Supported Au nanoparticles as Heterogeneous Catalyst for Organic Reactions

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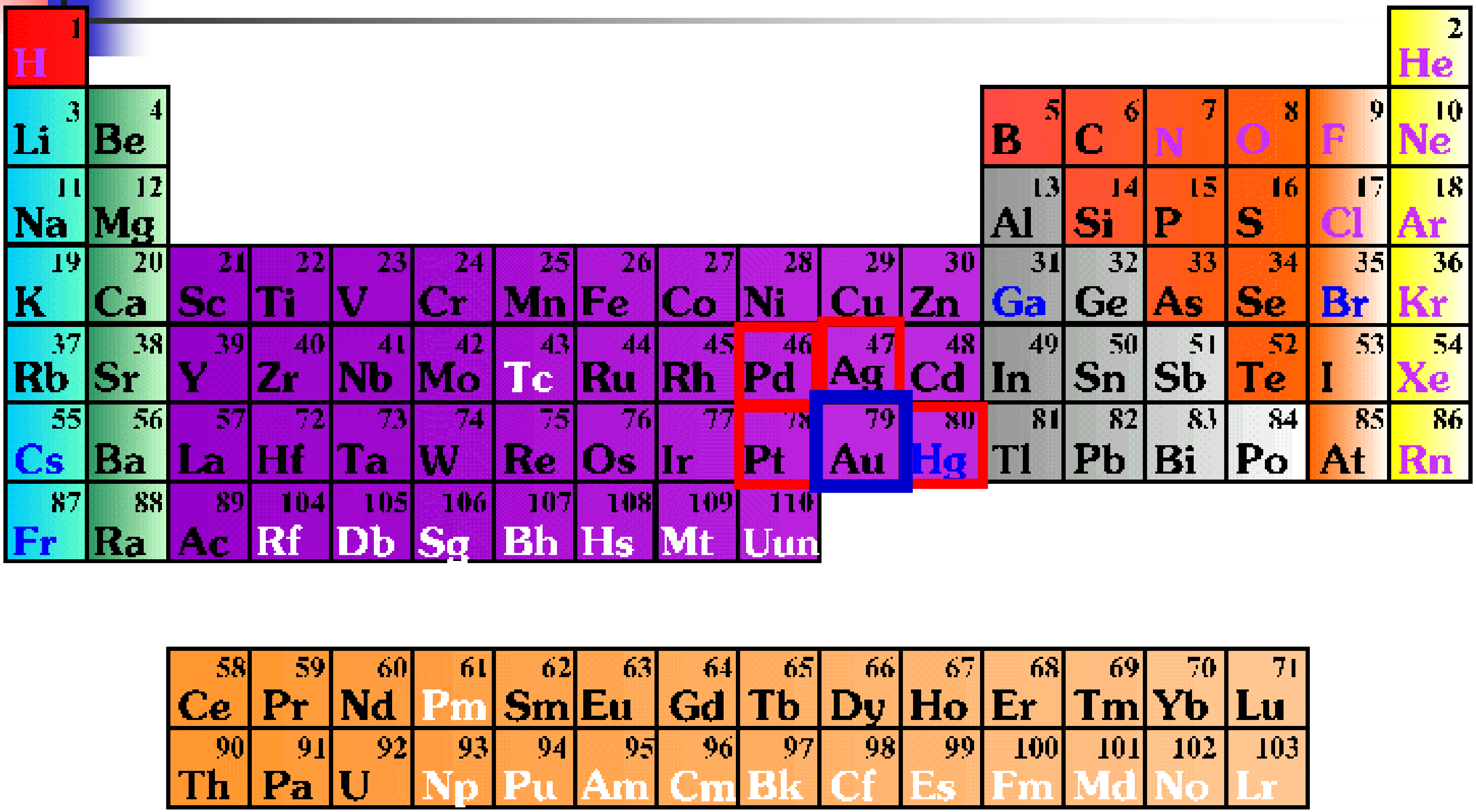
<u>Outline</u>:

Au NPs and Nanoscience
Au NPs as catalyst
  For aerobic oxidations
  For carbamoylation
  For tandem reactions
Role of impurities
Isolation of Au intermediates
Conclusions and Acknowledgements

Catalytic activity of noble metals



As the only exception in noble metals up to the 80s
Au was catalytically inactive

