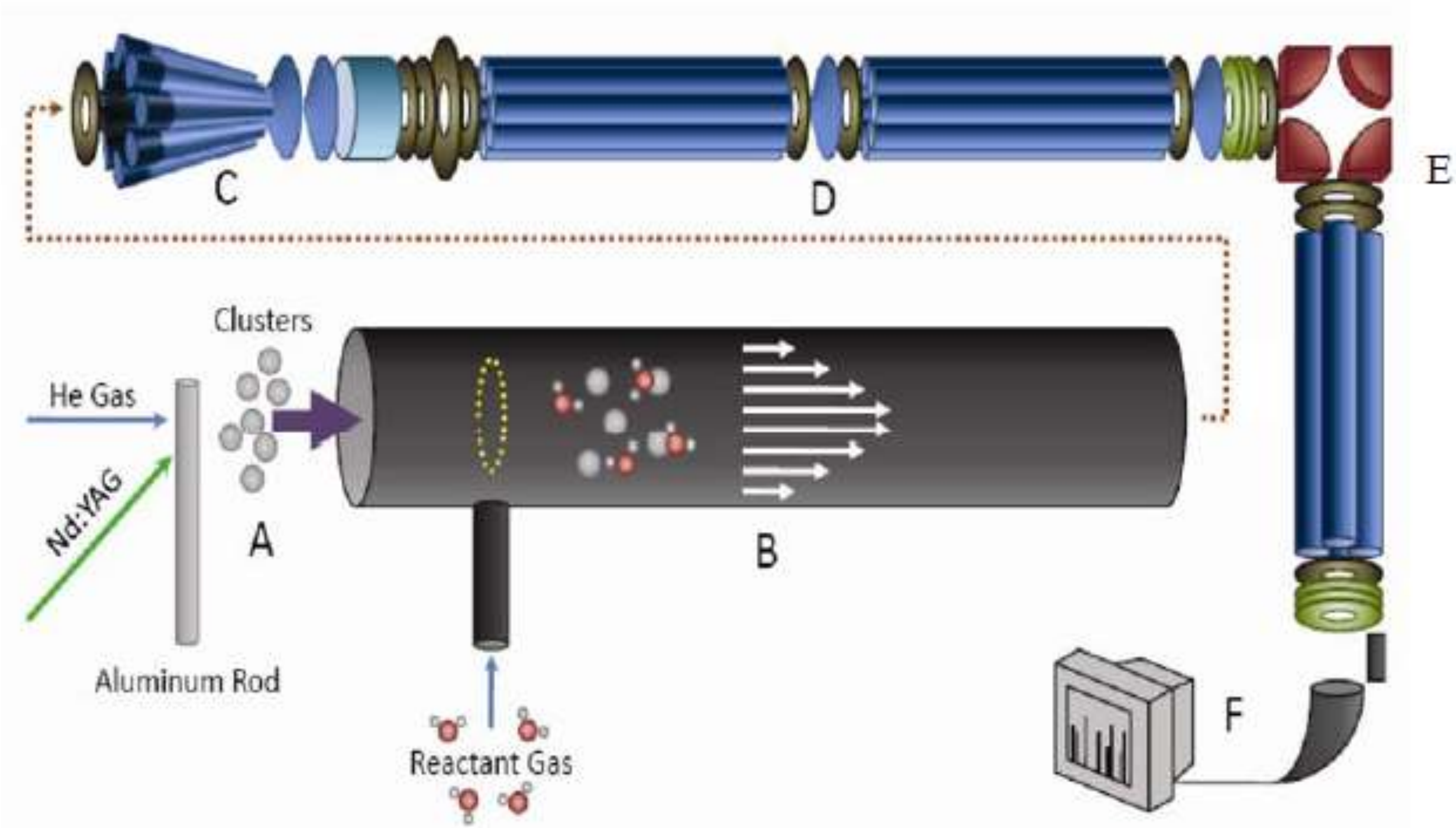


Figure | The Fast Flow Reactor.

Castleman, A. W. *et al., Science* **2009**, *323*, 492.

Is Super Atom really 'Super' ? (1)

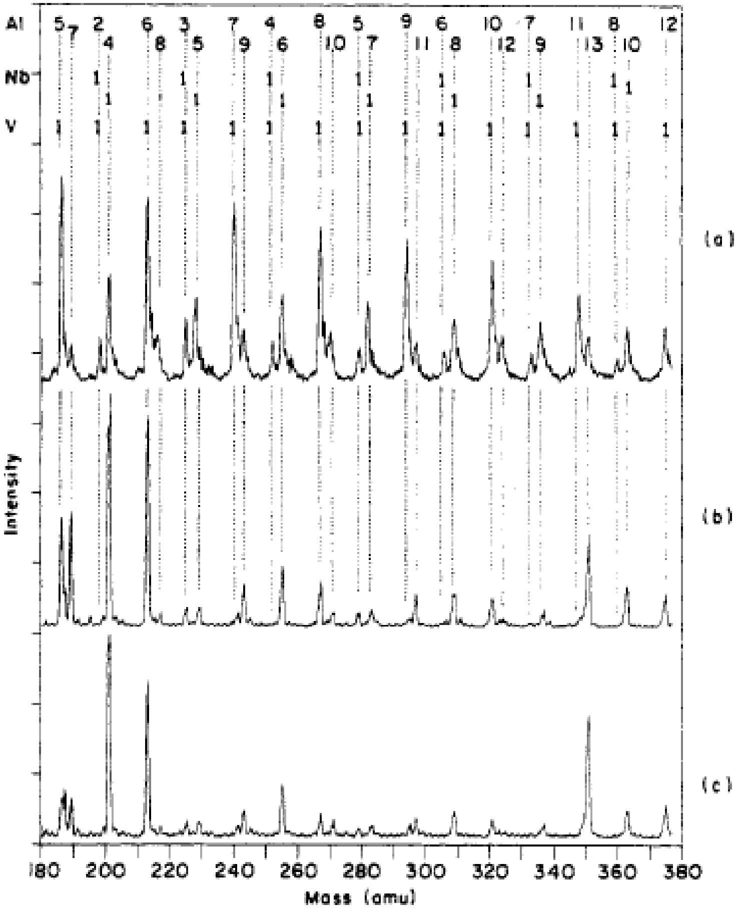


Figure | Substituting test to investigate the importance of the electronic contribution to stability

Electron valence of Atom

Al ($3s^2$ $3p^1$) Nb ($4d^4$ $5s^1$) V ($3d^3$ $4s^2$)

Sum of electron in Cluster

$1s^2$, $1p^6$, $1d^{10}$, $2s^2$, $1f^{14}$, $2p^6$, $1g^{18}$ …

Al_{13}^- (40) Al_{23}^- (70) Al_4Nb^- (18)

Al_5V^- (18) (V *provide two s electron*)

Al_7V^- (8) (Al *provide one p electron*)

Al_6Nb^- (20) (Nb *provide one s electron*)

Al_6V^- ???

Castleman, A. W. *et al., J. Am. Chem. Soc.* **1990**, *112*, 5673.

Is Super Atom really 'Super' ? (2)

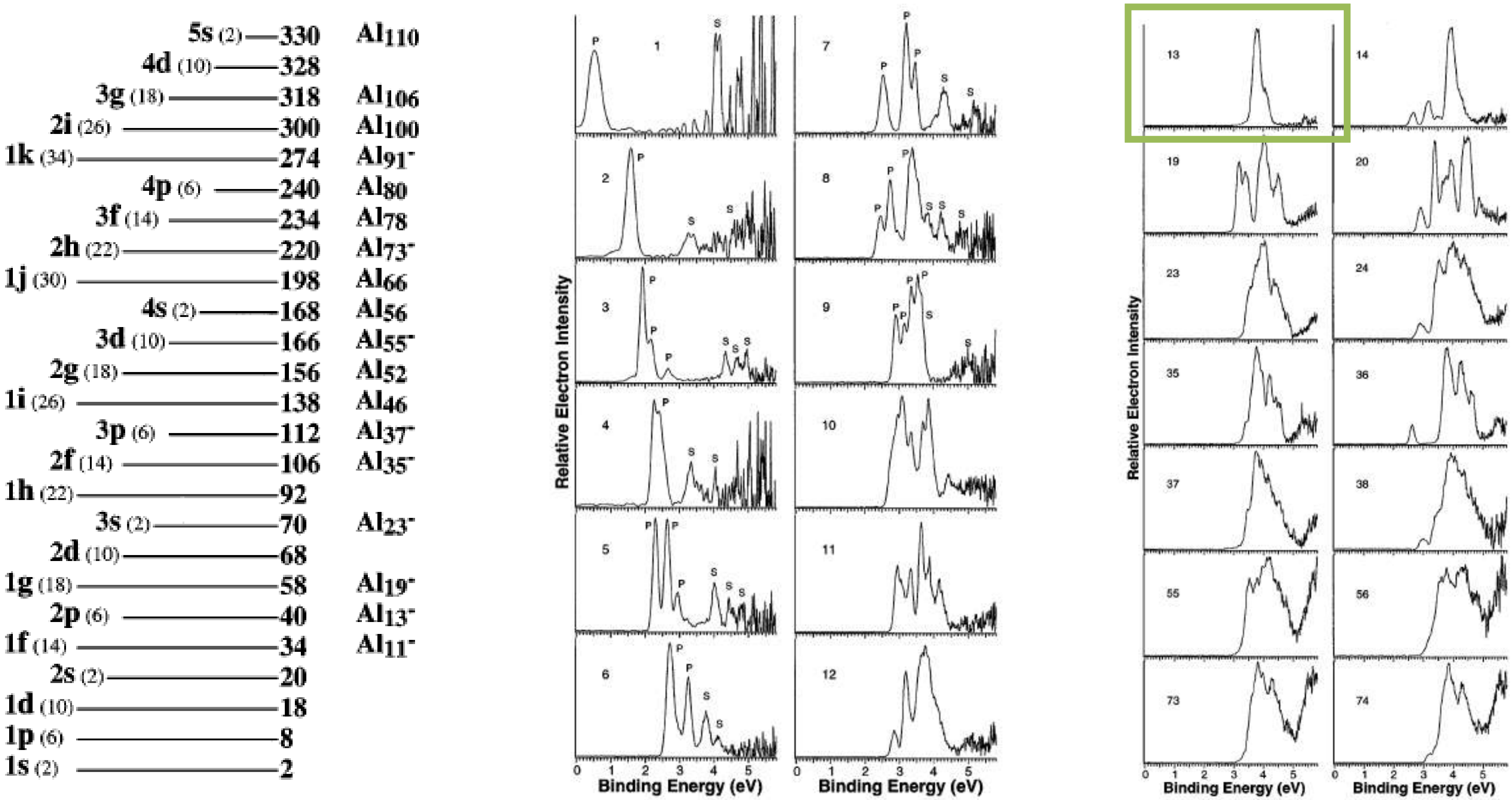
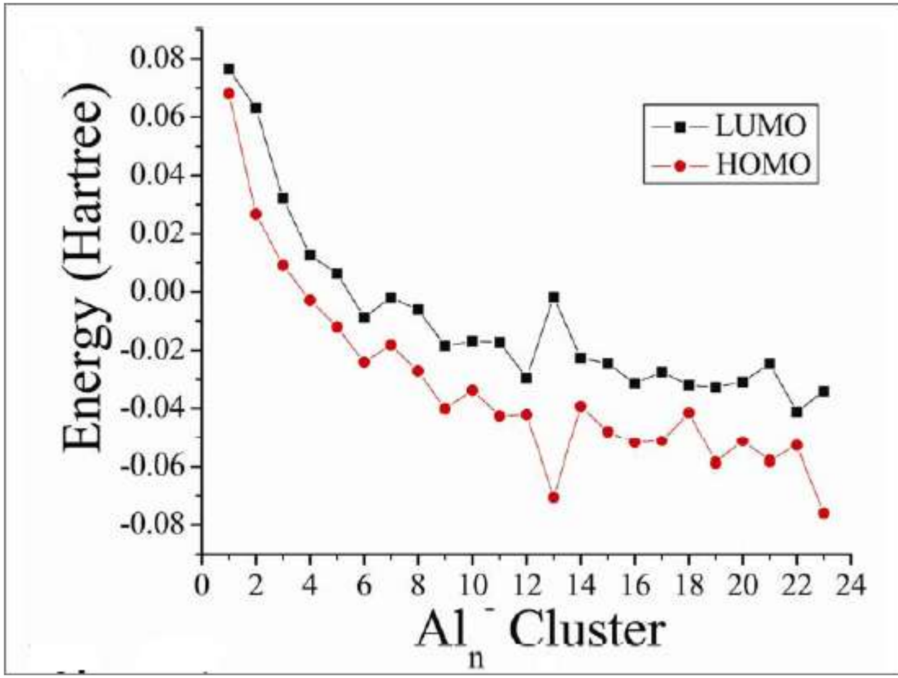
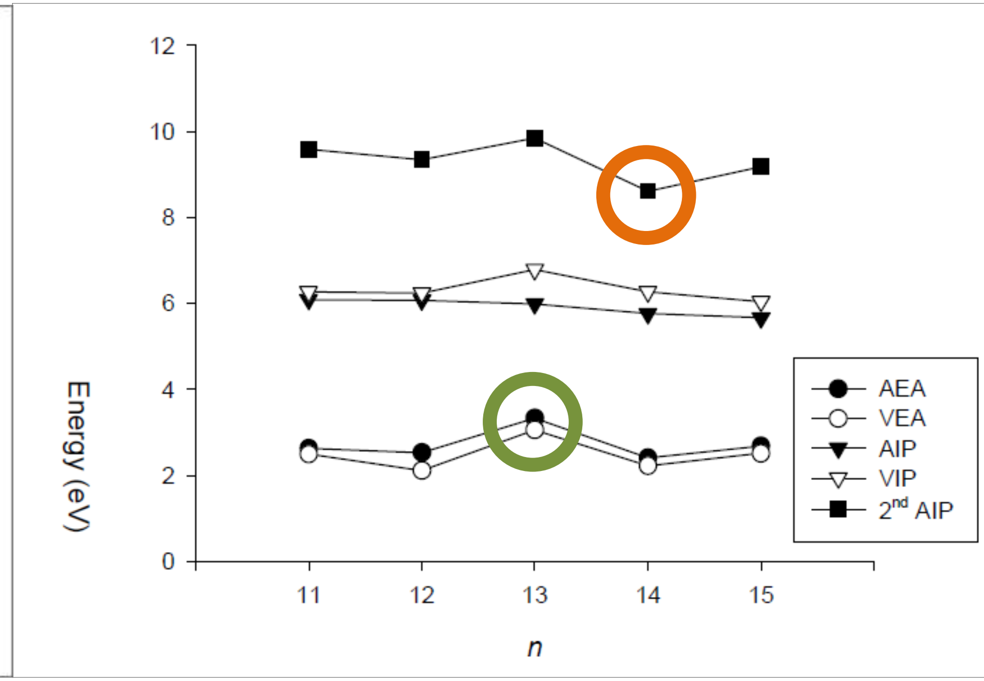


