Clusters
An introduction through case studies

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Literature Presentation
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“Calomel” has been known in India for hundreds of years. \( \text{Hg}_2\text{Cl}_2 \) was later proven to have a Hg-Hg bond.

1300s

Fe\(_2\)(CO)\(_9\) followed by a series of Fe, Mn clusters were discovered

Metal Carbonyl complexes

1907

Young Linus Pauling found \( \text{Mo}_6 \) Octahedral in \( \text{MoCl}_2 \)

1928

Alfred Stock: “Those are boranes in analogy to the alkanes.”

2023

Boron clusters

1937

Mainstream attention

F.A Cotton discovered \( \text{ReCl}_3 \) as \( \text{Re}_3\text{Cl}_9 \), followed by M-M multi bond

1960s

1990s

https://www.pharmaceutical-technology.com/features/history-of-als
It’s not a long story

History

“Calomel” has been known in India for hundreds of years. Hg₂Cl₂ was later proven to have a Hg-Hg bond.

1300s

Fe₂(CO)₉ followed by a series of Fe, Mn clusters were discovered

Metal Carbonyl complexes

1907

Young Linus Pauling found Mo₆ Octahedral in MoCl₂

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1937

1960s

2023

Mainstream attention

F.A Cotton discovered ReCl₃ as Re₃Cl₉, followed by M-M multi bond

Alfred Stock: “Those are boranes in analogy to the alkanes.”

Boron clusters

https://www.pharmaceutical-technology.com/features/history-of-als
Chemists have been discovering Clusters
But...
Much like we don’t get all natural products from animals
Can we make them?
The synthesis of clusters

General procedures

Metal salts → Steel pressure vessel → Autoclave (100-150°C) → Cluster crystal

Days

The synthesis of clusters

General procedures

Metal salts → Solution → Crystalization → Cluster crystal

The synthesis of clusters

General procedures

Metal salts

High-Temp reactor
(500-1200°C)

Cluster powder

The synthesis of clusters

General procedures

Oxidized salts → Metal reductant → Carbon monoxide → Carbonyl clusters
The synthesis of clusters

General procedures


Cu₃MoS₄
The synthesis of clusters

General procedures

Case study I:
“The important one”
$Au_{55}[P(C_4H_5)_{3}]_{12}Cl_6$
Case study I

$\text{Au}_{55}[\text{P(C}_4\text{H}_5)_3]_{12}\text{Cl}_6$

Case study I

$Au_{55}[P(C_4H_5)_3]_{12}Cl_6$

$Au_{55}[P(C_4H_5)_3]_{12}Cl_6$

**Synthesis**

\[
\text{Ph}_3\text{P} - \text{Au} - \text{Cl} \xrightarrow{\text{B}_2\text{H}_6} [\text{Au}_{9.2}(\text{PPh}_3)_2\text{Cl}]_n
\]

50-60°C

Benzene

---

**Translatable strategy**

$Au_{55}$, $Ru_{55}$, $Rh_{55}$, $Pt_{55}$, $Co_{55}$ can all be made similarly

Generate M(0) waste

Poor thermo stability
$Au_{55}[P(C_4H_5)_3]_{12}Cl_6$

**Synthesis**

\[ \text{Ph}_3\text{P} - \text{Au} - \text{Cl} \]

$B_2H_6$

\[ [\text{Au}_{9.2}(\text{PPh}_3)_2\text{Cl}]_n \]

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50-60°C
Benzene

**Translatable strategy**

**Au\textsubscript{55}, Ru\textsubscript{55}, Rh\textsubscript{55}, Pt\textsubscript{55}, Co\textsubscript{55}**
can all be made similarly

**Why 55?**
Generate M(0) waste

Poor thermo stablity
Metals really like to be close packed!

