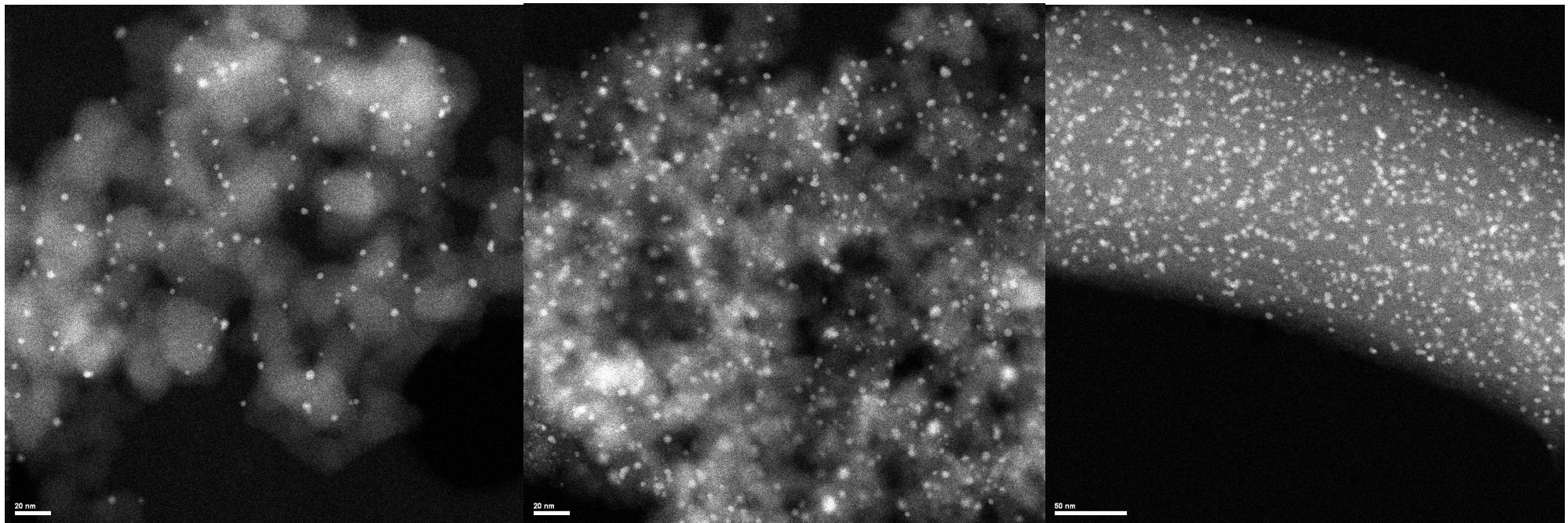


Preparation of Small, Monodisperse Supported Au Nanoparticles Via Strong Electrostatic Adsorption of Au Ethylenediamine

Sean Noble, Sean Barnes, Ritubarna Banerjee, John Regalbuto



What is the hypothesis?

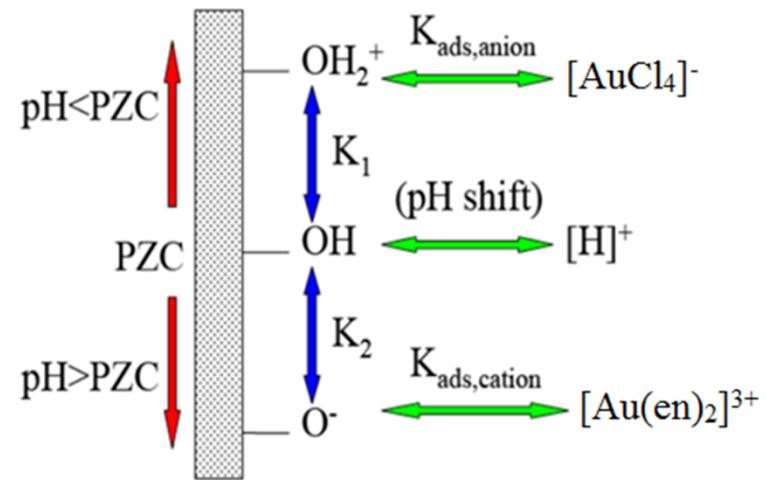
- Strong electrostatic adsorption (SEA) is a simple, scalable synthesis of ultra-small Au nanoparticles on a variety of supports using of gold bis-ethylenediammine, $\text{Au}(\text{en})_2\text{Cl}_3$.

Why Gold?

- CO oxidation[1]
- Low temperature Water Gas Shift using Au/FeO and Au/TiO₂[2,3]
- Selective oxidation of hydrocarbons
- NO reduction
- Acetylene Hydrochlorination to Vinyl Chloride Monomer with Au/C [4]
- Oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid with Au/C [5]

How do we do it?