Figure | (left) Spherical shell closings and the corresponding closed shell neutral and negative clusters of trivalent Al. (middle) Photoelectron spectra of Al_x^- (x = 1 ~12). (right) Photoelectron spectra of the expected closed shell Al_x^- anions compared to those of the Al_{x+1}^- clusters.

Wang, L. S. *et al., Phys. Rev. Lett.* **1998**, *81*, 1909.

Al_{13} is 'Ultra' Super Atom





EA: electron affinity, IP: ionizing potential

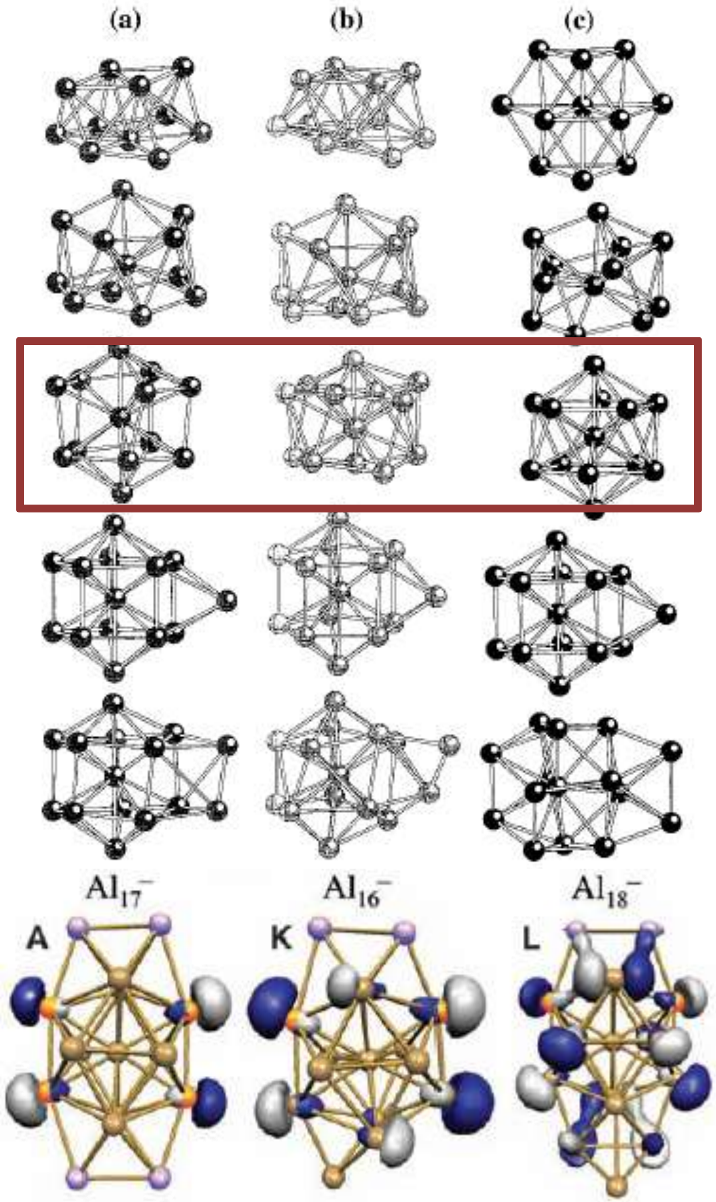
Figure | (left) The calculated absolute HOMO and LUMO levels of the Al_n^- clusters as a function of size (right) Ionization potentials and electron affinities for Al_n (n=11–15). A: Adiabatic, V: Vertical.

Among the elements of periodic table,
the highest EA element is Cl (3.61 eV) and the lowest 2nd IP element is Ba (10.0 eV).

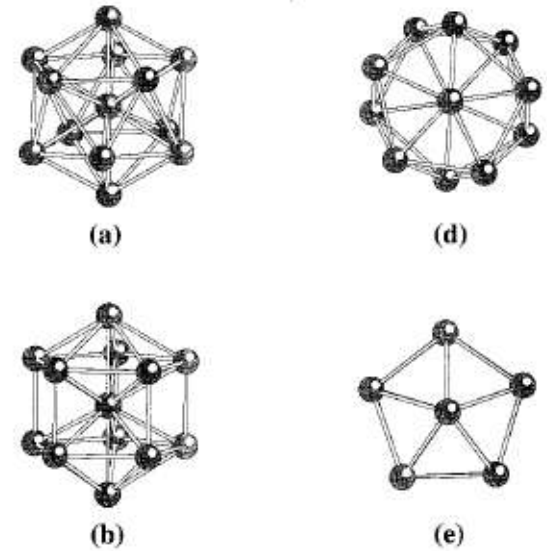
Castleman, A. W. *et al., Science* **2009**, *323*, 492.

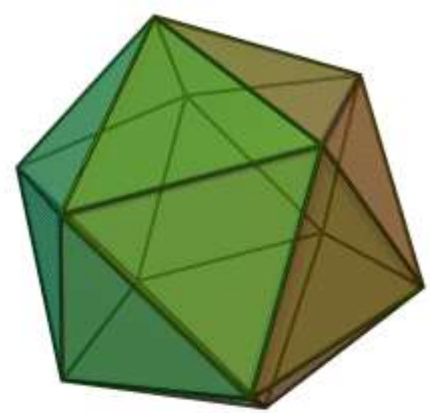
Han, Y. K. *et al., J. Am. Chem. Soc.* **2008**, *130*, 2.

Why is Al_{13}^- especially so stable?



Rao, B. K.; Jena, P., *J. Chem. Phys.* **1999**, *111*, 1890.

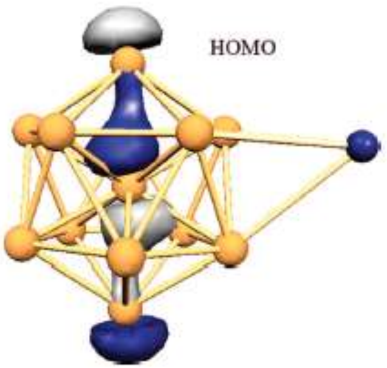


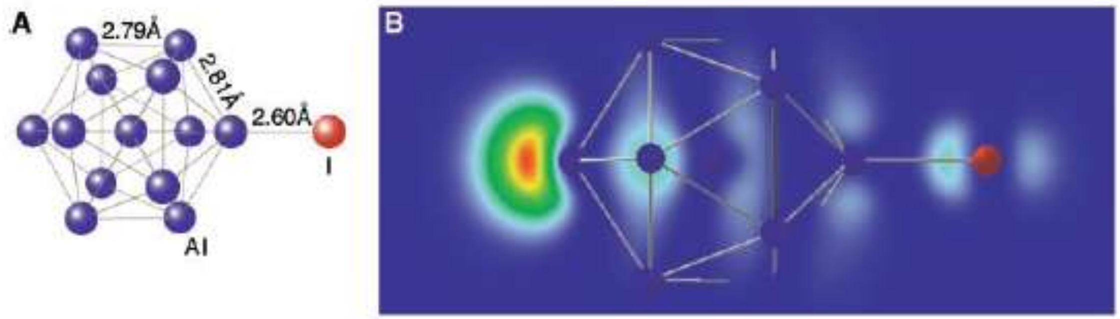


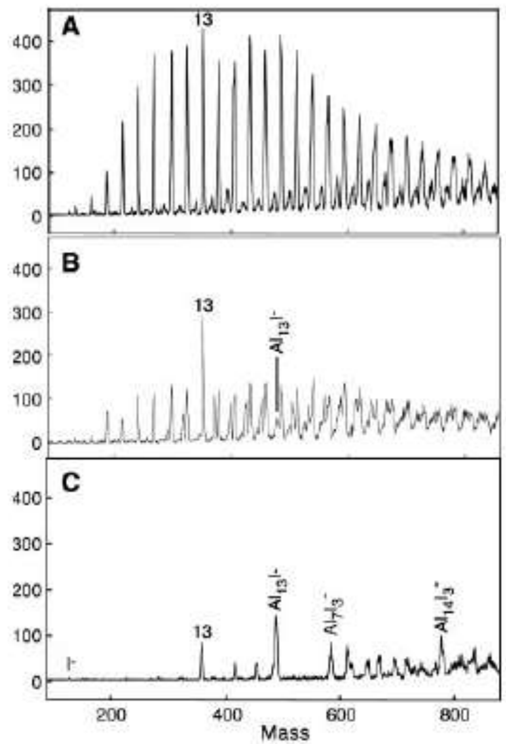
icosahedron

Reactions of Al_{13}^{-} cluster (1)

Reaction with HI







Al_{13} is a SUPERHALOGENE!!!

Figure | (upper left) Electron charge density of the HOMO in an $Al_{13}K$ cluster. Most of the electron density is located around the Al_{13} cluster. (upper middle & right) Charge density of the HOMO in $Al_{13}I^-$ showing that most of the charge is located around the Al_{13} moiety. (left) Mass spectra showing the reaction of aluminumclusters with HI: (A)0 sscm, (B) 25 sccm, (C) and 200 sccm of 10% HI seeded in He.

Castleman, A. W. *et al., Science* **2004**, *304*, 84.

Reactions of Al_{13}^- cluster (2)

Reaction with I_2 (1)

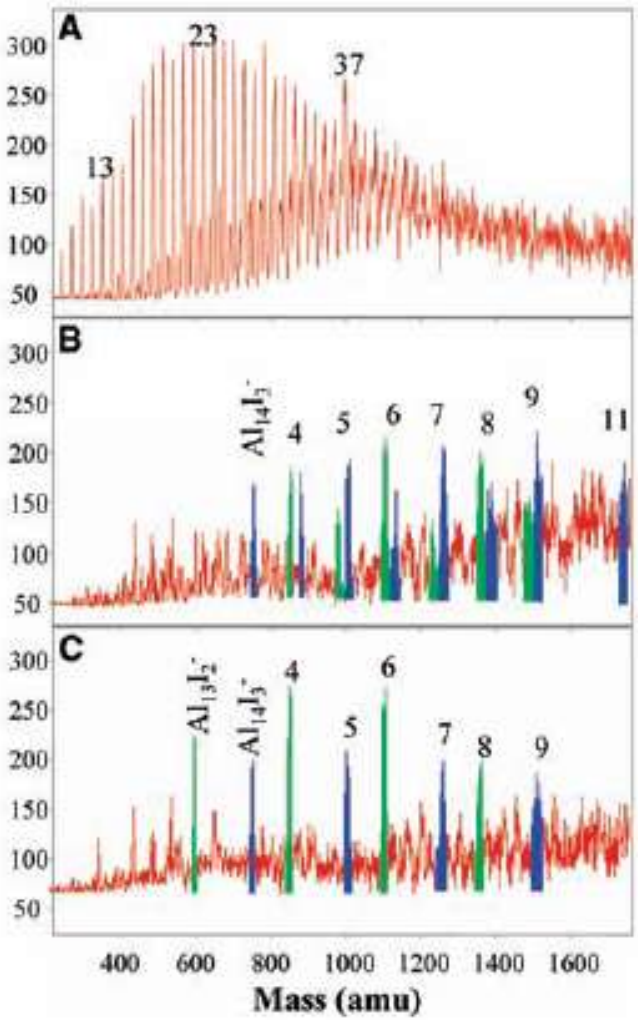


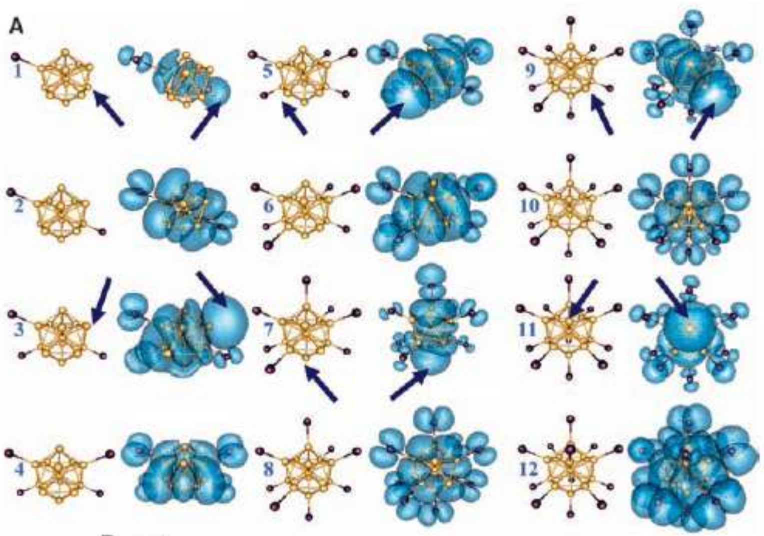
Figure | Mass spectra of (A) Al cluster anions (B) reacted with I_2 vapor and then (C) etched by O_2. Peaks shaded green fall into the $Al_{13}I_x^-$ family, whereas peaks shaded blue fall into the $Al_{14}I_x^-$ family.