Gold nanoparticles as catalyst

Hydrogen technology

$$C + H_2O \longrightarrow CO + H_2 \xrightarrow{H_2O} CO_2 + H_2$$

syngas

water gas shift

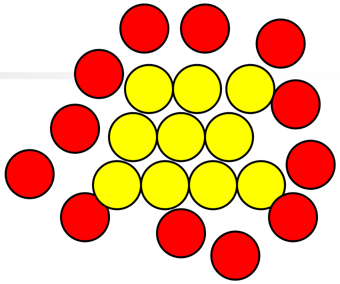
Low temperature, selective CO combustion:

the smaller the particle size, the higher the activity

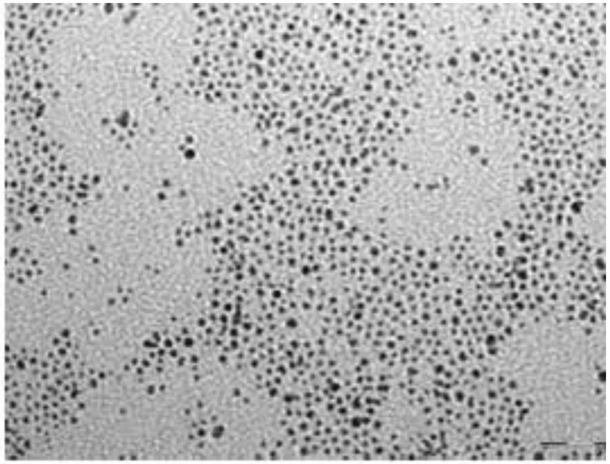
$$CO + O_2 \xrightarrow{Au} CO_2$$

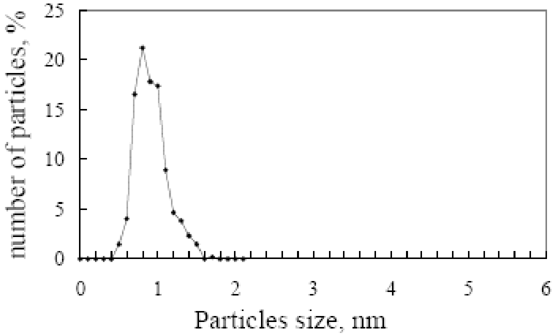
M Haruta, N Yamada, T Kobayashi, S Iijima: J. Cat. 115 (1989) 301-09.

Au NPs



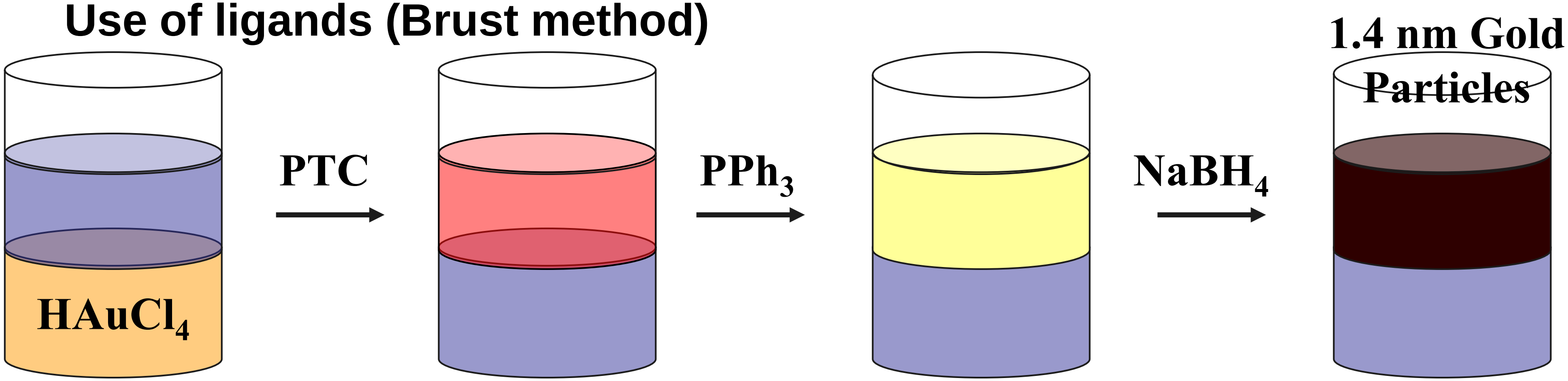
- They can be easily obtained.
- "Bare" small Au NPs (1-2 nm) tend to grow
- The key issue is to stabilize small Au NPs
- "Stabilized" nanoparticles are surrounded by a ligand shell or supported on a solid
- Typically, for bulk materials, surface atoms form a negligible part of the total number of atoms