Let’s expand the packing from the simplest repeating unit.
The Magic number

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2 layers → 3 layers → 4 layers

5 layers → 6 layers
The Magic number

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**The Magic number**

Let’s expand the packing from the simplest repeating unit.

\[ M_{13} \rightarrow M_{55} \rightarrow M_{147} \]

5 layers 6 layers
The Magic number

Let's expand the packing from the simplest repeating unit.

\[ M_{13} \rightarrow M_{55} \rightarrow M_{147} \rightarrow M_{309} \rightarrow \text{6 layers} \]
**The Magic number**

Let’s expand the packing from the simplest repeating unit.

\[ \text{M}_{13} \rightarrow \text{M}_{55} \rightarrow \text{M}_{147} \rightarrow \text{M}_{309} \rightarrow \text{M}_{561} \]

The Magic number

Let’s expand the packing from the simplest repeating unit.

\[ y = 10n^2 + 2 \]
\( Au_{55}[P(C_4H_5)_3]_{12}Cl_6 \)

*Heterogeneous catalysis*

\[ \text{Ph}_3P - Au - Cl \quad \text{[Au}_{9.2}(\text{PPh}_3)_2Cl]_n \]

Translatable strategy

\( Au_{55}, \text{Ru}_{55}, \text{Rh}_{55}, \text{Pt}_{55}, \text{Co}_{55} \)
can all be made similarly

Generate \( M(0) \) waste

Poor thermo stability
Unfortunately, a wide range of $M_{55}$ failed as efficient catalysts.

Generate M(0) waste

Poor thermo stablity
Unfortunately, a wide range of $\text{M}_{55}$ failed as efficient catalysts.

A translatable strategy

$\text{Au}_{55}, \text{Ru}_{55}, \text{Rh}_{55}, \text{Pt}_{55}, \text{Co}_{55}$ can all be made similarly.

Generate $\text{M}(0)$ waste

Poor thermo stability
Unfortunately, a wide range of M₅₅ failed as efficient catalysts

Translatable strategy

Poor thermo stablity

Au₅₅, Ru₅₅, Rh₅₅, Pt₅₅, Co₅₅ can all be made similarly

Generate M(0) waste
Unfortunately, a wide range of M$_{55}$ failed as efficient catalysts. Poor thermo stability. Au$_{55}$, Ru$_{55}$, Rh$_{55}$, Pt$_{55}$, Co$_{55}$ can all be made similarly. TON < 10.
Unfortunately, a wide range of $M_{55}$ failed as efficient catalysts.

**Poor thermo stability**

$Au_{55}, Ru_{55}, Rh_{55}, Pt_{55}, Co_{55}$ can all be made similarly

$120{^\circ}C$

$\text{TON} = 1$
Can we make more stable clusters?
The Magic number

M_{13}  M_{55}  M_{147}
M_{309}  M_{561}
The Magic number
Case study II:
The most studied cluster catalyst system
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The most studied cluster catalyst system
\[ \text{Pd}_{561}\text{L}_{60}(\text{OAc})_{180} \]
$Pd_{561}L_{60}(OAc)_{180}$

Synthesis

$Pd_{561}L_{60}(OAc)_{180}$

*Synthesis*

$Pd_{561}L_{60}(OAc)_{180}$

**Synthesis**

$\text{H}_2$

$\text{Pd(OAc)}_2$ $\rightarrow$ $[\text{Pd}_4\text{(OAc)}_2\text{phenH}_4]_n$

$\text{phen}$ $n = 100$

$[\text{Pd}_4\text{(OAc)}_2\text{phenH}_4]_n$ $\rightarrow$ $\text{Pd}_{561}\text{(OAc)}_{180}(\text{phen})_{60}$

$\text{O}_2$

Wait...I think it should be $Pd_{540}$
*Pd*$_{561}$*L*$_{60}$(*OAc*)$_{180}$

*Characterization*

How do we arrive at the formula

*Pd*$_{561}$*L*$_{60}$(*OAc*)$_{180}$?
$Pd_{561}L_{60}(OAc)_{180}$

Characterization
$Pd_{561}L_{60}(OAc)_{180}$

Characterization
Transmission electron microscopy (TEM)

How does it work?
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How does it work?