Castleman, A. W. *et al., Science* **2005**, *307*, 231.

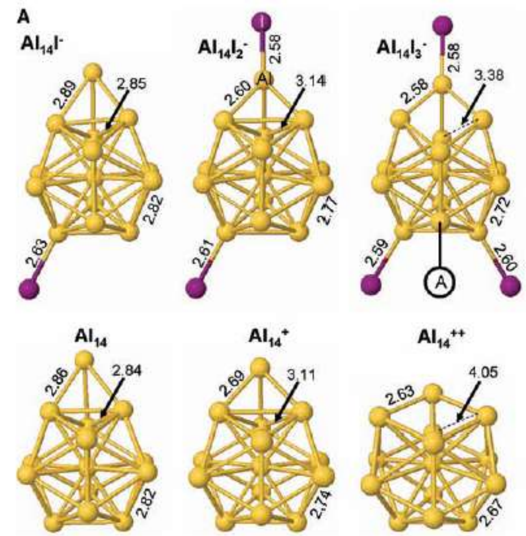
Reactions of Al_{13}^{-} cluster (3)

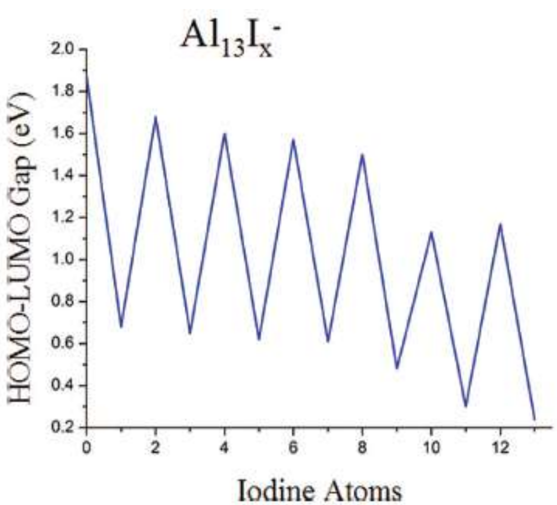
Reaction with I_2 (2)

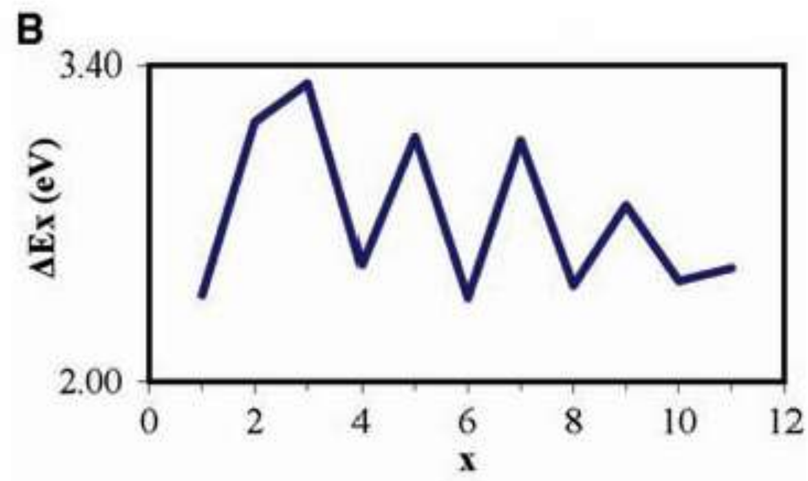
$Al_{13}I_x^{-}$ families



$Al_{14}I_x^{-}$ families

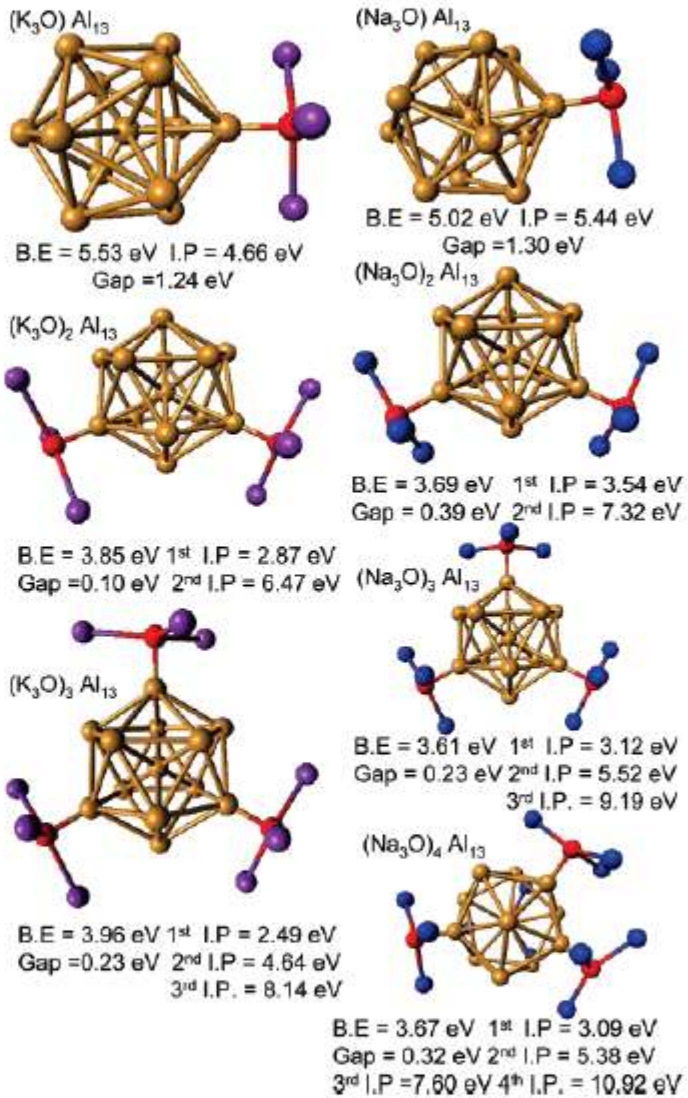






Recent examples of Magic cluster (1)

Superatomic Architectures



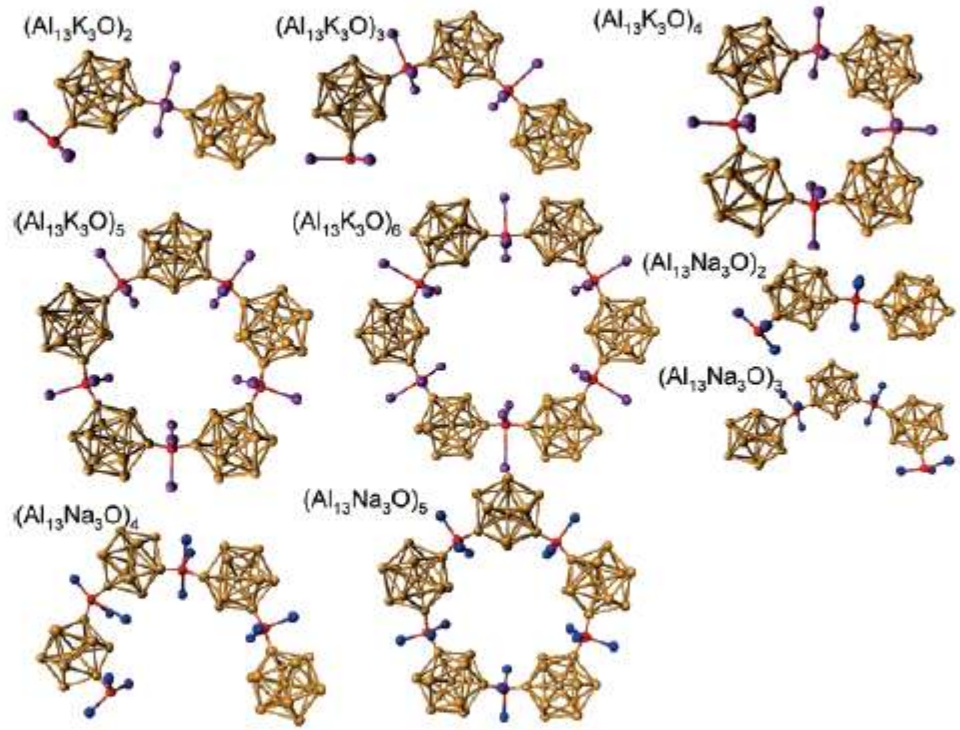
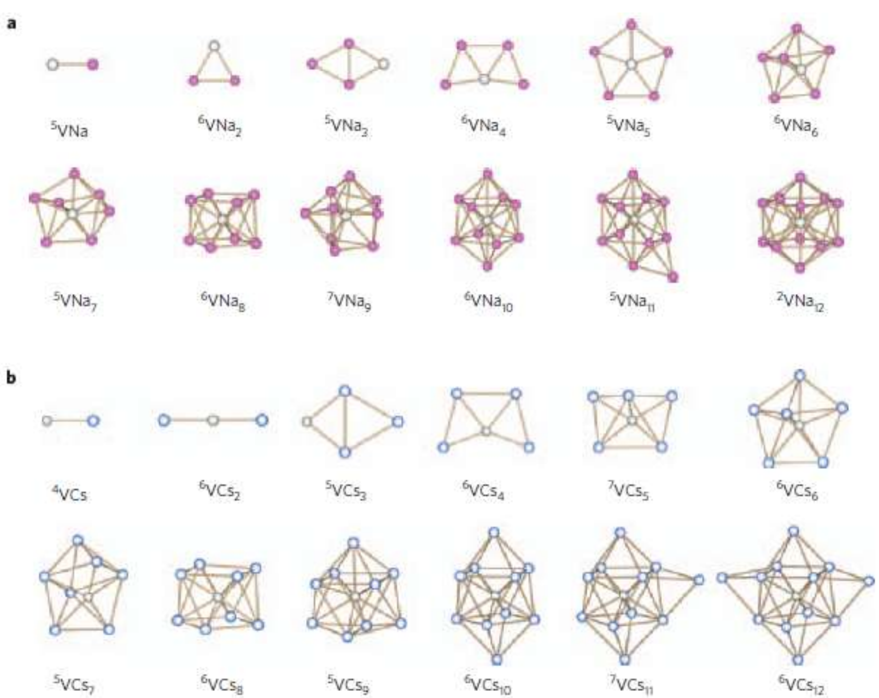


Figure | (left) Structure binding energy (B.E.), HOMO-LUMO gap (Gap), and ionization potentials (I.P.) for $Al_{13}(K_3O)$ and $Al_{13}(Na_3O)$ series. (upper) Assemblies of (A) $Al_{13}K_3O$ and (B) $Al_{13}Na_3O$ molecules

Khanna, S. N. *et al., J. Am. Chem. Soc.* **2007**, *129*, 10189.

