Synthesis of Ultra-Small PdAu Nanoparticles with homogenous Alloys on SiO_2 and Al_2O_3 via Electrostatic Adsorption

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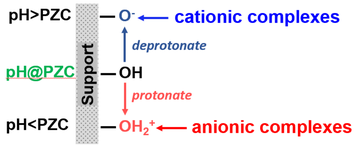
Motivations

- Pd based materials performed high activity in hydrogenation of alkene and alkyne; Au, as a promoter, has been reported to improve the selectivity.
- Small nanoparticles effectively improve the metal utilization.
- Strong Electrostatic Adsorption (SEA) is a generalizable and facile technique to synthesize ultra-small metal particles.
- Aims at extending SEA synthetic strategy to target ultra-small bimetal Pd-Au catalysts on high surface area silica and alumina.

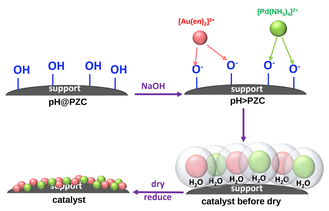
Catalysts Synthesis

Strong Electrostatic Adsorption (SEA)



- Support surface can be charged by adjusting solution pH.
- Oppositely charged metal complexes can be adsorbed onto the support surface.
- Strong interaction with support and metal.

Bimetallic catalysts preparation by co-SEA



strong metal-support interaction
↓
highly dispersed metal (s)
homogenous alloying
adjust metal concentration(s)
↓
controlled metal compositions

Bimetallic catalysts preparation by co-DI

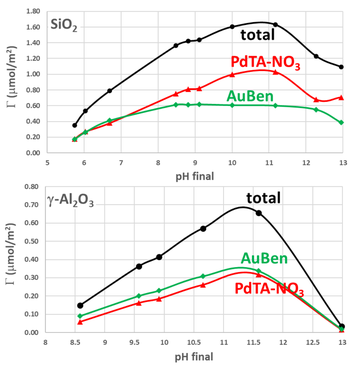
dry impregnation

- Advantages: simple procedure & controlled metal loadings
- disadvantages: poor metal-support interaction

↓

poor metal dispersion, inhomogeneity

Metal Adsorption Investigation



Support properties and uptake results

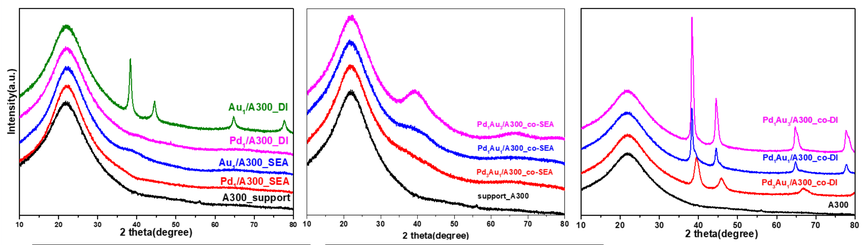
support	SiO_2	γ-Al_2O_3
SA (m_2/g)	280	277
PZC	3.6	8.3
SL (m^2/L)	1000	1000
max. Γ_{Au} (umol/m^2)	0.61	0.39
max. Γ_{Pd} (umol/m^2)	1.03	0.37

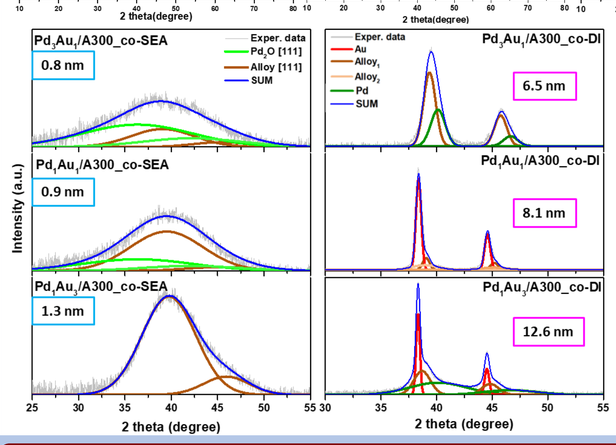
- Higher loadings of Pd and Au on SiO_2 than γ-Al_2O_3 due to the sufficient deprotonation of the surface.