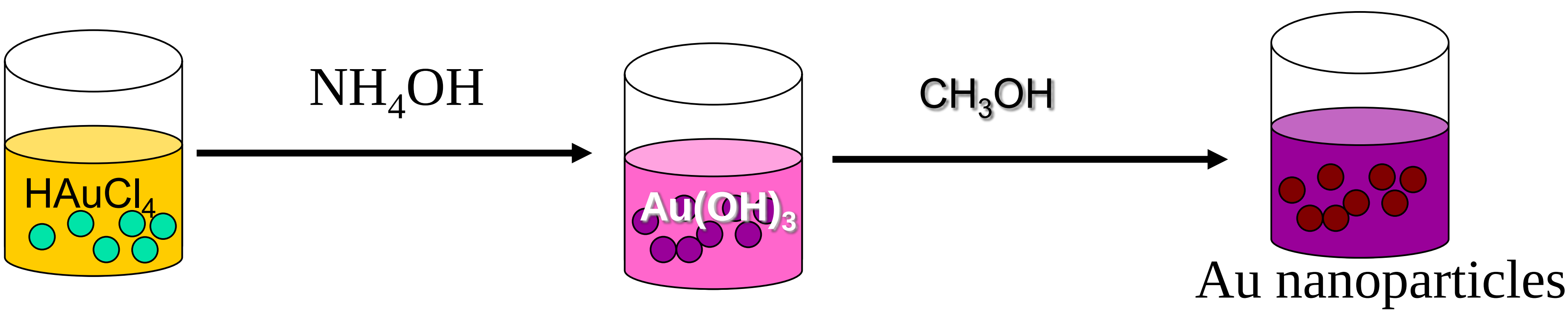


Stabilizing Gold Nanoparticles

Use of ligands (Brust method)