Recent examples of Magic cluster (2)

Designer Magnetic Superatom



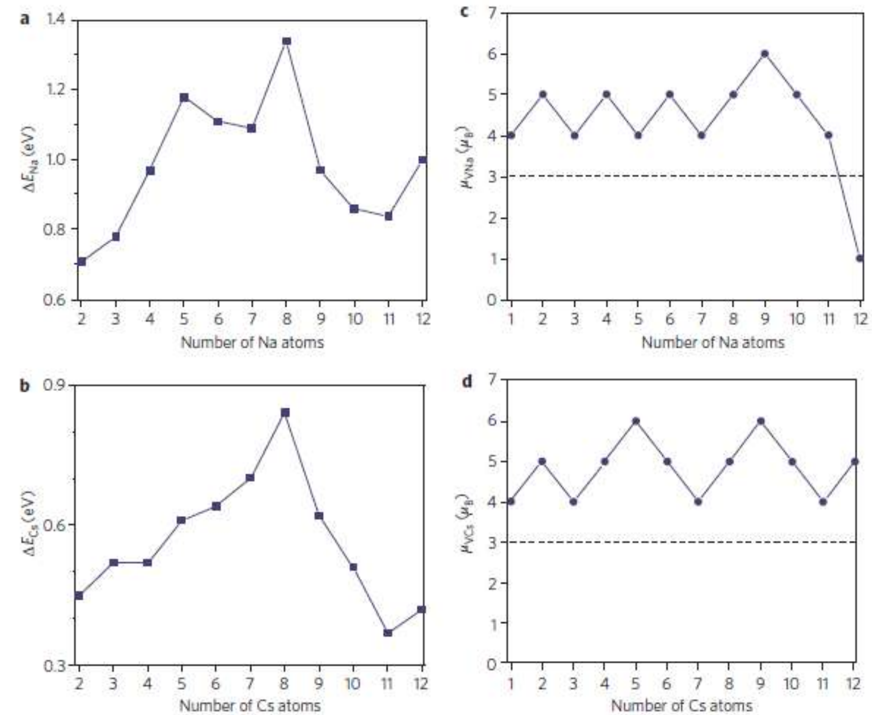
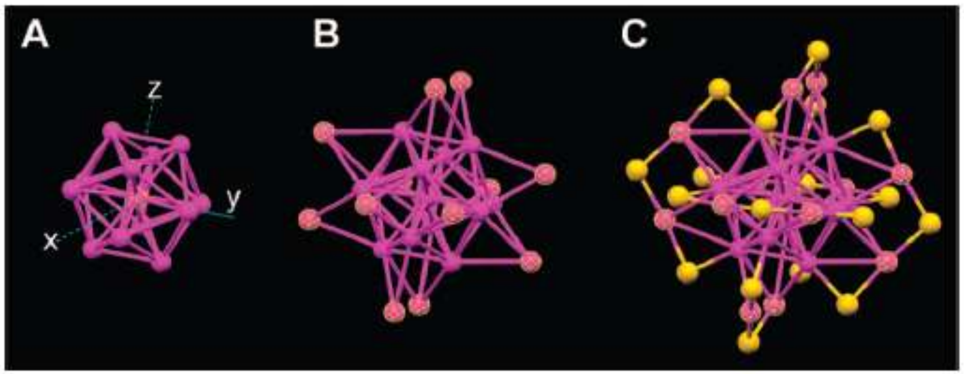


Figure | (left) Ground-state geometries of VNa_n and VCs_n clusters. a, VNa_n (n=1～12) clusters. b, VCs_n (n=1～12) clusters. Na: red, Ce: blue, V: grey. (right) Energetic and magnetic trends of VNa_n and VCs_n clusters. a,b, Variation of the gain in energy caused by alkali addition (DEA) with n in the (a) Vna_n and (b) VCs_n clusters. c,d, Variation of the magnetic moments (m) with n in the (c) Vna_n and (d) VCs_n clusters. The magnetic moment of the vanadium atom is also given as reference (dashed line).

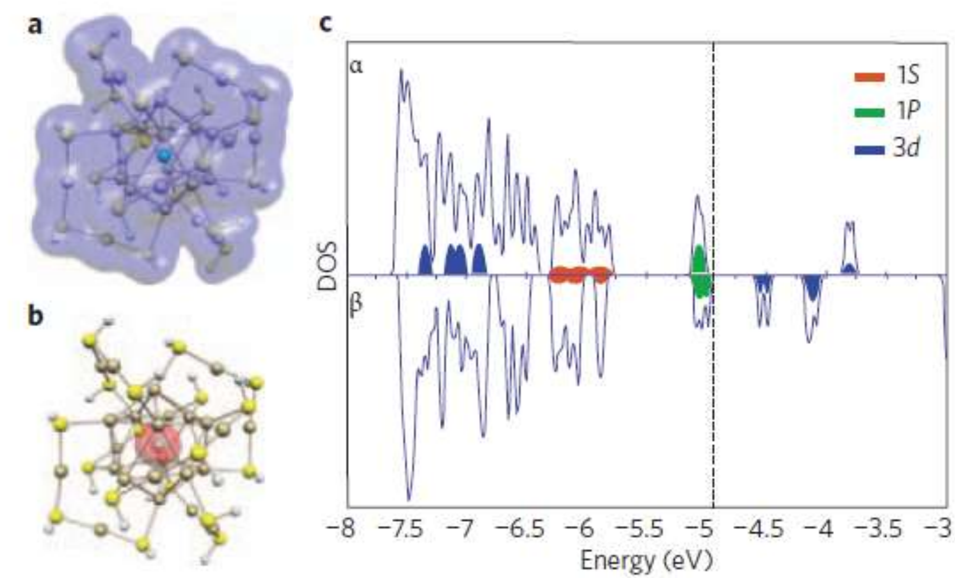
Khanna, S. N. *et al., Nature Chemistry* **2009**, *1*, 310.

Recent examples of Magic cluster (3)

Designer Magnetic Superatom & the Ligand-Stabilized Magic Gold Cluster



Jin, R. *et al., J. Am. Chem. Soc.* **2008**, *130*, 5883.



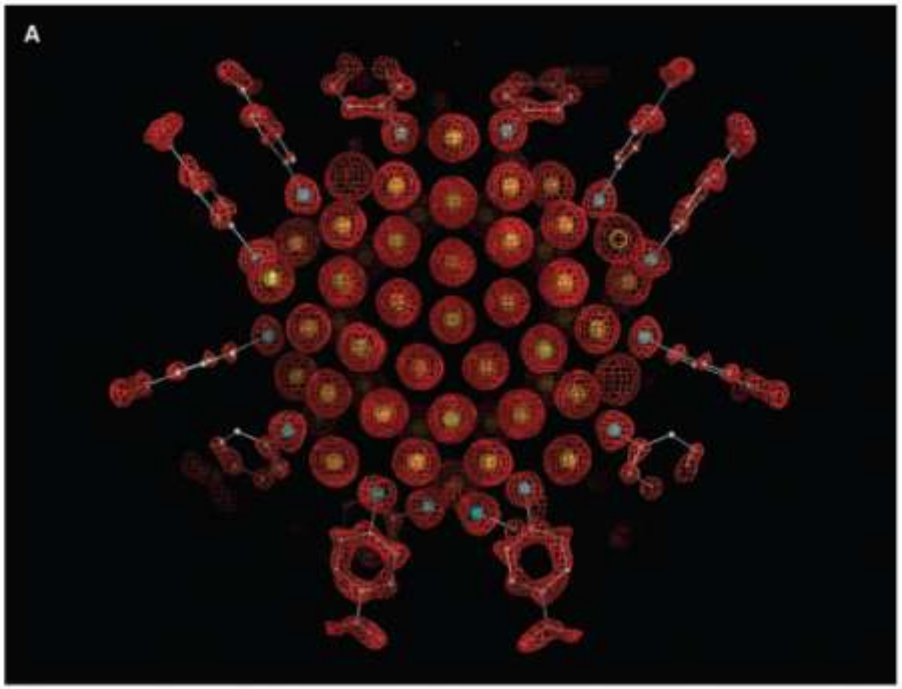
Khanna, S. N. *et al., Nature Chemistry* **2009**, *1*, 310.

Figure | (upper) Crystal structure of a $Au_{25}(SR)_{18}^-$ cluster (R = phenylethyl group): (A) the icosahedral Au_{13} core; (B) the Au_{13} core plus the exterior 12 Au atoms; (C) the whole Au_{25} cluster protected by 18 thiolate ligands (S: magenta, Au: yellow). (lower) Total and net spin electron density and density of states (DOS) of the $MnAu_{24}(SH)_{18}$ cluster. (a) Total electron density, (b) net spin electron density and (c) DOS obtained by broadening the molecular levels by Gaussians of width 0.017 eV (Mn: blue, Au: gold, S: yellow, H: white). The delocalized 1S and 1P electronic shells and localized 3d atomic orbitals are marked in orange, green and blue areas, respectively.

Recent examples of Magic cluster (4)

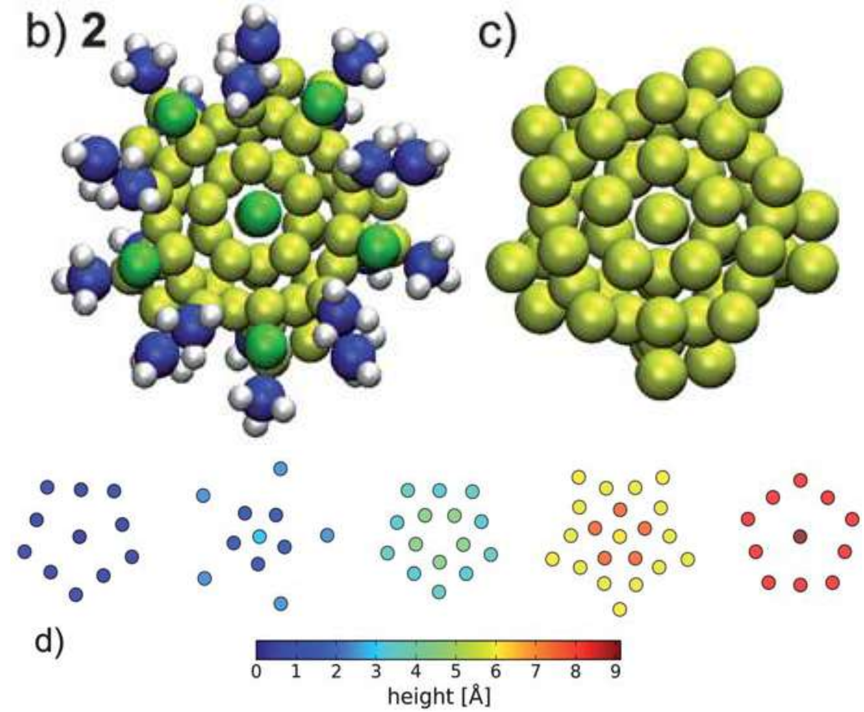
the Ligand-Stabilized Magic Gold Cluster

Au_{102} (p-MBA)$_{44}$



Jadzinsky, P. D. *et al., Science* **2007**, *318*, 430.

$[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$



Walter, M. *et al., Chem. Sci.* **ASAP.**

Figure | (left) X-ray crystal structure determination of the Au_{102} (p-MBA)$_{44}$ nanoparticle. Au: yellow, p-MBA: framework with small spheres (S: cyan, C: gray, O: red) (p-MBA = p-mercaptobenzoic acid). (right) (b) Structure of the $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$, (Au: yellow, Cl: green, P: blue, H: white) and (c) the gold-core and (d) the split layers of different height perpendicular to the paper plane.

Further study of Super Atom

Mini review

Castleman, A. W.; Khanna , S. N. *J. Phys. Chem. C* ***2009,*** *113*, 2664.

Reactions of Aluminum clusters with

HCl

Schnockel, H. *et al., J. Am. Chem. Soc.,* ***2006,*** *128*, 7904.

O_2

Schnockel, H. *et al., Science,* ***2008,*** *319*, 438.

Khanna, S. N. *et al., J. Am. Chem. Soc.* ***2007,*** *51*, 16098.

H_2O

Castleman, A. W. *et al., Science,* ***2009,*** *323*, 492.

Is Superatom model realy suitable?

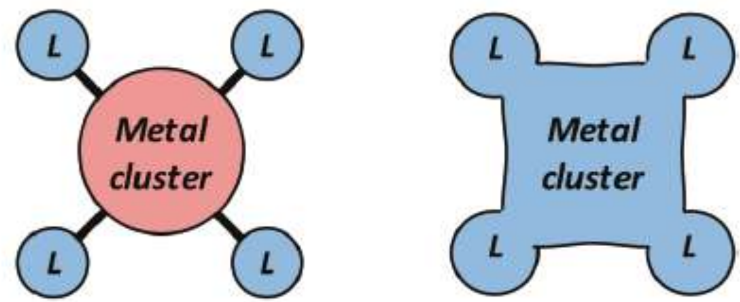
Han, Y. K. *et al., J. Am. Chem. Soc.* ***2008,*** *130*, 2.

Reimers, J. R.; Cankurtaran, B. O *et al., J. Am. Chem. Soc.* ***2010,*** *132*, 8378.

Han, Y. K. *et al., J. Am. Chem. Soc.* ***2011,*** *133*, 6090.

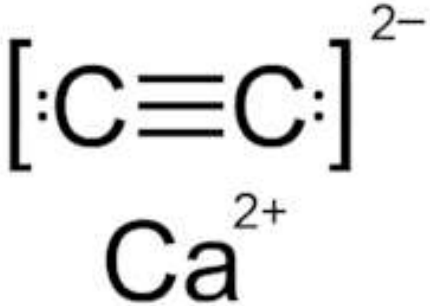
Summary of Super Atom

Although it seems too simple, Jellium closing shell model explains well.
As far as I research, Al_{13} is the only non ligand-stabilized cluster which has been studied enthusiastically and therefore can be regarded as 'Superatom'.
To obtain extra ordinal stability, which is necessary for the cluster functioning as 'Superatom', the cluster needs both closing electron shell and highly symmetric geometry.
This steric demand will cause mismatch between clusters and small but relatively complex molecule.



(a) (b)

What's Transition Metal Carbides?