*pH was adjusted by HCl and NaOH

Results: X-ray diffraction

supported on SiO_2



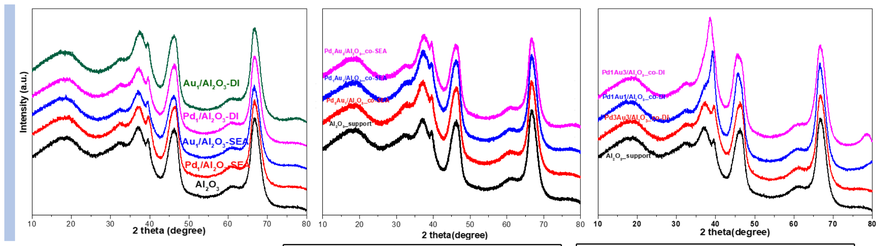


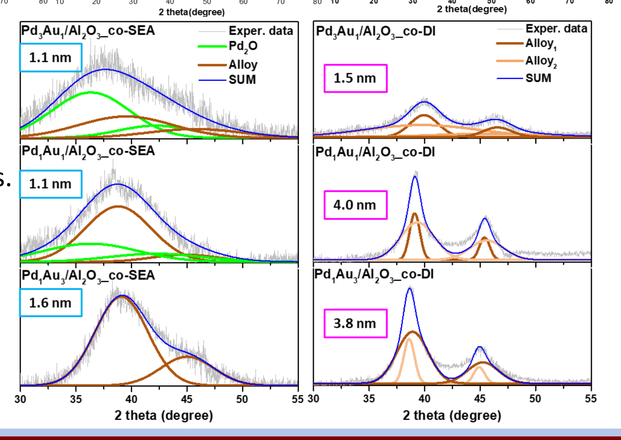
Pd [111]	40.12
Pd [200]	46.66
Pd [220]	68.12

Au [111]	38.19
Au [200]	44.39
Au [220]	64.58

- **co-SEA**: very broad peaks in XRD patterns.
  ultra-small particles (<2nm).
  homogenous alloys.
- **co-DI**: sharp peaks in XRD patterns.
  larger particles.
  more than two alloys (inhomogeneity)