- **Strong Electrostatic Adsorption (SEA)**
- pH at which surface hydroxyl groups are neutrally charged: Point of Zero Charge (PZC)
- Protonate or deprotonate hydroxyl groups on support surface by adjusting pH of solution
- Use cationic $\text{Au}(\text{en})_2\text{Cl}_3$ precursor for low PZC supports



Mechanism of electrostatic adsorption for the case of Au over a charged support surface

What supports do we use?

- Low and mid PZC supports
- Low and high surface area
- Maximum Au Wt% from 1 cycles of SEA
- Comparison with Dry Impregnation

Support	Surface Area (m ² /g)	PZC	Au Wt (%)
Silica			
A90	93	4.2	1.4
A300	330	4.2	5.1
Graphite			
Ashbury	115	5.2	2.1
Mesoporous Silica			
SBA-15	574	4.2	8.2
Titania			
Sach	345	4	5.1
P25	50	4	1
Alumina			
$\gamma\text{-Al}_2\text{O}_3$	277	8.4	0.74
Niobia			
Nb_2O_5 (Amorph)	159	2.5	4.3
Zirconia			
ZrO_2	22	7	0.3
Ceria			
CeO_2	97	8.4	0.7

Why do we use $\text{Au}(\text{en})_2\text{Cl}_3$?

- Cationic $\text{Au}(\text{en})_2^{3+}$ ($2+$)
- Stability over 1 month period (no precipitation)
- 3+ state to 2+ state with increasing pH verified with XANES and EXAFS

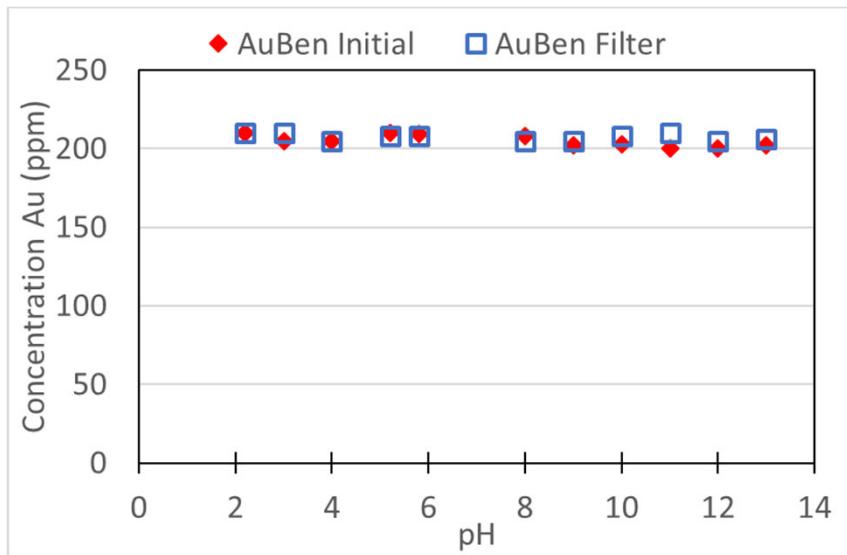


Figure 1) Stability study of $\text{Au}(\text{en})_2\text{Cl}_3$ analyzed by ICP-OES

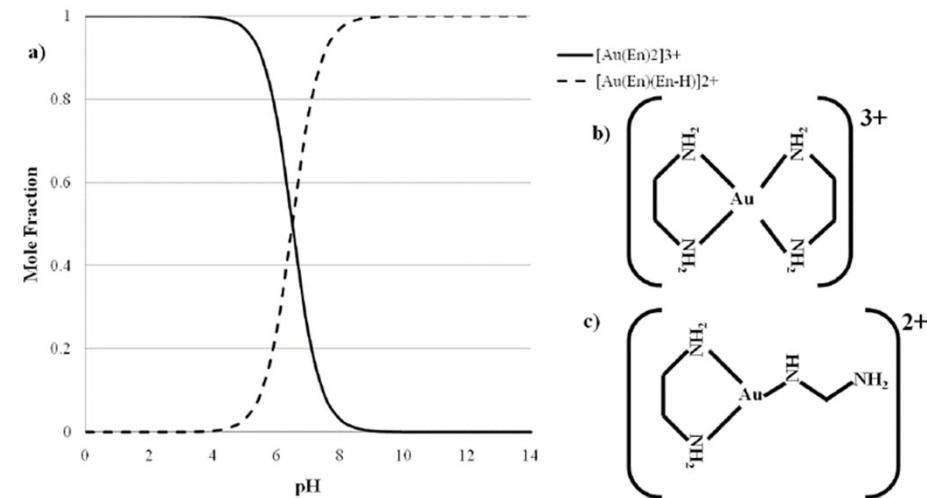


Figure 2: a) Speciation curves of ethylenediamine in aqueous solution

What are the adsorption Kinetics of $\text{Au}(\text{en})_2\text{Cl}_3$ onto supports?