Orders of magnitude more resolution than optical spectroscopy
Transmission electron microscopy (TEM)
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(TEM)
Transmission electron microscopy (TEM)
TEM data shows 3 kinds of Pd:
1) majority of Pd are in FCC environment
2) Distorted five-fold axis indicates icosahedral
3) Low symmetry sites were identified
TEM data shows 3 kinds of Pd:
1) Majority of Pd are in FCC environment
2) Distorted five-fold axis indicates icosahedral
3) Low symmetry sites were identified

The Pd$_{540}$ accounts for only the first and second kind
So there are more than 540 Pd atoms

Supported by other microscopy and element analysis
The formula was deducted to be Pd$_{570\pm30}$L$_{63\pm3}$(OAc)$_{190\pm10}$

The magic number 561 was suspected to be the result of averaging the ensemble of clusters in different sizes
The Pd-561 is significantly more competent as a catalyst

$Pd_{561}L_{60}(OAc)_{180}$

Heterogeneous catalysis
Can we add stability by other means?
Case study III: Stabilize by ethers
Boënnemann’s nanocluster systems

Case study IV: Stabilize by inorganic
Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters
Bönnemann’s nanocluster systems

Synthesis

Boßnemann’s nanocluster systems

Boënnemann’s nanocluster systems

Synthesis

Boønnemann’s nanocluster systems

Synthesis

\[
\text{MX}_v \quad \overset{\text{ether, } < 50^\circ \text{C}}{\longrightarrow} \quad \text{ether M (cluster)} + \text{vNR}_4X + \text{vBE}_3 + 0.5\text{vH}_2
\]

Translatable strategy

Cr, Co, Mo, etc can all be made as stable cluster solutions

Ether is rather important for stability

Participate out under H\textsubscript{2} makes it ineffective catalyst

Can we fix that?
Importance of support

Dipping support in Cluster solutions

Support materials

SMCs
Supported clusters
Heterogeneous catalysis

SMCs play important role in heterogeneous catalysis

Me\text{CN} \rightarrow \text{Industrial Rh} \rightarrow \text{Charcoal} \rightarrow \text{MeCH}_{2}\text{NH}_{2}

\[ A_{\text{rel}} = 1 \]

Me\text{CN} \rightarrow \text{12-22 Å Rh} \rightarrow \text{Charcoal} \rightarrow \text{MeCH}_{2}\text{NH}_{2}

\[ A_{\text{rel}} = 2.44 \]
By using chiral NR₄X in the synthesis asymmetric catalyst can be obtained. Supported clusters
Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

Synthesis

Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

Synthesis

Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

Synthesis

750 H₂

300[(COD)Ir₂P₂W₁₅Nb₃O₆₂]⁸⁻ → 300 COD + Ir(0)₃₀₀·₃₀₀(P₂W₁₅Nb₃O₆₂)⁹⁻ + 300H⁺

“Clean” metal cluster

Highly catalytically reactive

Counter ion is restricted

Rigorous air/moisture free synthesis required

Iridium based hydrogenation catalysts

Very interesting observation

\[
\text{[(COD)Ir}_2\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-} + \text{H}_2 \rightarrow \text{COD} + \text{Catalyst} + 300\text{H}^+
\]

\[
\text{Catalyst} + \text{H}_2 \rightarrow \text{COD} \quad \text{TON > 1500}
\]
Iridium based hydrogenation catalysts

Very interesting observation

\[
\text{H}_2 \\ [(\text{COD})\text{IrP}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-} \rightarrow \text{COD} + \text{Catalyst} + 300\text{H}^+
\]

- 1 equiv of COD was generated in 10 hrs.
- Hydrogenation of cyclohexane has an induction period ~2 hrs
- After 6 hrs, only 45% of COD was generated but >85% of cyclohexane.