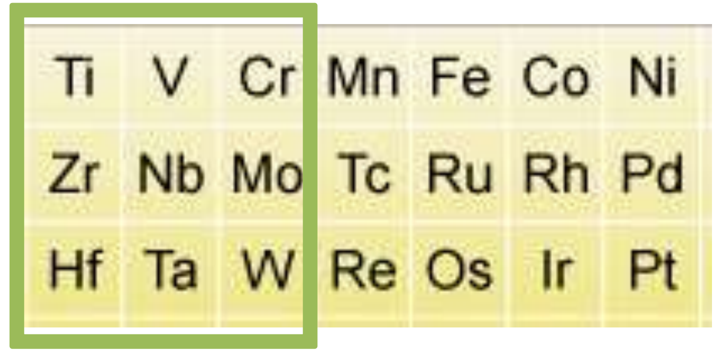
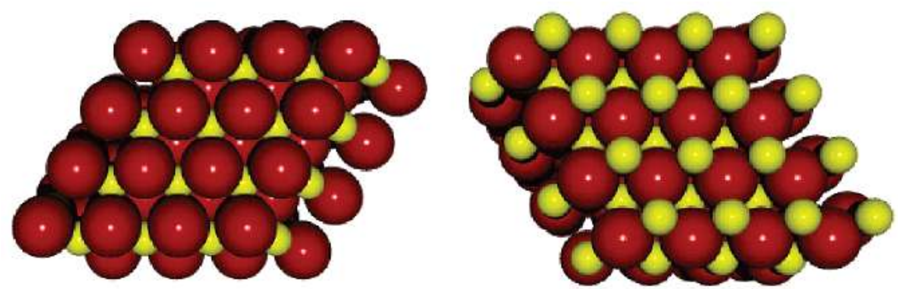


Figure | Calcium carbide



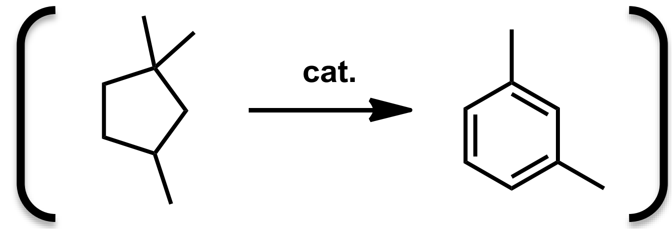
(a) Ti-Terminated TiC(111) (b) C-Terminated TiC(111)

(c) Mo-Terminated $Mo_2C(0001)$ (d) C-Terminated $Mo_2C(0001)$

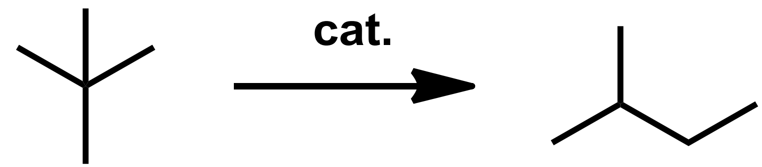
Precedent work

Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis

1. $H_2 + O_2 \xrightarrow[\text{r.t.}]{\text{cat.}} H_2O$



2. $WO_3 \xrightarrow[H_2\ \text{flow}]{\text{cat.}} H_xWO_3$

3. 

Catalyst	Pretreatment	Reaction temperature (°C)	Rate (μmol m^{-2} sec^{-2})	
			r_h	r_i
Platinum	Flowing H_2, 300°C, 2 hours	300	5.4*	2*
Tungsten	Flowing H_2, 300°C, 2 hours	460	0	0
Tungsten	Flowing H_2, 750°C, 25 hours	460	~ 10^{-3}	0
Tungsten carbide (WC)	Flowing H_2, 300°C, 2 hours	370	~ 2×10^{-2}	~ 2×10^{-4}

Levy, R. B.; Boudart, M. *Science,* ***1973,*** *181*, 547.

TMC & Pt-Group Metal Surface

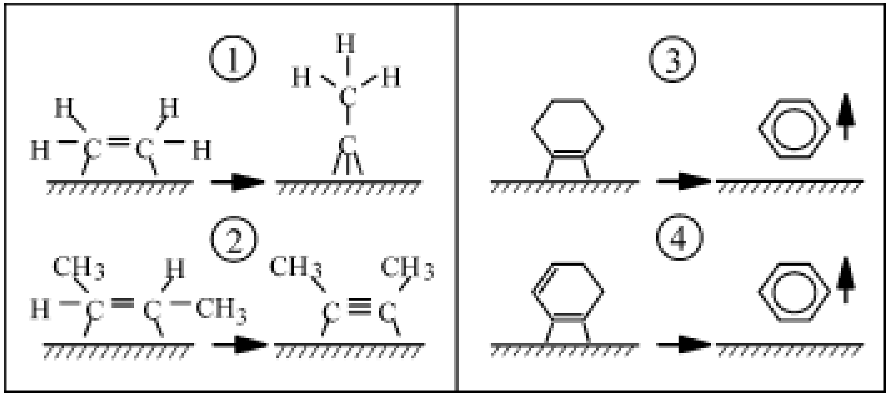


Figure | the probe reactions to determine whether TMC surfaces possessed the "Pt-like" chemical properties.

① Ti/C showed the conversion of ethylene to ethylidyne.

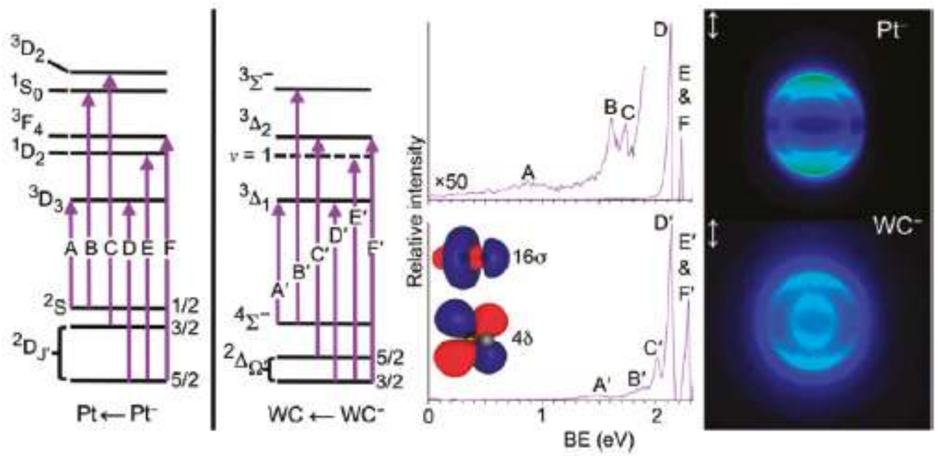
② Mo/C showed the selective activation of the R-C-H bond of *cis*- and *trans*-2-butene to 2-butyne.

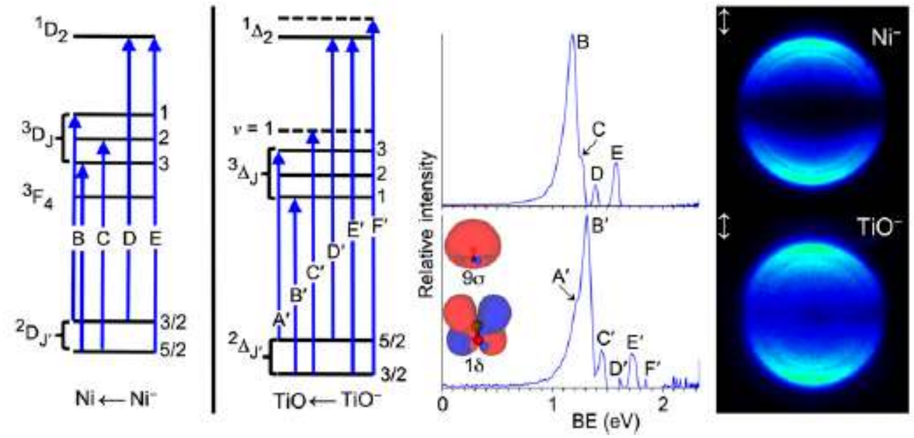
③&④ TMCs showed the selective dehydrogenation of cyclohexene and cyclohexadiene to benzene.

The formation of carbides on groups 4-6 metals reduces the degree of interaction between adsorbates and TMC surfaces, leading to a modified surface activity that more closely esembles the Pt-group metals than the parent metals.

Hwu, H. H.; Chen, J. G. *Chem. Rev.,* ***2005,*** *105*, 185.

$WC^{-} = Pt^{-}$?





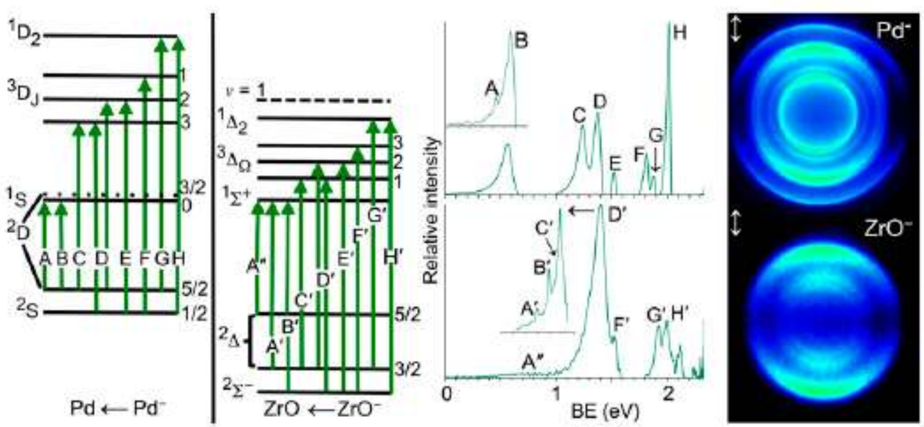
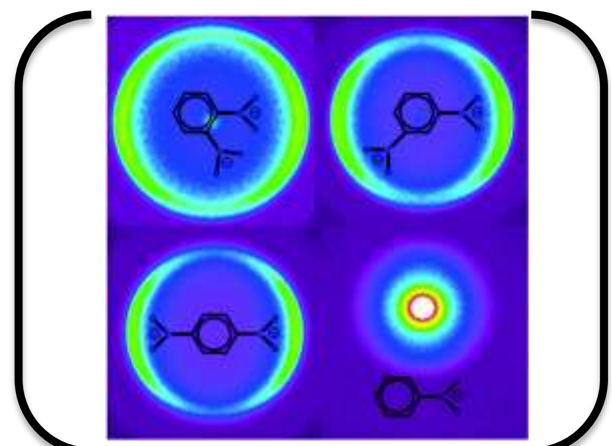


Figure | Energy level diagrams, binding energy (BE) spectra, and raw hotoelectron images of (upper left) Pt^{-} & WC^{-}, (upper right) Ni^{-} & TiO^{-}, (left) Pd^{-} & ZrO^{-}.



Castleman, A. W. *et al., P.N.A.S* **2010**, *107*, 975.

Summary of TMC

Although carbon atom changes the properties of early transition metals and TMCs show similar catalytic functionalities as Pt-group metals, the electronic surface of both are completely different.
And, there aren' t any alchemical elements in TMCs.
Recently, however, the reports is appearing that show the similarity of the photoelectron signatures and angular distributions in the acquired images between negative ions of the group 10 noble metals and that of their isoelectronic early transition metal heterogeneous diatomic molecule.