- A300 (silica) and Asbury (Graphitic Carbon)

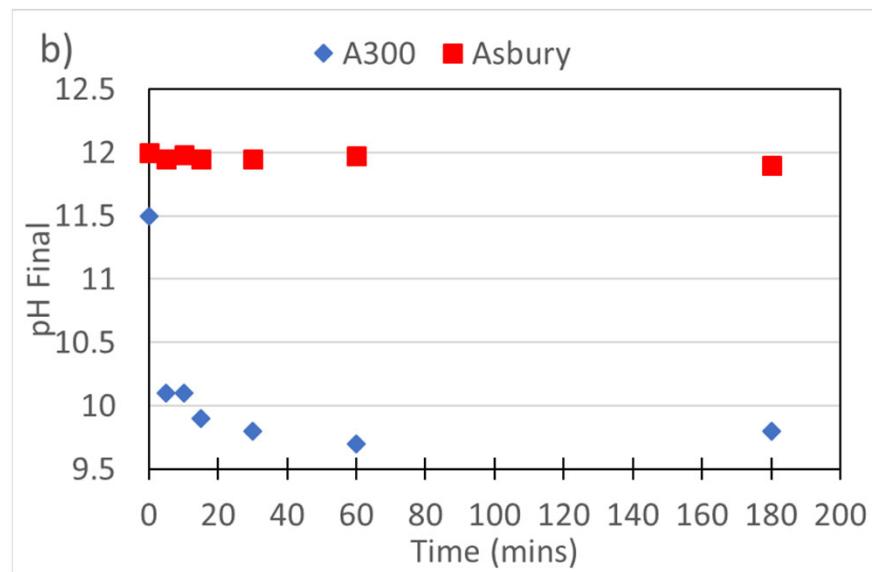
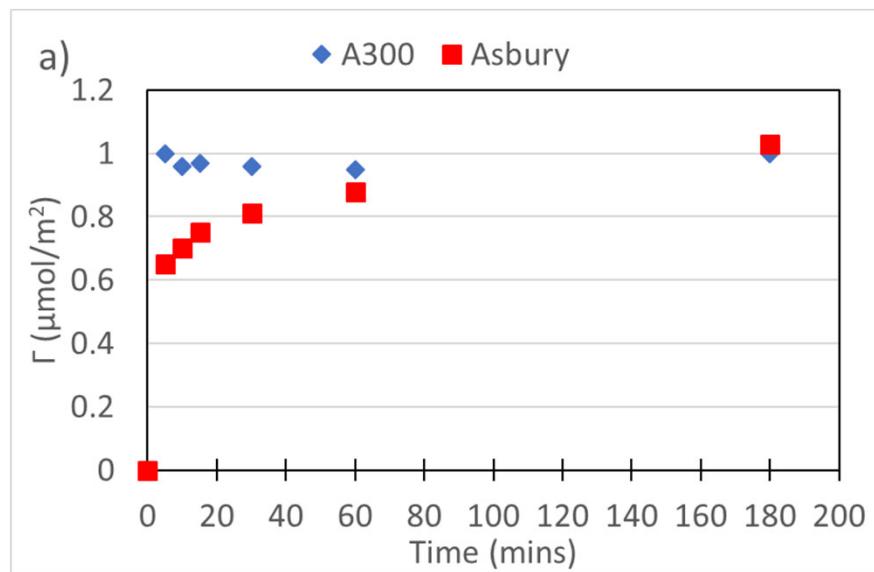


Figure 3: Adsorption kinetics measurement of $\text{Au}(\text{en})_2\text{Cl}_3$ on A300 and Asbury at pH initial of 12: a) uptake of $\text{Au}(\text{en})_2\text{Cl}_3$ as time is varied, b)pH change as time is varied

How much $\text{Au}(\text{en})_2\text{Cl}_3$ adsorb onto each surface at various pH?

- Max adsorption in basic pH range
- Retardation at pH of 13 due to high ionic strength
- High PZC supports have low density of surface hydroxyl groups deprotonated

