

Catalytically Active Transition-Metal Nanoclusters Prepared in Solution.

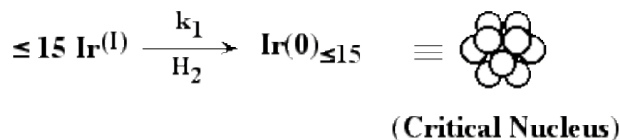
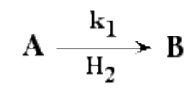
Illustration of the State-of-the-Art [1,2,3,4] via:

- (I) What We Do Know About Their Mechanism of Formation, and
 (II) A Partial List of What Is Still Needed / What We Cannot Yet Do**

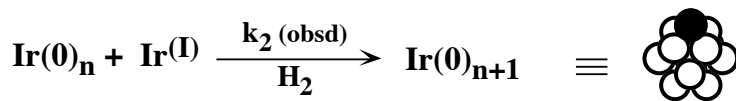
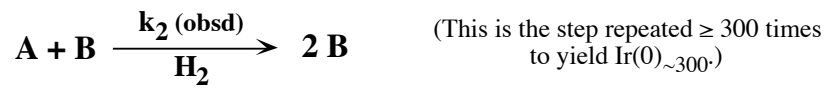
(I)(a) Compelling Product, Balanced Reaction Stoichiometry and Kinetic Evidence Is Available Elsewhere [5] for the Following Mechanism of Transition-metal Nanoparticle Formation Under Reducing Conditions:

Pictorial View of the Proposed, Minimum Mechanism of Formation of Ir(0) and Other Transition-metal Nanoclusters Prepared Under H₂ (Adopted from Figure 13 on p. 44 published elsewhere [1])

A) Nucleation (slow, continuous, homogeneous)

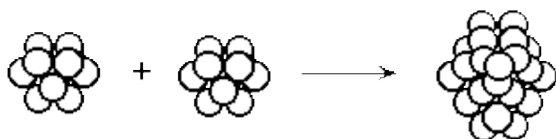


B) Autocatalytic Surface Growth



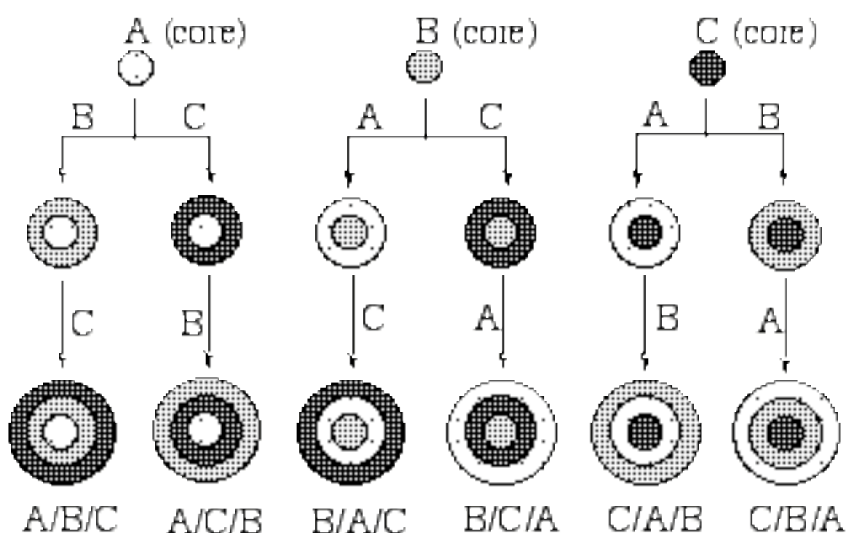
$$\text{Where } k_2 \text{ (obsd)} = k_2 \left[\frac{1 + x_{\text{growth}}}{2} \right]$$

C) Diffusive Agglomerative Growth



(I)(b) The Slow, Continuous Nucleation, Fast Autocatalytic Surface Growth Mechanism Explains Why “Magic Number” (Full Shell) Nanoclusters Tend to Form [6]. It Provides the Mechanistic Rationale for, and Insights How to Best Use [7], the Seed Growth Method [6], and It Predicts Easily Tested Synthetic Routes to All Possible Geometric Isomers (“Nano-onions”) of Multimetallic Nanoclusters [6]. The Latter is Illustrated Below:

Illustration of the Living-metal Polymer Approach to the Synthesis of Multi-metallic Nanoclusters (“nano-onions”) of, at Least in Principle, Well-defined Initial Structures and Layer Thickness. (Adopted from Figure 16 elsewhere [1], where some caveats about symmetry or lattice mismatch, mound or island growth, or atomic / layer migrations are also discussed [1])



(II) A Partial List of What Is Still Needed / What We Cannot Yet Do (Re: Catalytically Active Transition-Metal Nanoclusters Prepared in Solution)

(A) Fundamental Understanding / Basic Physical Properties / Some Synthetic Goals

- Which stabilizers, of a myriad of anions, cations, solvents, polymers, dendrimers and so on being continually reported, truly provide the *best* synthetic recipes? That is, a quantitative ranking of nanocluster stabilizers is needed—for both stabilization and catalytic activity [8].
- What anions, counter cations, solvents, added ligands and other stabilizers provide the best combination of catalytic activity, selectivity, lifetime vs its probable trade-off with stability [8]?
- How to achieve higher temperature stability nanocluster catalysts in solution (currently limited to ca. 130-160 °C [9])
- What is the *exact chemical composition*, and how does that relate to the catalytic or other physical properties, of a given TM nanocluster?
- Initially “Naked Nanoclusters”, of controlled size, shape and, eventually, desired ligand additives, that would be ideal for preparing more active [10], supported heterogeneous catalysts (i.e., the Naked Nanocluster problem [11]).
- Effects of trace impurities, notably O₂, on size, structure and catalytic activity ala classic studies in heterogeneous catalysis (e.g., Abhaya Datye’s studies of supported Rh)
- The definitions [1] and distinguishing features between *nanoclusters* and *nanocolloids* (e.g., Bradley’s important Pt nanos where reduction of nH₂PtCl₆ + PVP to give Pt(0)_n•PVP and 6nHCl results in ±670% catalytic *irreproducibility*. Yet, when the excess HCl was removed by dialysis, a ±15% *reproducible, more active catalyst* was obtained—that is, Bradley showed how to transformed a nano-colloid into a modern nano-cluster [12])
- Scaled-up (≥ 1gm), reproducible, checked, *Inorganic or Materials Syntheses* procedures for the best, catalytically active TM nanoclusters identified from above
- All geometric isomers of multimetallic nanoclusters (“nano-onions”) rationally prepared by the autocatalytic surface growth (living-metal polymer) mechanism [6]
- “catalyst bank” of well-characterized, prototype nanoclusters for use in rapid survey experiments by others in catalysis
- Most types of more complicated, *catalytically active*, 2D and 3D superstructures incorporating nanoclusters
 - Multifunctional, multi-catalytic cycle, tandem / “hand-off” or “assembly line” catalysts

- Compartmentalized catalysts of all types
- Vectorial e^- / H^+ or other *bio-mimetic* catalysts
(Witness N_2 ase and its [4Fe-4S], P-cluster, FeMoCofactor mediated, room temperature reduction of N_2)
- Coupling of other sources of energy to accomplish difficult catalysis
(e.g., as N_2 ase does:
$$N_2 + 8 H^+ + 8 e^- + 16 \text{ Mg ATP} \rightarrow 2 NH_3 + H_2 + 16 \text{ MgADP} + 16 \text{ Pi}$$
)
- And so on

- *Directed assembly* (vs the much cruder self-assembly)—witness the fantastic structures and complexity of gene-product-directed biomineralization, for example

Lead References

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[10] The active sites in Rh(0) nanoclusters are $\geq 2.3 - 23$ fold more active than the active sites in 5% Rh/Al₂O₃ by CS₂ titration studies: "Nanoclusters in Catalysis: A Comparison of CS₂ Catalyst Poisoning of Polyoxoanion- and Tetrabutylammonium-Stabilized 40 ± 6 Å Rh(0) Nanoclusters to 5% Rh/Al₂O₃, Including an Analysis of the Literature Related to the CS₂ to Metal Stoichiometry Issue", Hornstein, B. J.; Aiken III, J. D.; Finke, R. G. *Inorg. Chem.*, **2002**, *41*, 1625.

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