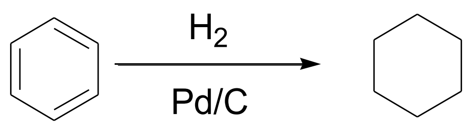


Supporting on a solid: Deposition-Precipitation method

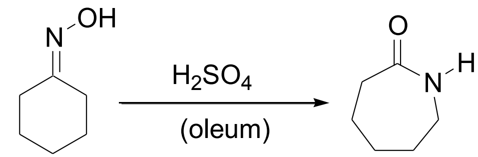


Organic reaction types

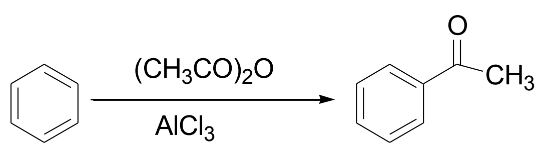
Hydrogenations



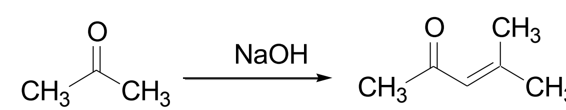
Brönsted acids



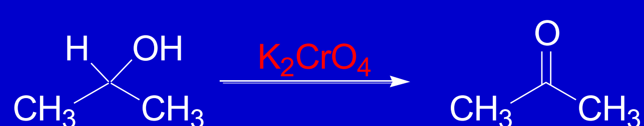
Lewis acids



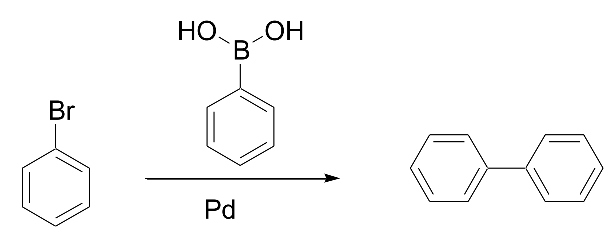
Bases



Oxidations



Transition metal catalysts

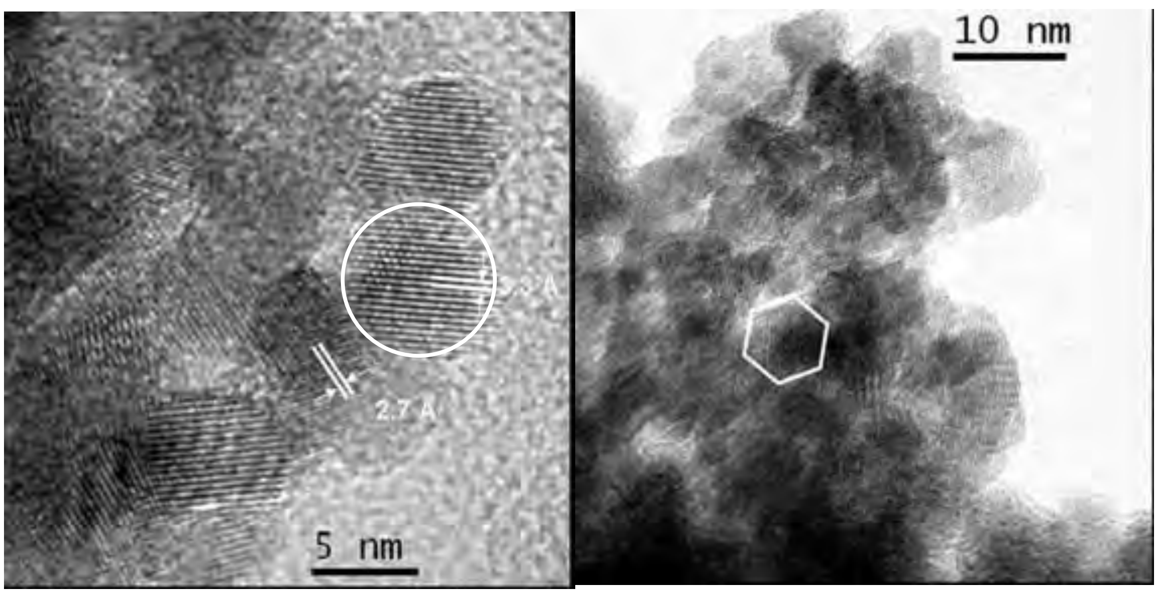


Au NPs supported on nanoparticulated ceria

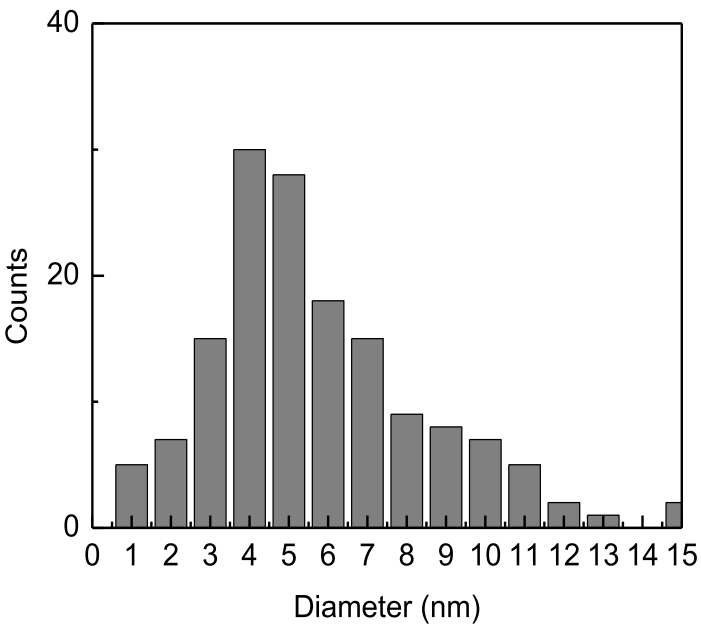
CeO_2 nanoparticles

- **Increasing Ce^{III} population**
- **Creation of oxygen vacancies**
- **From insulator to semiconductor**

Interplanar distance of Au



Particle size distribution



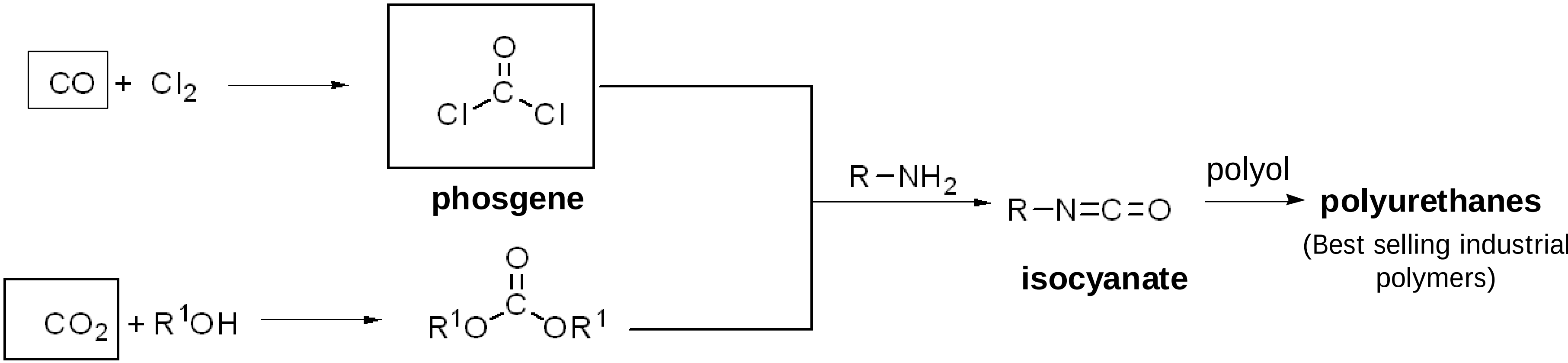
Solventless, aerobic (1 atm) oxidation of alcohols by Au/CeO_2