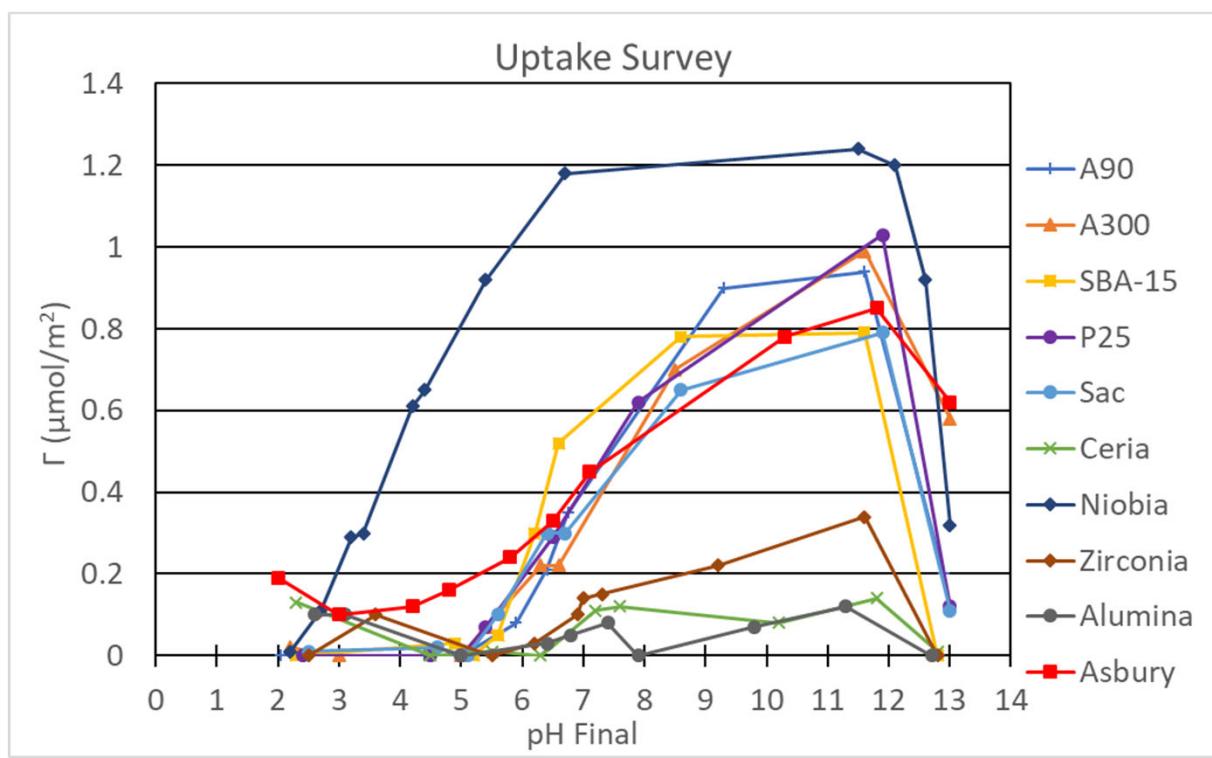


Figure 4: Adsorption survey experiments with various support materials

What are the results?

Support	Surface Area (m ² /g)	PZC	DI Au (%)	DI XRD d _{avg}	SEA Au (%)	SEA STEM d _{avg}	SEA XRD d _{avg}
A90	93	4.2	1.4	18.5	1.4	2.6	2.9
A300	330	4.2	5.1	19.7	5.1	2.8	2.4
SBA-15	574	4.2	8.2	24.4	4.3	2.9	2.4
Ashbury	115	5.2	2.1	19.1	1.4	2.2	2.2
Sachtleben	345	4.0	5.1	27.4	4.0	2.7	1.9
P25	50	4.0	1.0	31.6	1.0	4.7	2.6
Nb ₂ O ₅ (Amorph)	159	2.5	4.3	8.9	4.3	4.2	4.3
γ-Al ₂ O ₃	277	8.4	0.74	5.3	0.74	1.7	2.7
ZrO ₂	22	7.0	0.3	17.6	0.3	1.6	<1.5
CeO ₂	97	8.4	0.7	24.2	0.7	1.3	<1.5

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How do we determine the particle size from XRD?