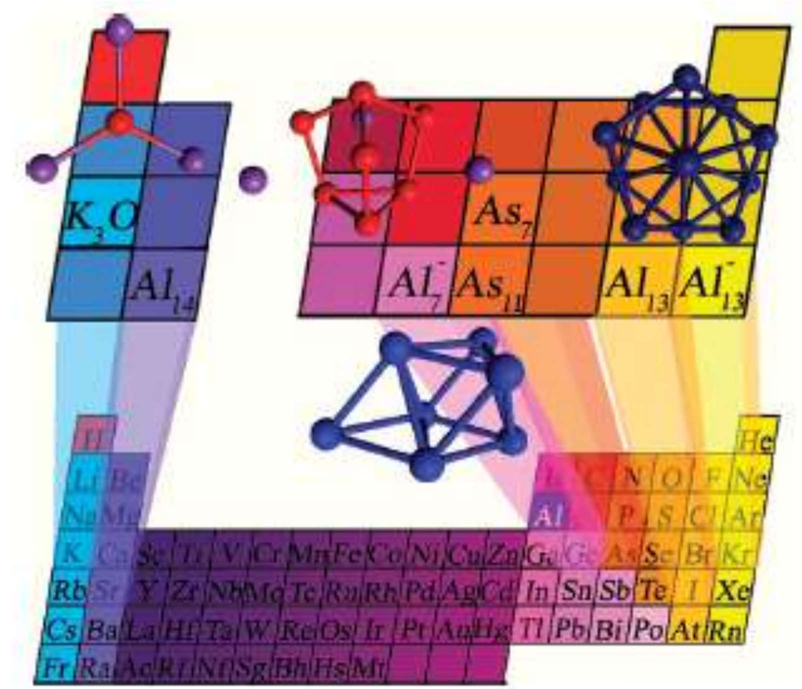
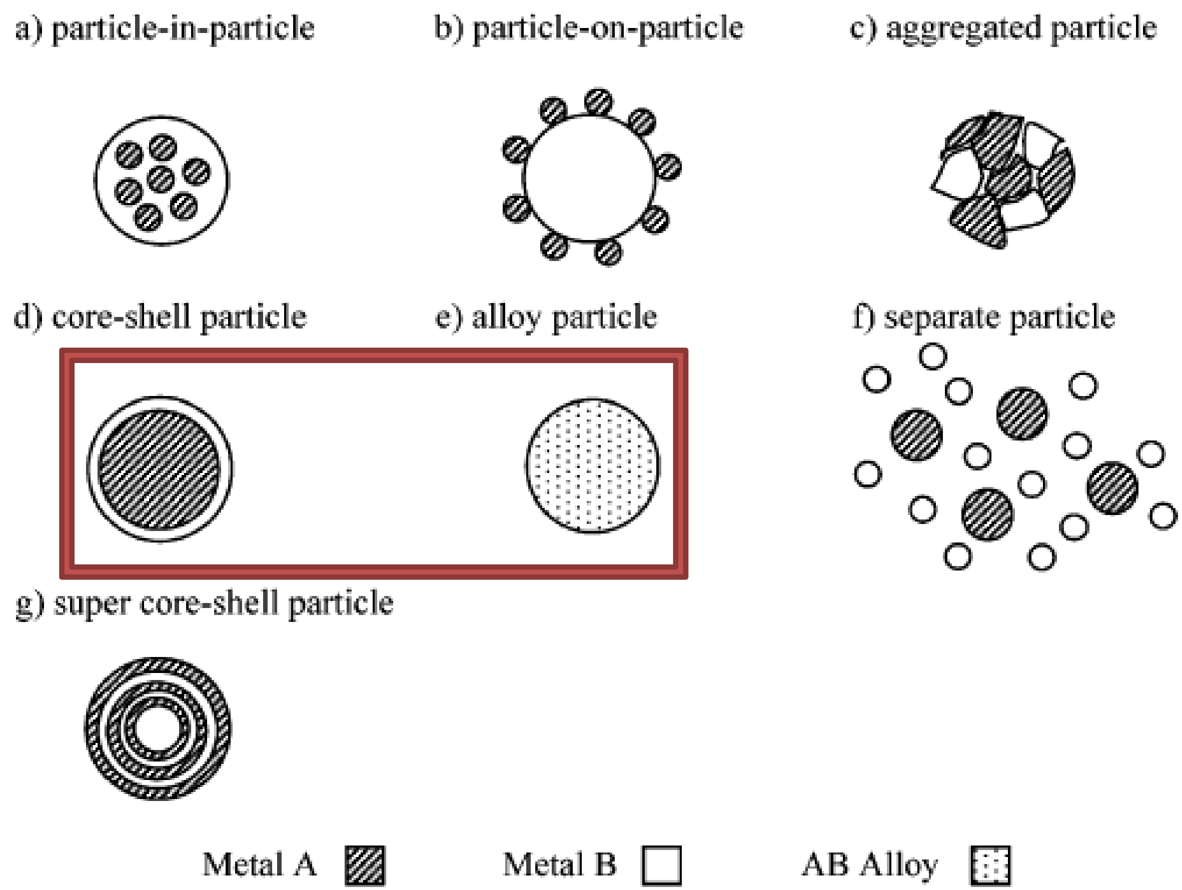


Figure | Three dimensional periodic table of cluster elements!

What's Bimetallic Nanoparticles?

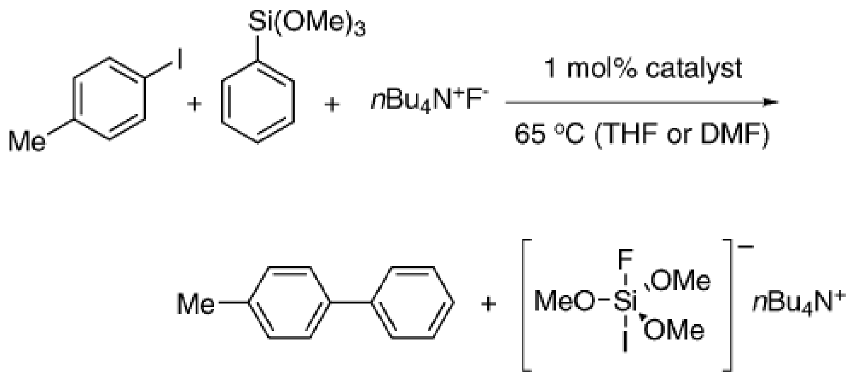


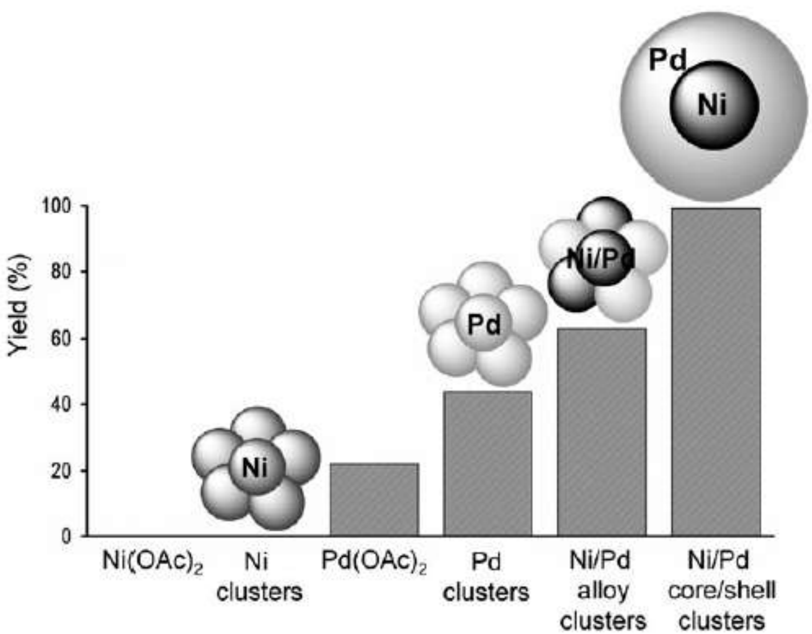
Increasingly, the shape, size, composition, and architecture of a nanoparticle are being recognized as important control parameters for tailoring new bimetallic nanoparticle systems.

Kunitake, T. *et al., J. Am. Chem. Soc.* ***2003,*** *125*, 11034.
Ferrando, R. *et al. Chem. Rev.,* ***2008,*** *108*, 845.

Pd–Ni

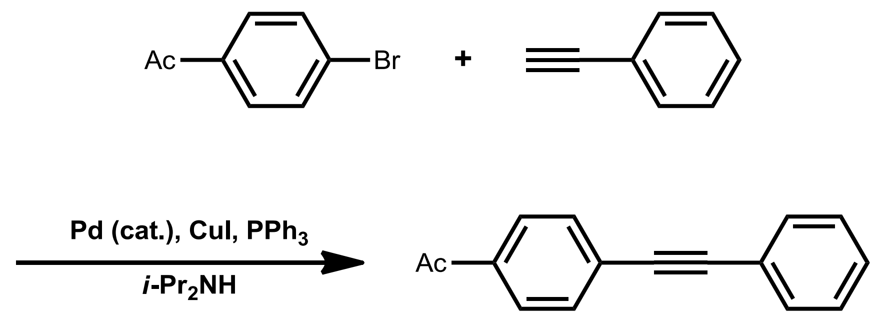
Hiyama coupling

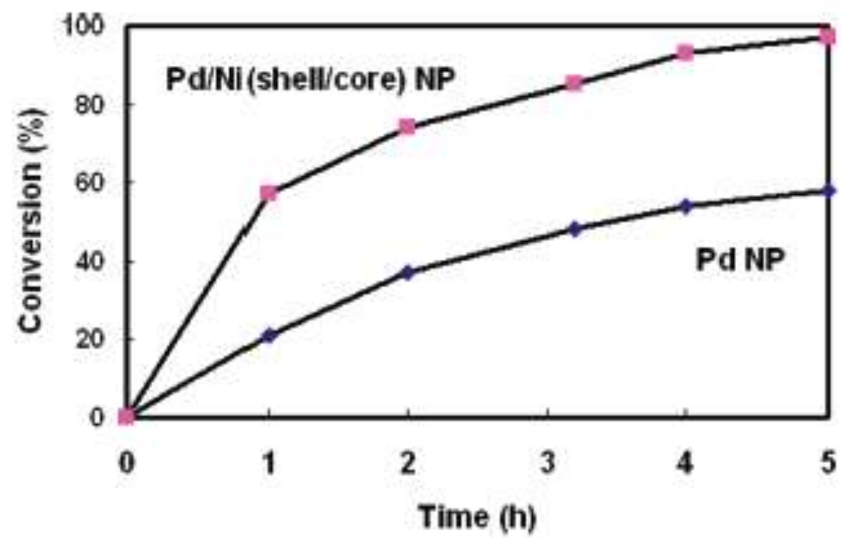




Rothenberg, G. *et al., Phys. Chem. Chem. Phys.* ***2006,*** *8*, 151.

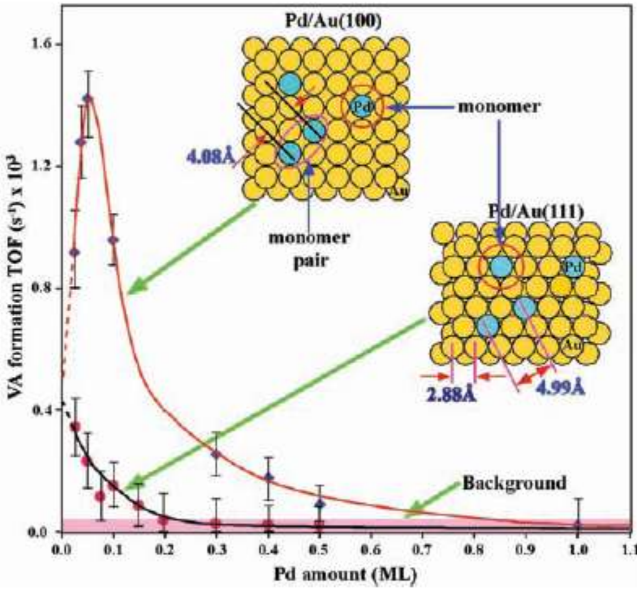
Sonogashira coupling

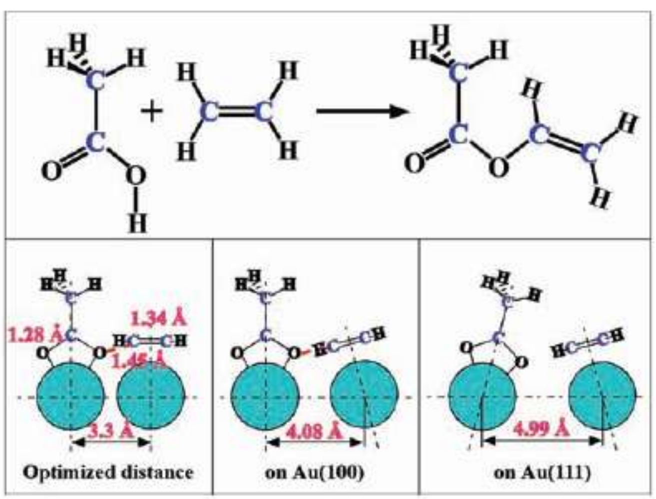




Hyeon, T. *et al., J. A. C. S.* ***2004,*** *126*, 5026.

Pd-Au





Benzyl alcohol oxidation

Catalyst	Conversion (%) 0.5 hour	Conversion (%) 8 hours	Benzaldehyde selectivity (%) 0.5 hour	Benzaldehyde selectivity (%) 8 hours	Benzaldehyde productivity* [mol/(hour/kg_{cat})]	H_2O_2 productivity [mol/(hour/kg_{cat})]
2.5% Au–2.5% Pd/Al_2O_3	2.6	83.3	90.5	86.6	174	23
2.5% Au–2.5% Pd/TiO_2	3.7	74.5	95.2	91.6	165	64
2.5% Au–2.5% Pd/SiO_2	3.6	35.7	97.3	88.0	76	80
2.5% Au–2.5% Pd/Fe_2O_3	3.6	63.4	74.9	66.4	102	16
2.5% Au–2.5% Pd/C	2.9	69.2	53.9	46.4	78	30
2.5% Au/TiO_2	0.6	15.3	96.7	63.9	24	<2
2.5% Pd/TiO_2	13.4	60.1	51.3	54.4	79	24

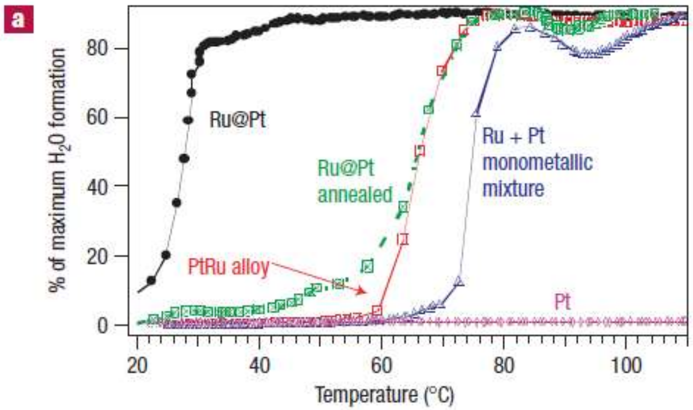
*Calculated for 8 hours of reaction.