	Substrate	Time [h]	Conversion[a] [%]	Product	Selectivity[%]
1[b]	3-octanol	2.5	97	3-octanone	96
2[b]	sec-phenylethanol	2.5	92	acetophenone	97
3[b]	2,6-dimethylcyclohexanol	2.5	78	2,6-dimethylcyclohexanone	94
4[b]	1-octen-3-ol	3.5	80	1-octen-3-ona	>99
5[b]	cinnamylalcohol	7	66	cinnamaldehyde	73
6[b]	3,4-dimethoxybenzyl alcohol	7	73	3,4-dimethoxybenzaldehyde	83
7[b]	3-phenyl-1-propanol	6	70	3-phenylpropyl- 3-phenylpropanoate	98
8[c]	vanillin alcohol	2	96	vanillin	98
9[c]	2-hydroxybenzyl alcohol	2	>99	2-hydroxybenzaldehyde	87
10[c]	3,4-dimethoxybenzyl alcohol	2	>99	3,4-dimethoxybenzylic acid	>99
11[c]	cinnamyl alcohol	3	>99	cinnamylic acid	98
12[d]	n-hexanol	10	>99	hexanoic acid	>99
13[e]	n-hexanol	10	>99	hexanoic acid	>99
14[c]	sec-phenylethanol	5	>99	acetophenone	51

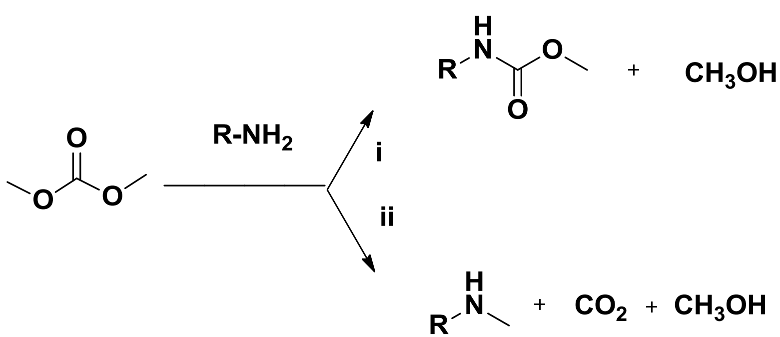
Solventless aerobic alcohol oxidation and the green chemistry principles

1. **Avoid wastes (minimise E factor)**.
2. **Use tolerable reagents and produce non-toxic products**.
3. **Use environmental friendly processes**.
4. **Use renewable feedstocks.**
5. **Develop more active and selective catalysts.**
6. Avoid derivatisation, protecting groups and isolations.
7. **Maximise the atomic economy.**
8. **Use environmentally friendly solvents.**
9. Minimise energy consumption
10. Use self- or bio- degradable products
11. Real time analyses
12. **Minimise hazards**