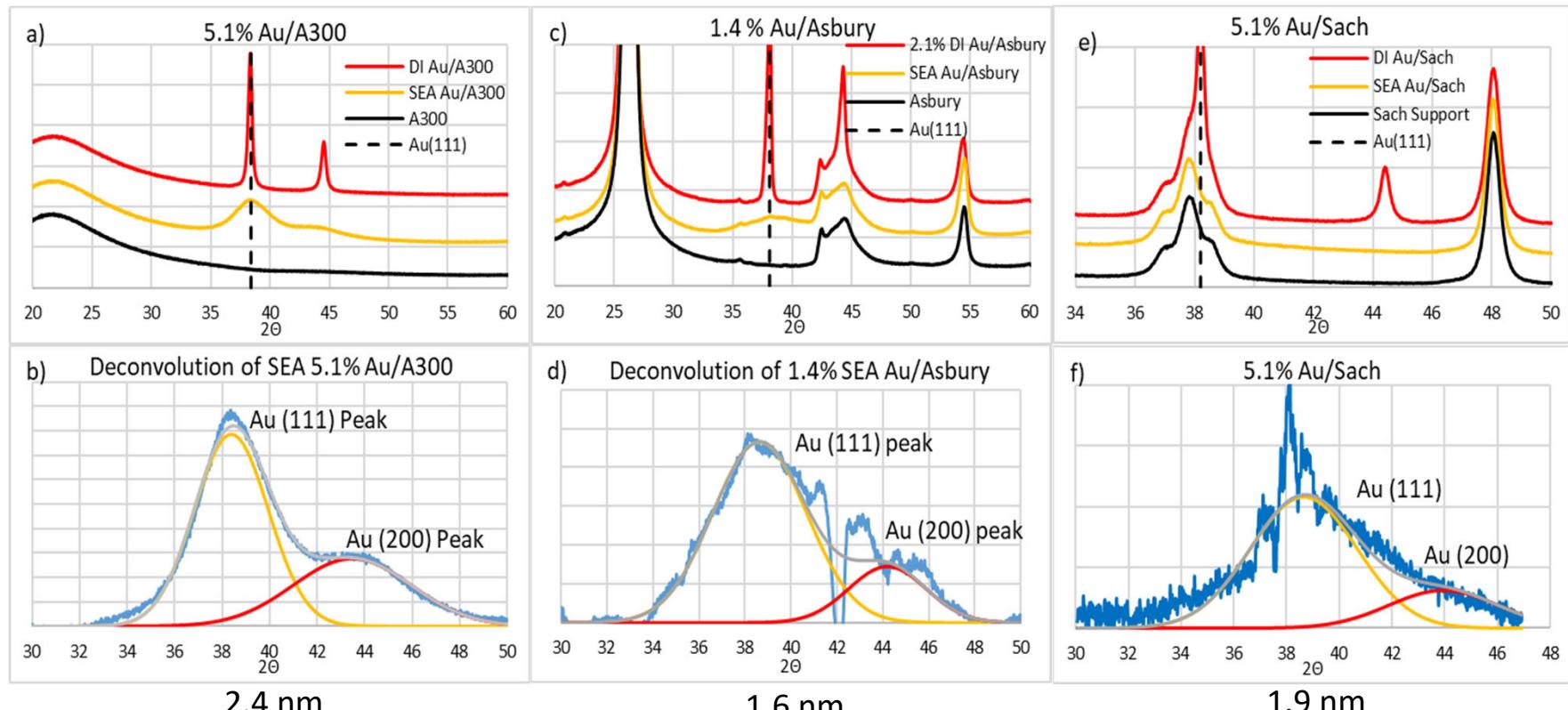


Figure 6: XRD of SEA and DI Au on various supports and deconvolution supported Au from SEA XRD spectra

How do we determine the particle size from XRD?