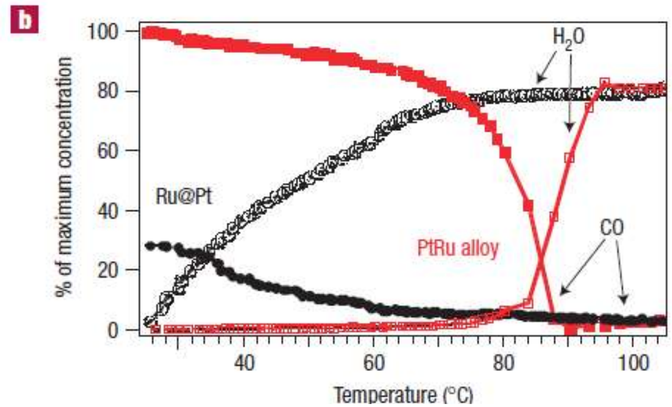
Figure | (*upper left*) **Vinyl acetate (VA) formation rates (TOFs) as a function of Pd coverage on Au(100) and Au(111). (left) Schematic for VA synthesis from acetic acid and ethylene. The optimized distance between the two active centers for the coupling of surface ethylenic and acetate species to form VA is estimated to be 3.3 A° . With lateral displacement, coupling of an ethylenic and acetate species on a Pd monomer pair is possible on Au(100) but implausible on Au(111). (upper right) Comparison of the catalytic activity for alcohol oxidation to the corresponding aldehyde. Substrates are oxidized without solventunless specified.**

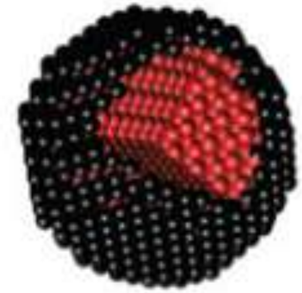
Goodman, D. W. *et al., Science,* ***2005,*** *310*, 291.

Hutchings, G. J. *et al., Science,* ***2006,*** *311*, 362.

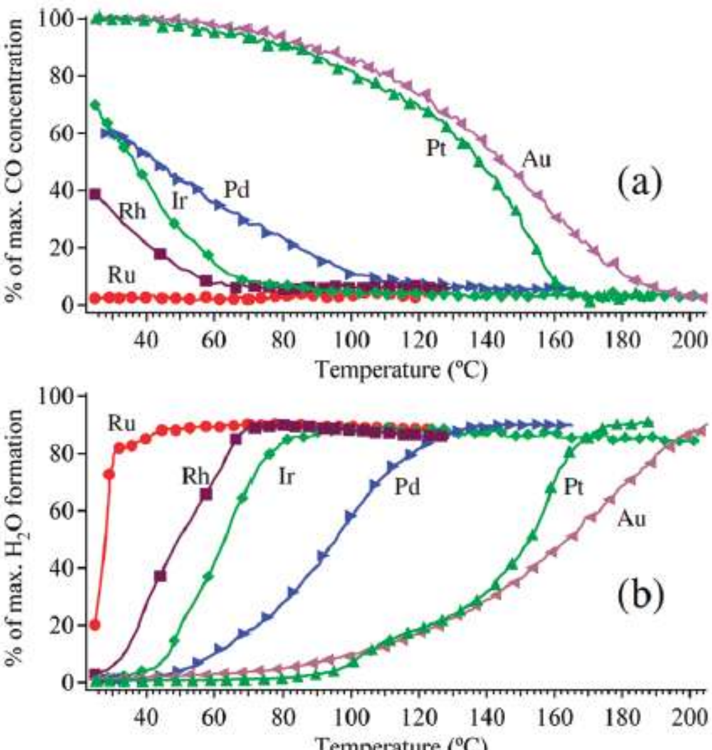
Ru-Pt (1)

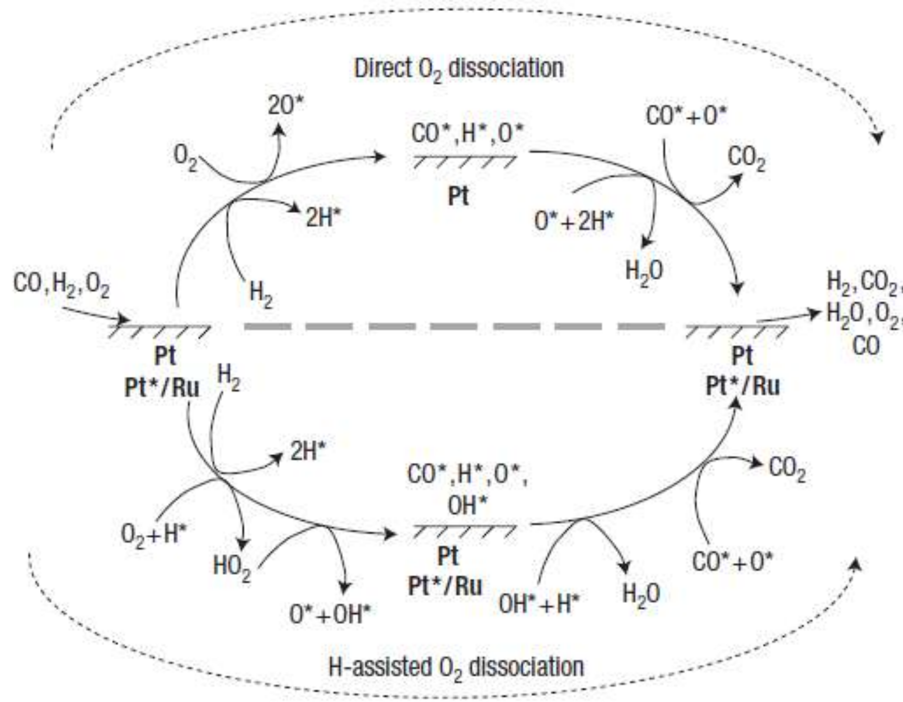






Ru@Pt core–shell





Pd-Pt

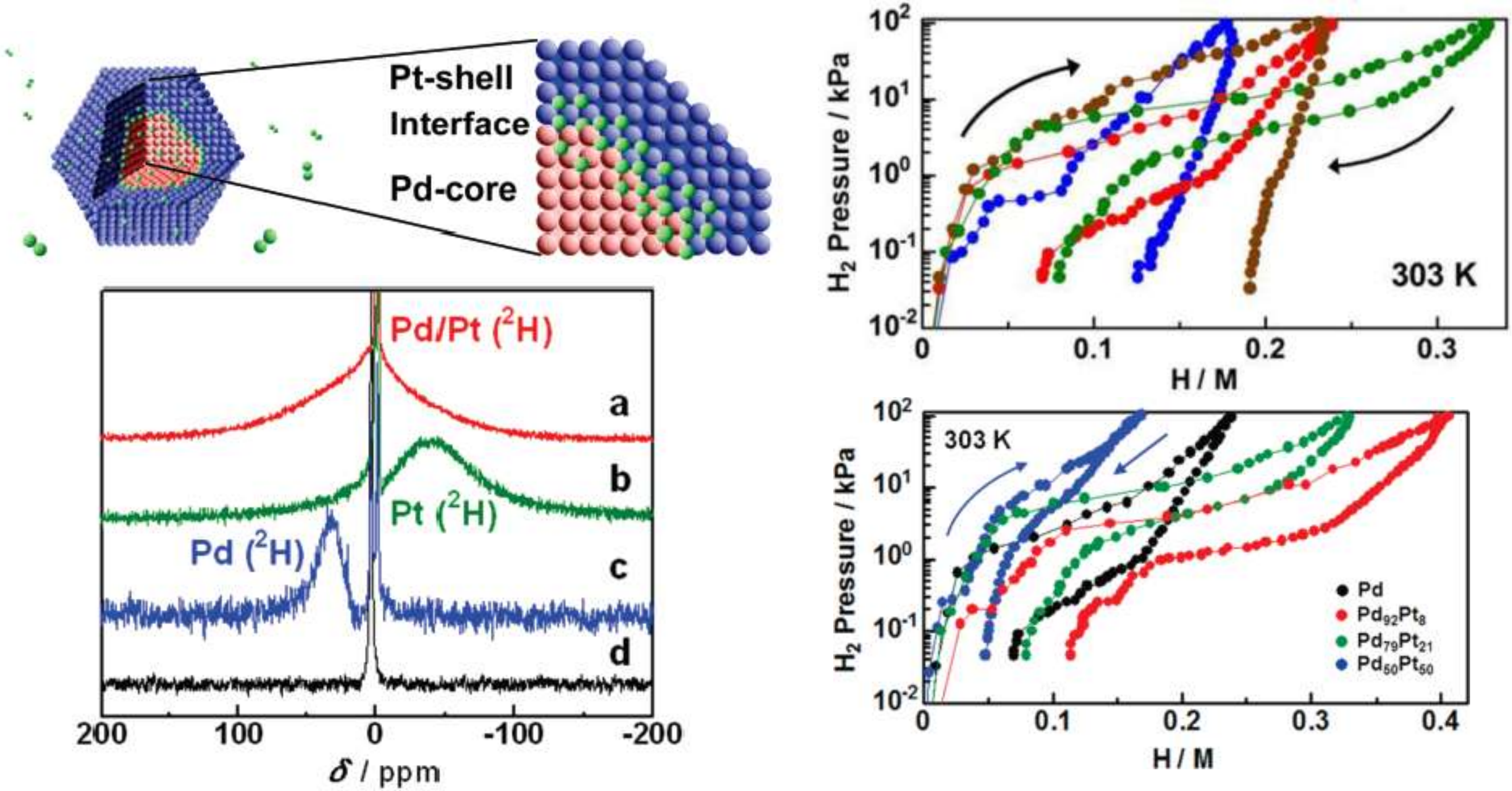
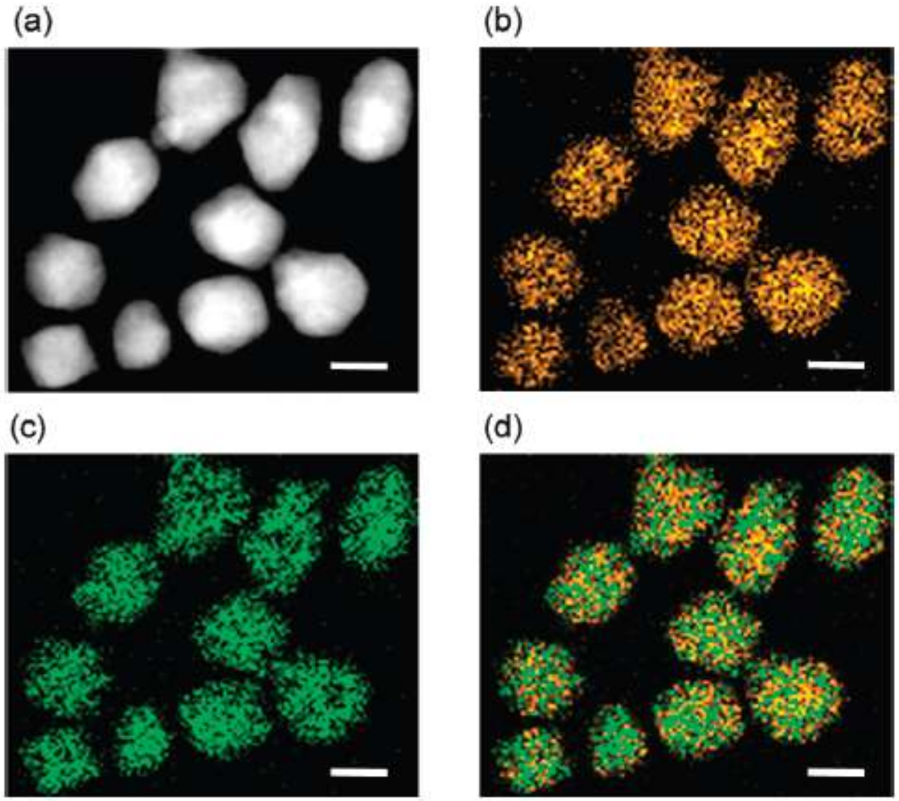


Figure | (upper right) PC isotherms of Pd (red), Pt (blue), $Pd_{79}Pt_{21}$ core/shell (brown) and $Pd_{79}Pt_{21}$ alloy (green). (lower right) PC isotherms of Pd, $Pd_{92}Pt_8$, $Pd_{79}Pt_{21}$, and $Pd_{50}Pt_{50}$ alloy.

Kitagawa, H. *et al., J. Am. Chem. Soc.* ***2008,*** *130*, 1818.

Kitagawa, H. *et al., J. Am. Chem. Soc.* ***2010,*** *132*, 5576.

(Rh + Ag) ÷ 2 = Pd?