Replacement of toxic phosgene: Catalytic carbamoylation of aromatic diamines



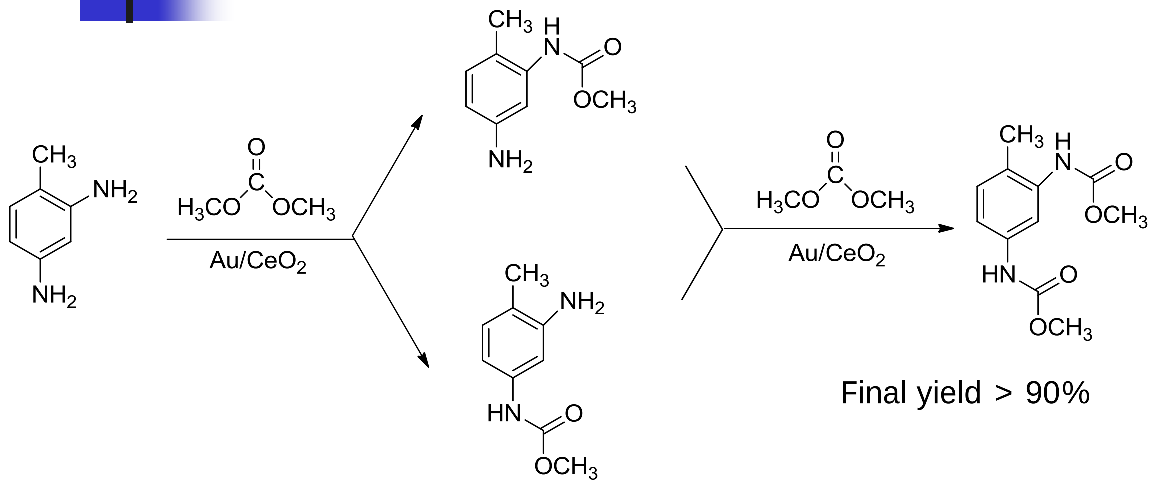
- Problem: development of a catalyst



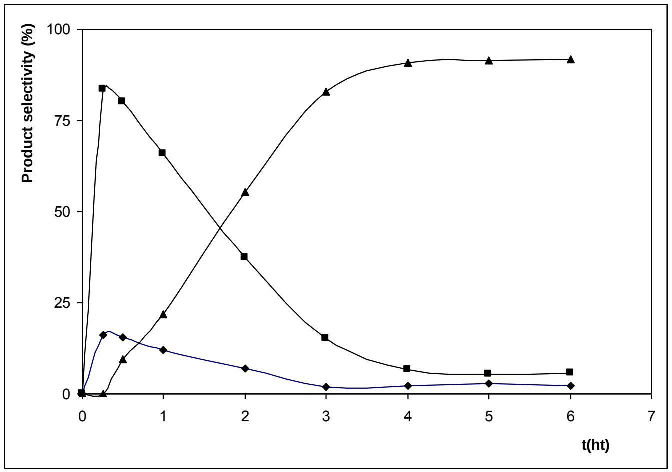
i; N-carbamoylation (unfavorable for aromatic amines)

ii, N-Alkylation

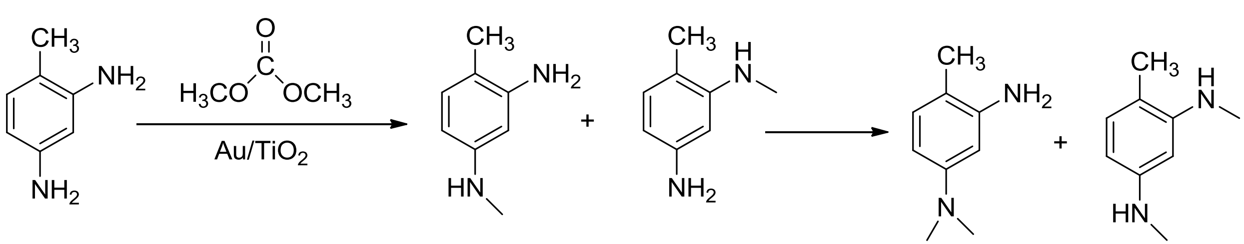
Carbamoylation of 2,4-diaminotoluene



Final yield > 90%

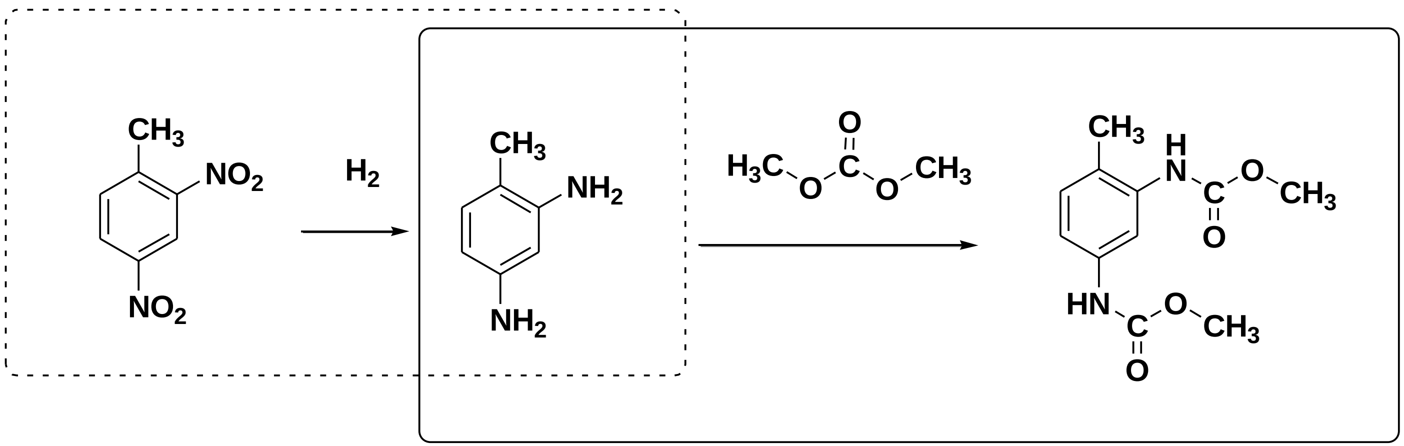


Au NPs on other supports give rise to N-methylation products:

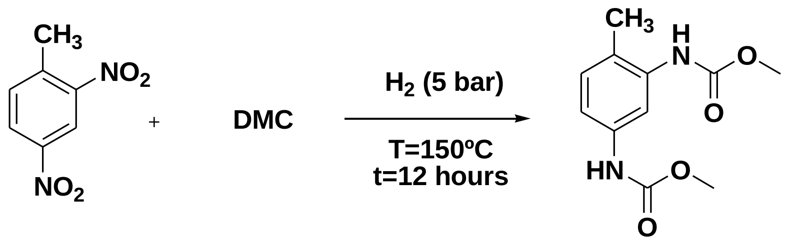


Tandem reaction

*Two steps, **two processes**:*



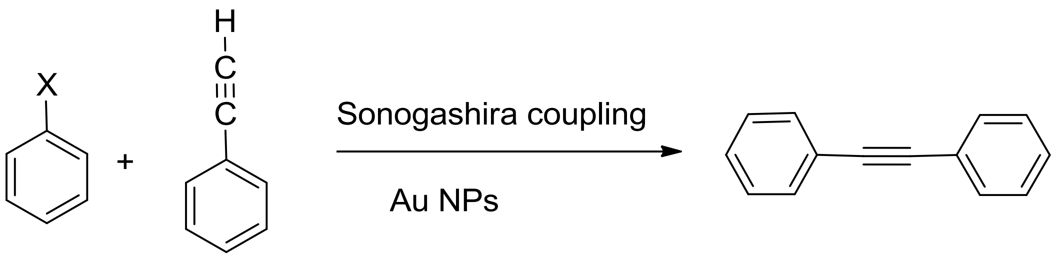
*or two-steps **one process**:*



Conversion = 95.2

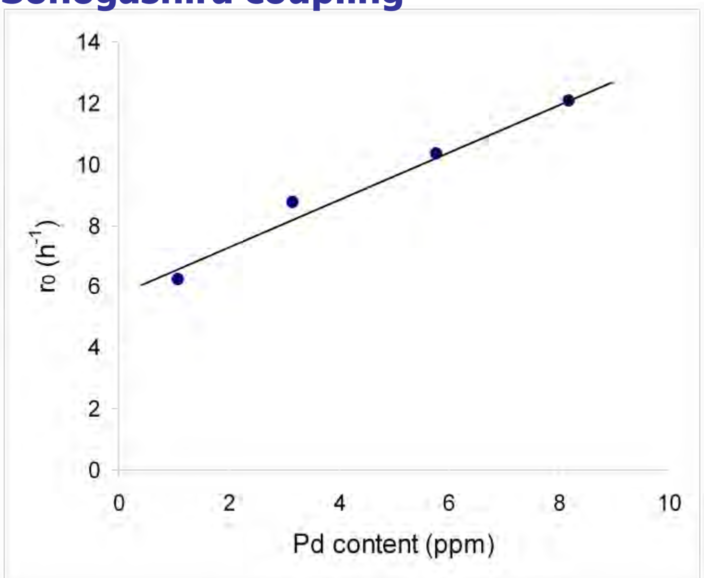
Selectivity = 98.3

Role of Pd impurities in Au catalysis

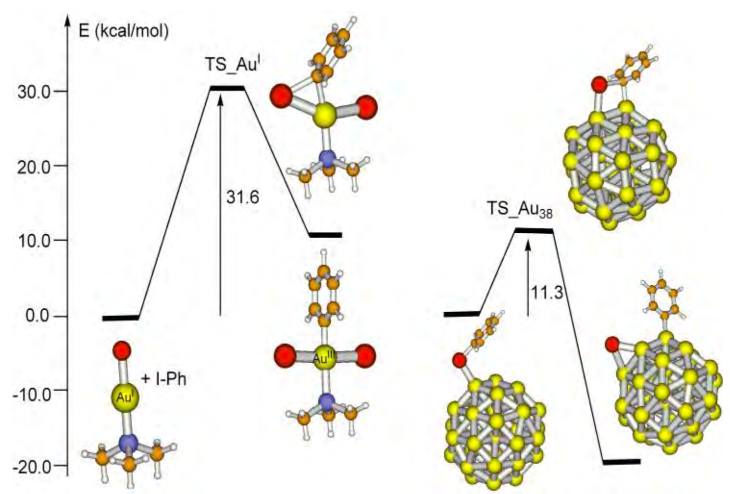


- Pd is a very efficient catalyst
- Au contains 5-10 ppm of Pd
- Has Au intrinsic activity?