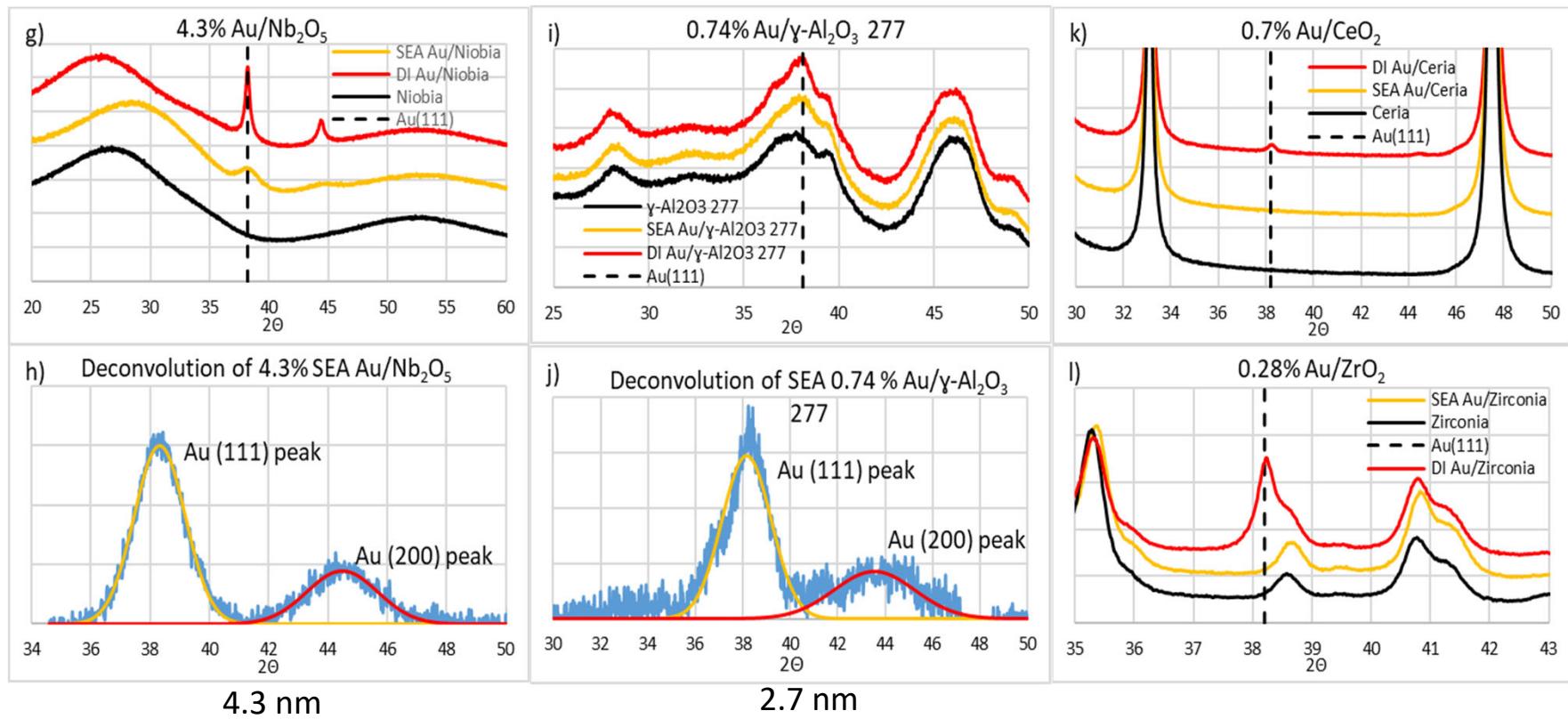


Figure 7: XRD of SEA and DI Au on various supports and deconvolution supported Au from SEA XRD spectra

What do the STEM images look like?

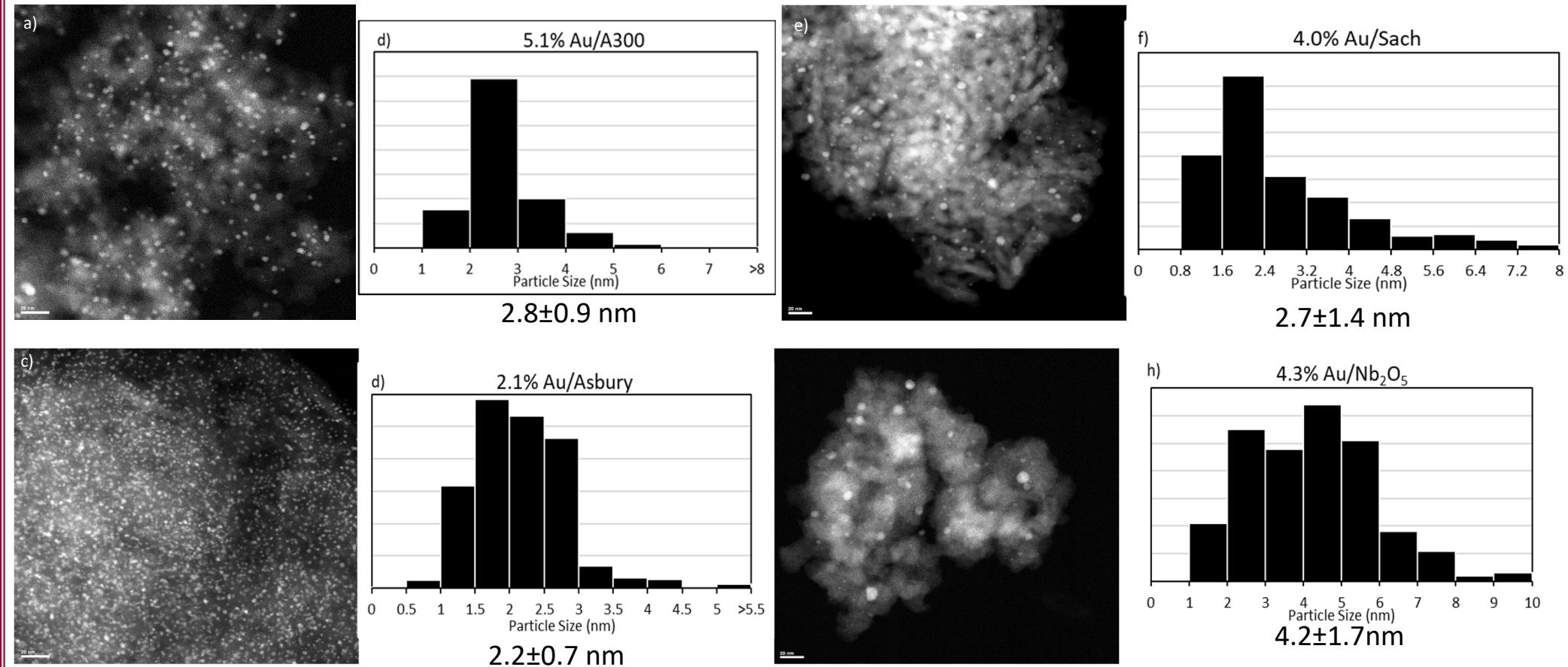


Figure 8: STEM images of SEA Au on a,b) A300 c,d) Asbury e,f) Sachtleben, g,h) Nb_2O_5 and corresponding particle size

What do the STEM images look like?