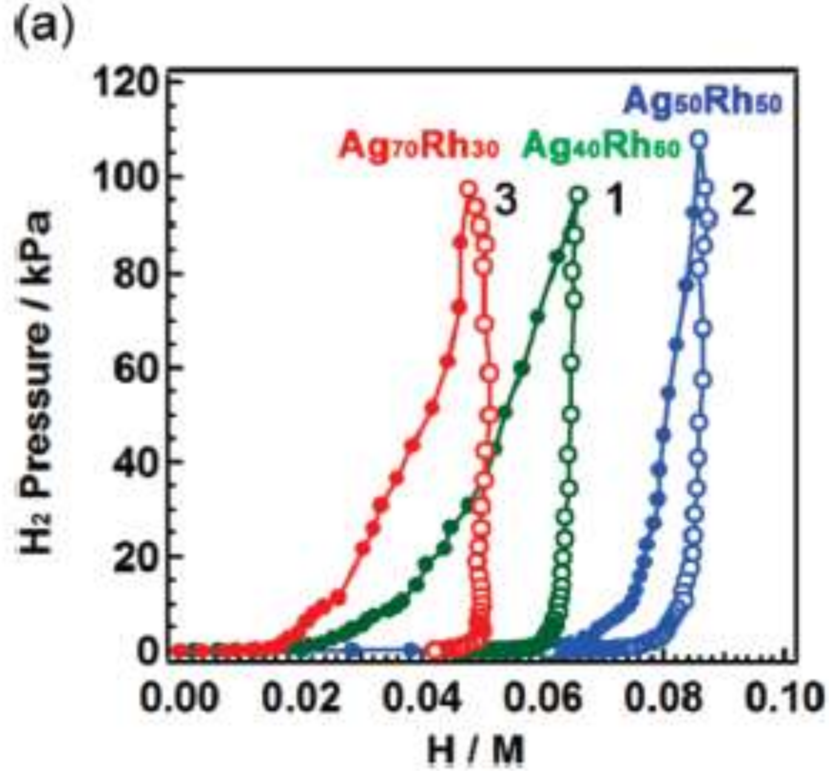
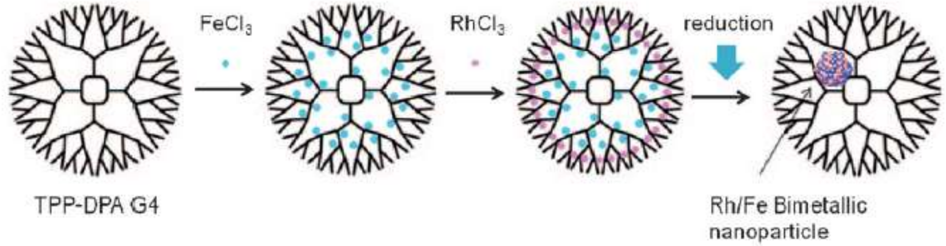


Figure | (left) (a) HAADF-STEM image, (b) Ag-L STEM-EDX map, and (c) Rh-L STEM-EDX map obtained from a group of prepared $Ag_{50}Rh_{50}$ nanoparticles. (d) Reconstructed overlay image of the maps shown in panels (b) and (c) (Rh: green, Ag: orange). The scale bars correspond to 10 nm. (right) Pressure-composition isotherms of (1) $Ag_{40}Rh_{60}$, (2) $Ag_{50}Rh_{50}$, and (3) $Ag_{70}Rh_{30}$ nanoparticles (open symbol: absorption at 303 K, close symbol: desorption at 303 K).

Kusada, K.: Kitagawa, H. *et al., J. Am. Chem. Soc.* ***2010,*** *132*, 15896.

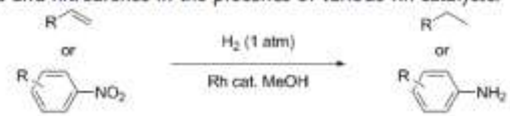
Summary of Bimetallic Nanoalloy

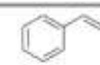
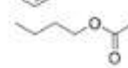
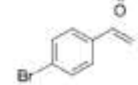
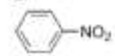
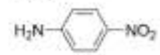
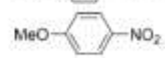
The shape, size, composition, and architecture of a nanoparticle are being recognized as important control parameters for tailoring new bimetallic nanoparticle systems.
And, analyzing and tuning these parameter are just enabled recently.
In many cases, the minor metals serve as 'spice'.
But in some cases, two metals are mixed to show completely new properties.



Scheme 1. The preparation of $Rh_{32}Fe_{28}$@TPP-DPA G4.

Table 1: Turnover frequencies (TOFs [h^{-1}]) of the hydrogenation of olefins and nitroarenes in the presence of various Rh catalysts.

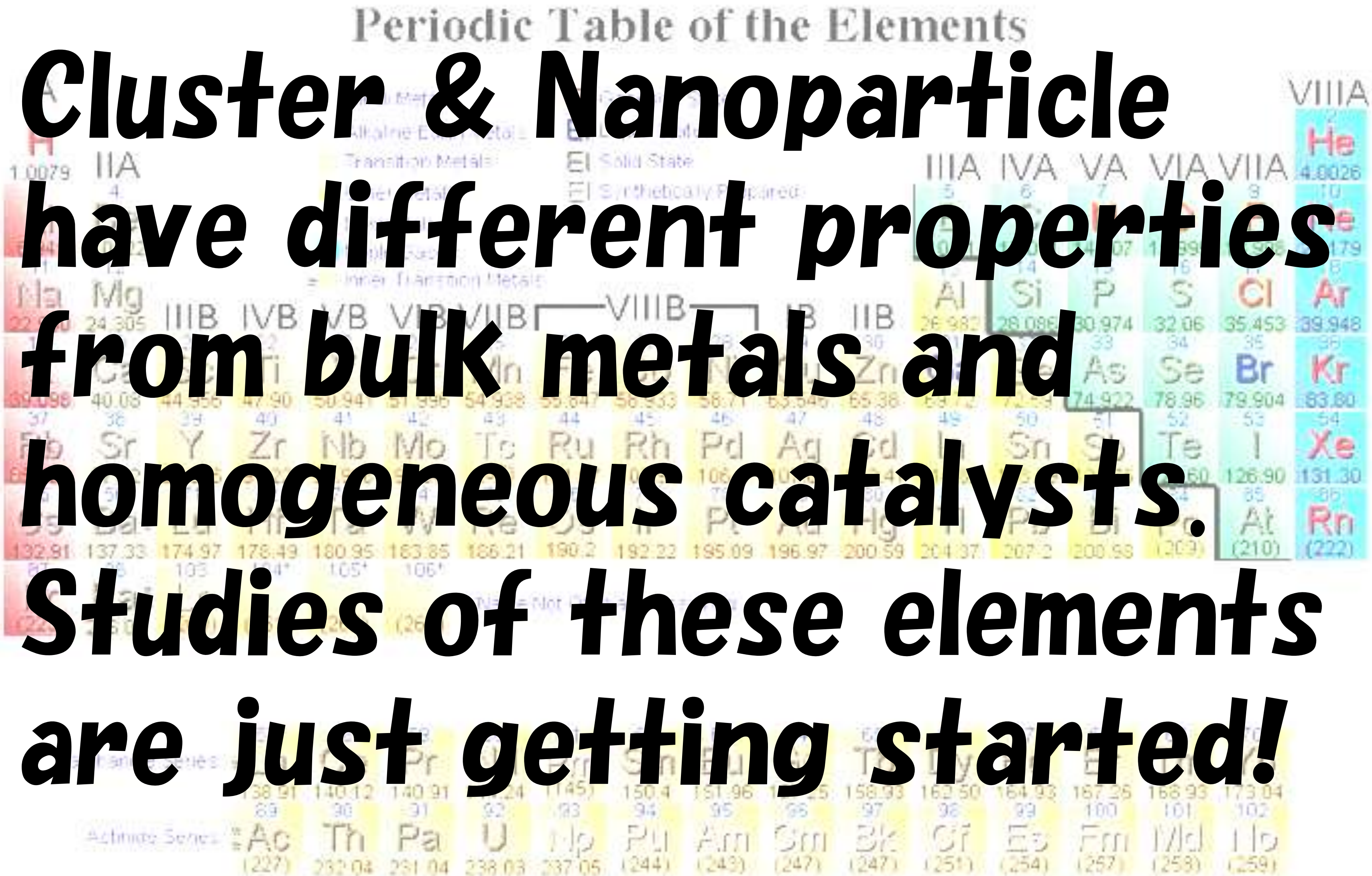


Entry	Substrate	Wilkinson	Rh_{60}@TPP-DPA[c]	$Rh_{32}Fe_{28}$@TPP-DPA[c]
1[a]		8	173 (10380)	**510 (30600)**
2[a]		12	292 (17520)	**500 (30000)**
3[a]		57	78 (4680)	**139 (8340)**
4[b]		0	2 (120)	**11 (660)**
5[b]		0	2 (120)	**17 (1020)**
6[b]		0	5 (300)	**11 (660)**

[a] 1.75 mmol olefinic substrate, 0.3 mol% catalyst (based on metal), 5 mL MeOH under H_2 (1 atm). [b] 0.7 mmol aromatic nitro compound, 0.3 mol% catalyst, 5 mL MeOH under H_2 (1 atm). [c] The TOF in parentheses is corrected for the total metal content (calculated as 60 atoms/cluster). Highest values highlighted in bold.

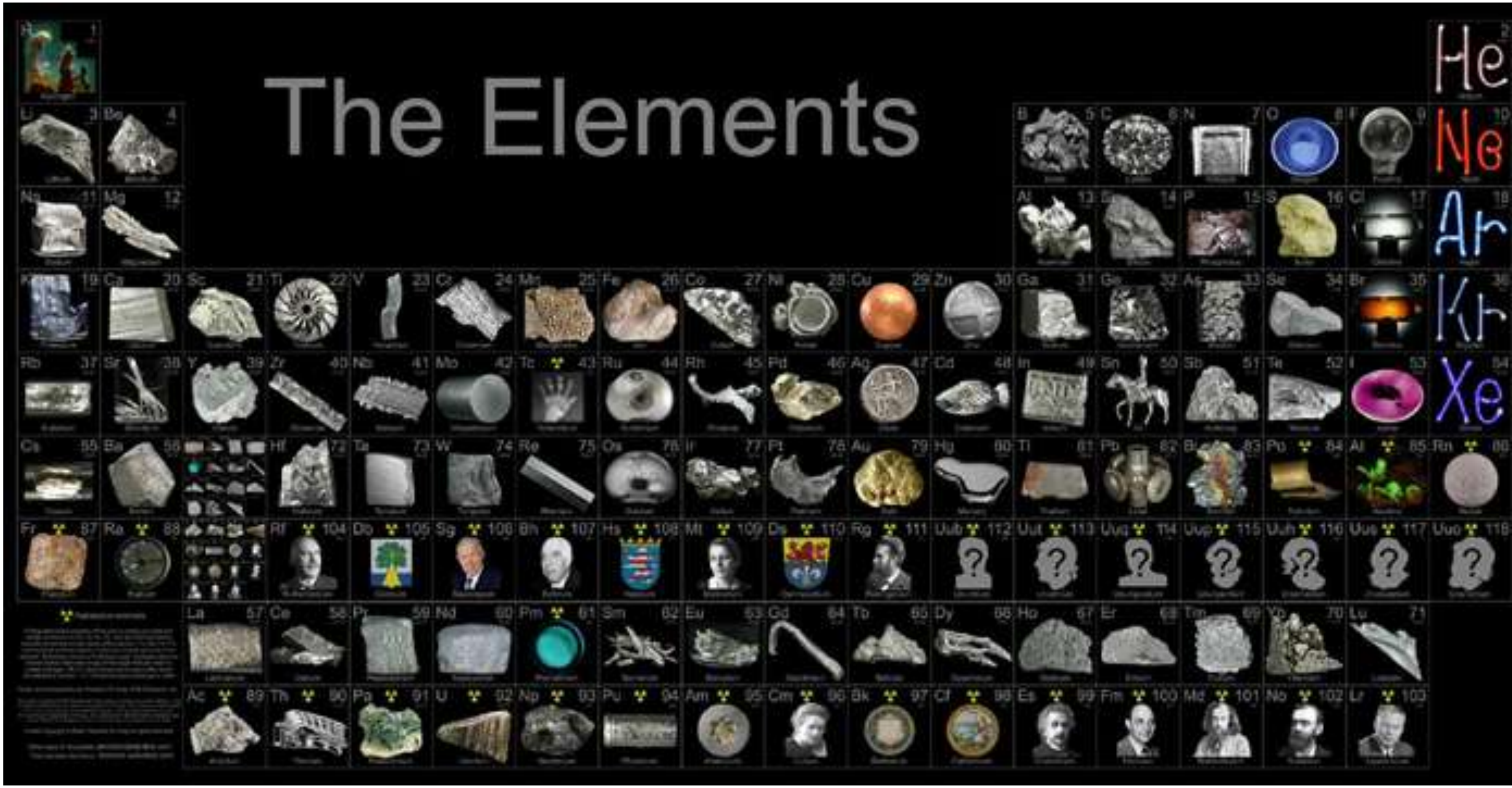
Yamamoto, K.; Nishihara, H. *et al. Angew. Chem. Int. Ed.* **ASAP**

Summary



Cluster & Nanoparticle have different properties from bulk metals and homogeneous catalysts. Studies of these elements are just getting started!

How do you think?



The Most Beautiful Periodic Table Poster in the World

By Theodore Gray