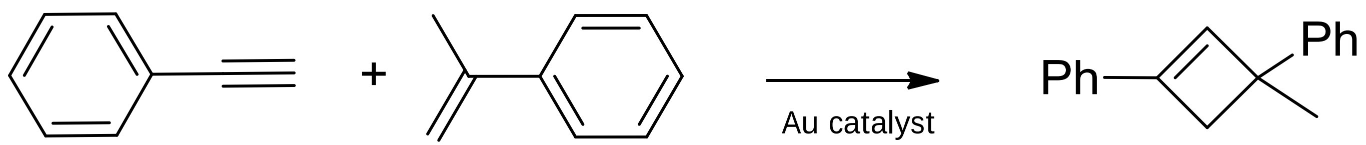
High purity Au is also active for Sonogashira coupling

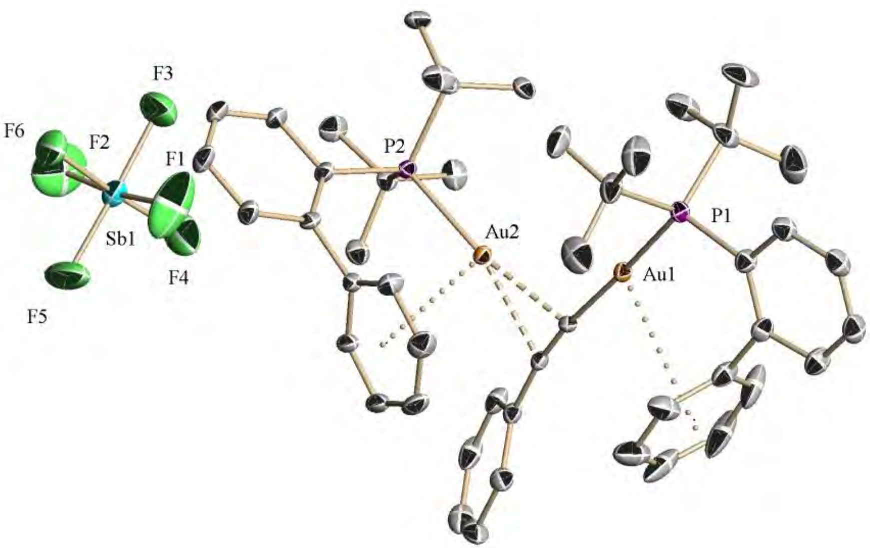


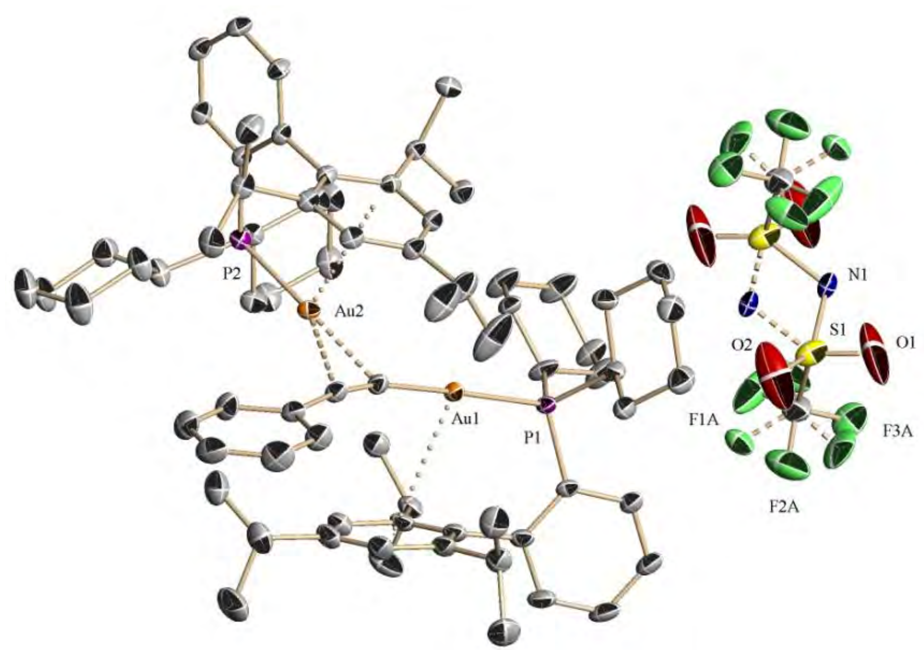
- Au complexes of a single atom is not able to promote Sonogashira
- Au NPs are active



Isolation of Au intermediates







Conclusions and Acknowledgements

Supported small sized Au NPs are highly active catalysts

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