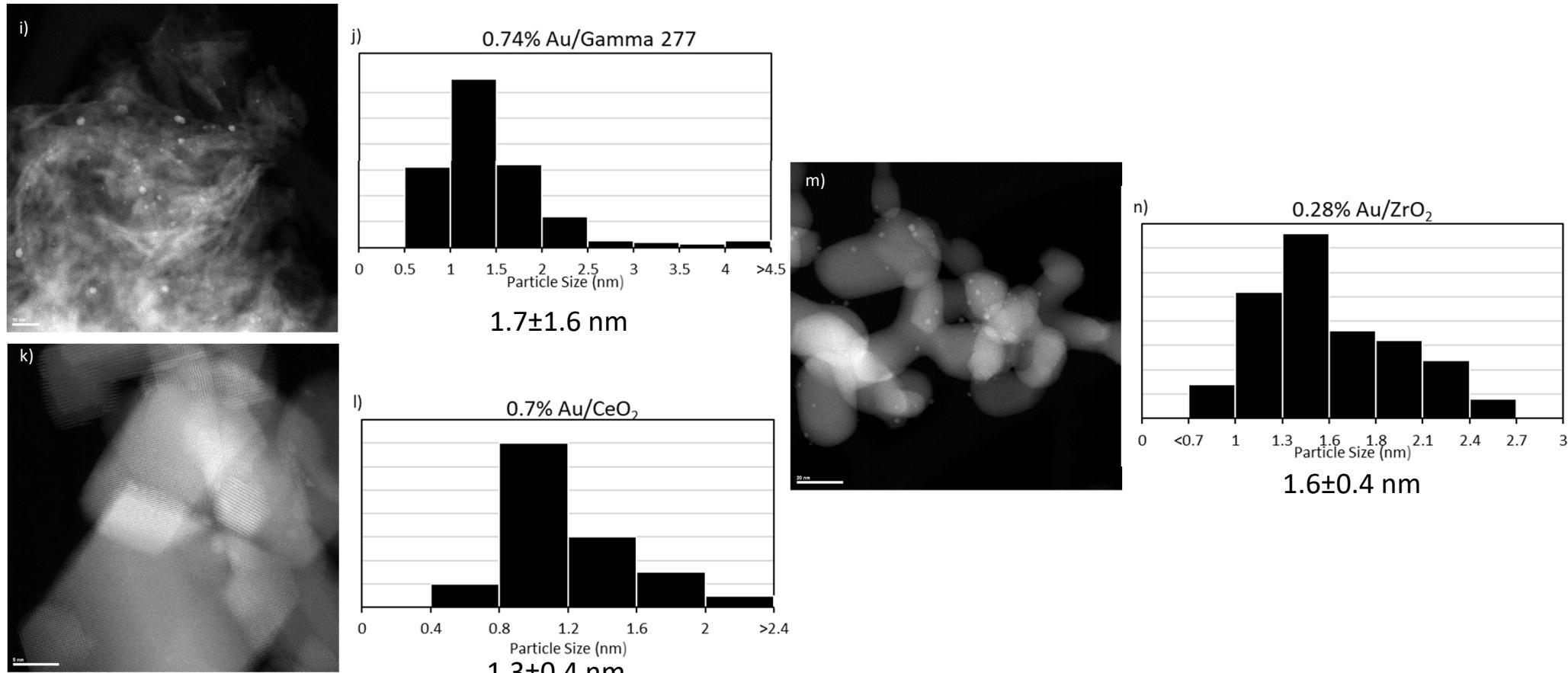


Figure 9: STEM images of SEA Au on *i,j)* $\gamma\text{Al}_2\text{O}_3$ *k,l)* CeO_2 and *m,n)* ZrO_2 and corresponding particle size