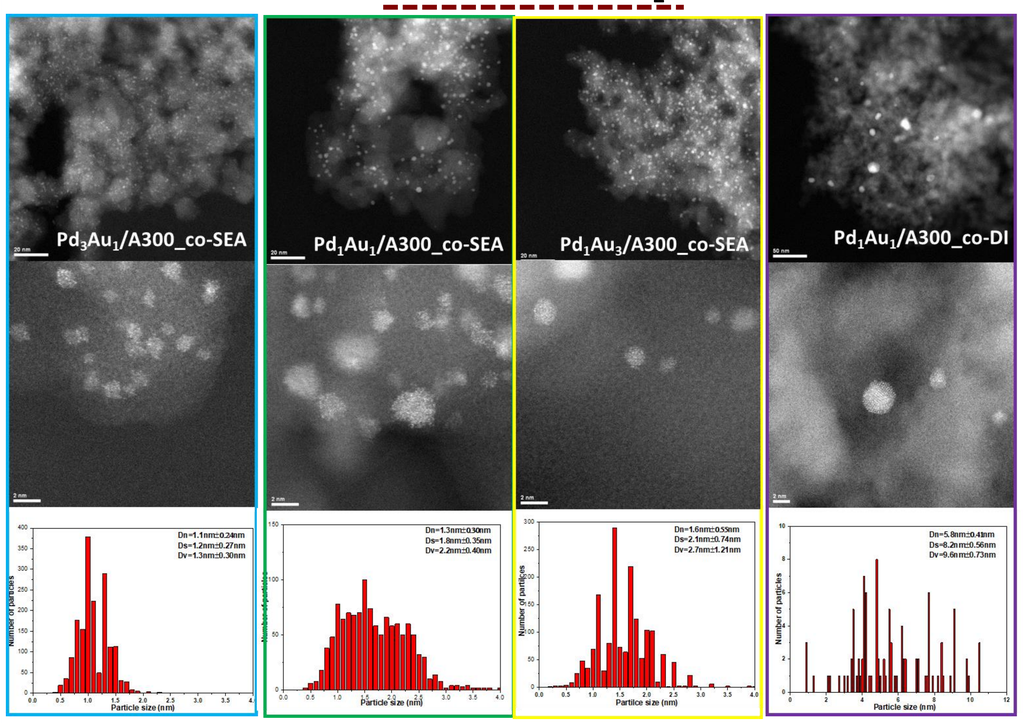
supported on γ-Al_2O_3



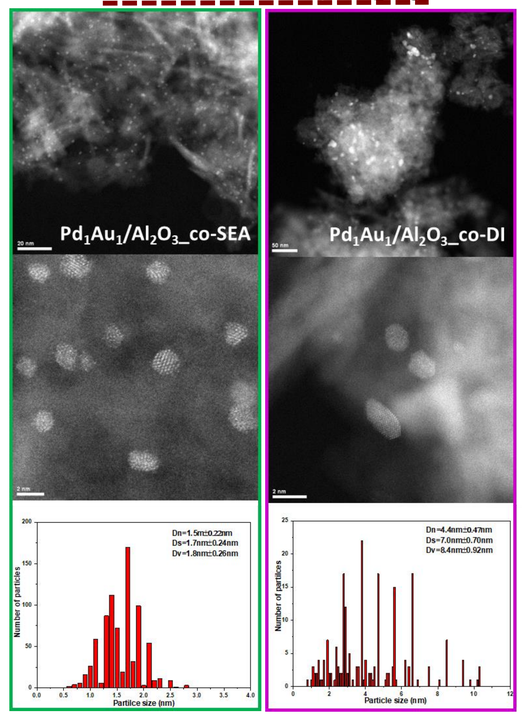


Results: STEM

supported on SiO_2



supported on γ-Al_2O_3

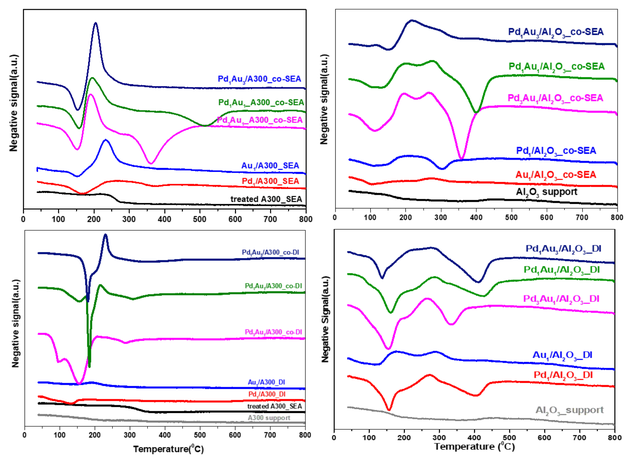


co-SEA:
ultra-small.
regularity.
speckling effects.

co-DI:
larger particles.
inhomogeneity.

Results: TPR

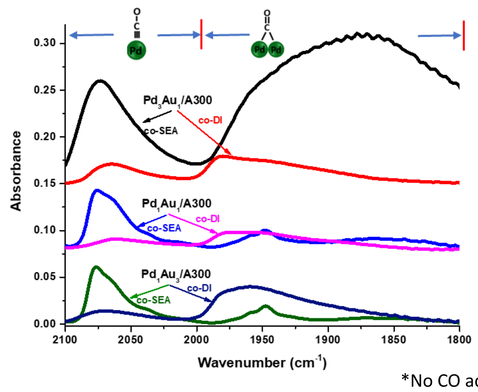
Temperature programmed reduction at 5^0C/min



- Broader peak by co-SEA suggesting stronger M-S interaction

Results: CO-FTIR

***in-situ* CO-FTIR**: in-situ reduced a 180^0C



*No CO adsorbed on Au

- More Pd atoms on the surface due to the smaller particles by co-SEA.
- Less Pd loading, better Pd distribution in Au cluster.

Conclusions

- Simultaneous strong electrostatic adsorption (**co-SEA**) is an effective and facile technique to synthesize **ultra-small** PdAu nanoparticles with **homogenous alloys.**
- **Stronger** metal-support **interaction** can be achieved by **co-SEA** than co-DI.
- **Increased** amount of Pd atoms on particle surface can be obtained by **co-SEA**.

References

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