What’s happening here?

\[
\text{Cyclohexene} \\ \text{H}_2 \\ \text{Catalyst} \rightarrow \text{Cyclohexane} \\
\text{TON} > 1500
\]
**Very interesting observation**

Iridium based hydrogenation catalysts

\[
[(\text{COD})\text{Ir}_{2}\text{P}_{2}\text{W}_{15}\text{Nb}_{3}\text{O}_{62}]^{8-} + \text{H}_2 \rightarrow \text{COD} + \text{Catalyst} + 300\text{H}^+ 
\]

Only a small fraction of active catalyst is enough

- After 6 hrs, only 45% of COD was generated but >85% of cyclohexane.

What's happening here?

\[\text{Cyclohexane} + \text{H}_2 + \text{Catalyst} \rightarrow \text{Cyclohexane} \text{+ Other products} \]

TON > 1500
**Iridium based hydrogenation catalysts**

*Very interesting observation*

\[
\text{H}_2 \\ [(\text{COD})\text{Ir}\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-} \rightarrow \text{COD} + \text{Catalyst} + 300\text{H}^+ 
\]

Only a small fraction of active catalyst is enough

The active catalyst is catalyzing the catalyst formation

\[
\text{H}_2 \\ \text{Catalyst} \\ \text{TON} > 190000 
\]

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\[
\text{H}_2 \quad \text{Catalyst} \\
\text{TON} > 190000
\]
Iridium based hydrogenation catalysts

Very interesting observation
Iridium based hydrogenation catalysts

Very interesting observation

\[
\begin{array}{c}
x \\
[ \begin{array}{c} A \rightarrow_{k_1} B \end{array} ]
\end{array}
\]

Nucleation
**Iridium based hydrogenation catalysts**

*Very interesting observation*

\[
\begin{align*}
x & \left[ A \xrightarrow{k_1} B \right] \\
1 - x & \left[ A + B \xrightarrow{k_2} 2B \right]
\end{align*}
\]

*Nucleation*

*Autocatalysis*
Iridium based hydrogenation catalysts

Very interesting observation

\[ x \begin{array}{c} A \xrightarrow{k_1} B \end{array} \]

\[ 1 - x \begin{array}{c} A + B \xrightarrow{k_2} 2B \end{array} \]

\[ \sim 1400 \begin{array}{c} B + \text{cyclopentene} + H_2 \xrightarrow{k_3 \text{Fast}} B + \text{cyclohexane} \end{array} \]

Nucleation

Autocatalysis

Fast hydrogenation
Very interesting observation

Iridium based hydrogenation catalysts

Auto catalysis enables fast turnover after induction period
Iridium based hydrogenation catalysts

Very interesting observation

\[
\begin{align*}
&x \left[ \begin{array}{c} A \rightarrow k_1 \rightarrow B \\ \end{array} \right] \\
&1 - x \left[ \begin{array}{c} A + B \rightarrow k_2 \rightarrow 2B \\ \end{array} \right] \\
&\sim 1400 \left[ \begin{array}{c} B + \text{cyclohexene} + H_2 \rightarrow k_3 \text{Fast} \rightarrow B + \text{cyclohexane} \\ \end{array} \right] \\
\text{Sum: } &A + \sim 1400 \text{cyclohexene} + \sim 1400 \text{H}_2 \rightarrow k_{\text{obs}} \rightarrow B + \sim 1400 \text{cyclohexane}
\end{align*}
\]
Cluster Chemistry
Challenges- 4S
For more active, long-live, and selective catalysis

- Scalability
  - retaining isolability and catalytic activity remains challenging on gram scale synthesis.

- Stability
  - lack of physical chemical understanding lead to not having a general protocol to predict and synthesize stable clusters

- Synthesis
  - poor understanding of cluster formation kinetics needs to be improved to provide chemists with more controlled synthesis of clusters in particular size or shape.

- Single active site heterogeneous catalysts
  - Limiting a cluster to only one single active site to achieve theoretically 100% selectivity is one of the biggest promise of cluster chemistry to catalysis, methods of which to achieve that is still in the air.
The yet to be explored chemical space in clusters may have treasures within

Yu, A.; Choi, Y. H.; Tu, M. Pharmacol Rev 2020, 72, 862.