Conclusion

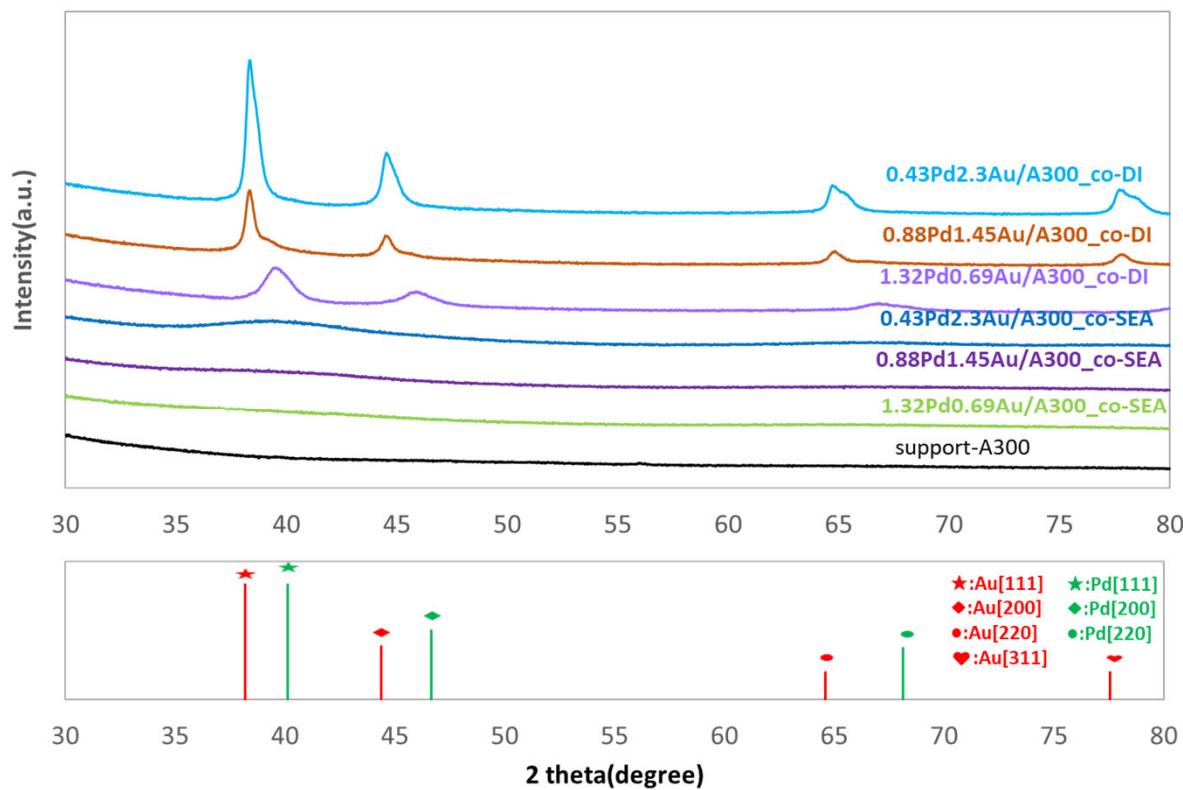
- $\text{Au}(\text{en})_2\text{Cl}_3$ is a stable complex in solution for long periods of time
- SEA can be used to prepare supported metal catalysts using the cationic gold complex $\text{Au}(\text{en})_2\text{Cl}_3$
- Adsorption mechanism over Silica is electrostatic in nature while carbon shows signs of additional reductive mechanism
- SEA samples had much smaller Au nanoparticles than DI at similar wt loadings
- SEA samples displayed high dispersion and small particle sizes
- co-SEA is possible with $\text{Au}(\text{en})_2\text{Cl}_3$ and $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ on A300 and Al_2O_3

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1. Kobayashi, T.; Haruta, M.; Sano, H.; Nakane, M. A Selective CO Sensor Using Ti-Doped α -Fe₂O₃with Coprecipitated Ultrafine Particles of Gold. *Sensors and Actuators* **1988**, *13* (4), 339–349.
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5. Donoeva, B.; Masoud, N.; De Jongh, P. E. Carbon Support Surface Effects in the Gold-Catalyzed Oxidation of 5-Hydroxymethylfurfural. *ACS Catal.* **2017**, *7* (7), 4581–4591
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7. Hao, X.; Spieker, W. A.; Regalbuto, J. R. A Further Simplification of the Revised Physical Adsorption (RPA) Model. *J. Colloid Interface Sci.* **2003**, *267* (2), 259–264.

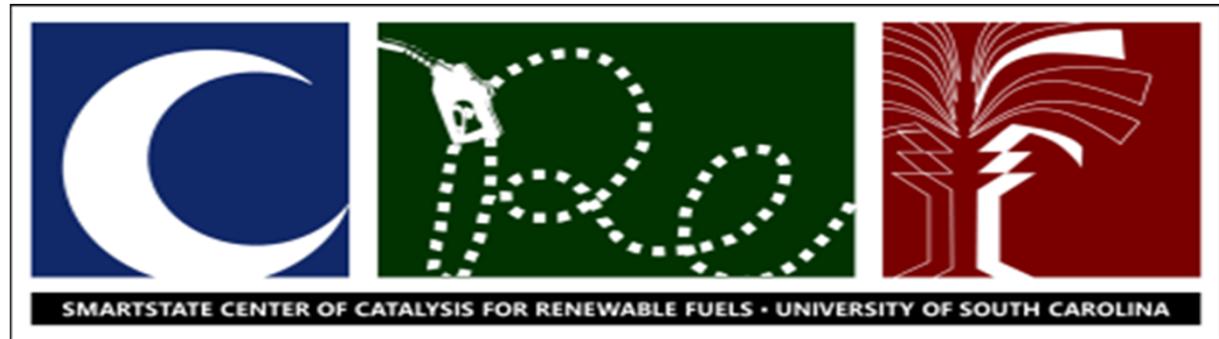
Can we do co-SEA with Au and Pd?

- AuPd/A300 and AuPd/ Al_2O_3
- Pd based systems for hydrogenation of alkenes and alkynes due to their high catalytic activity
- Au, as a promoter, has been reported to improve alkene selectivity.
- Broad peaks indicate small particles
- Au-Pd alloy confirmed by STEM



Acknowledgements

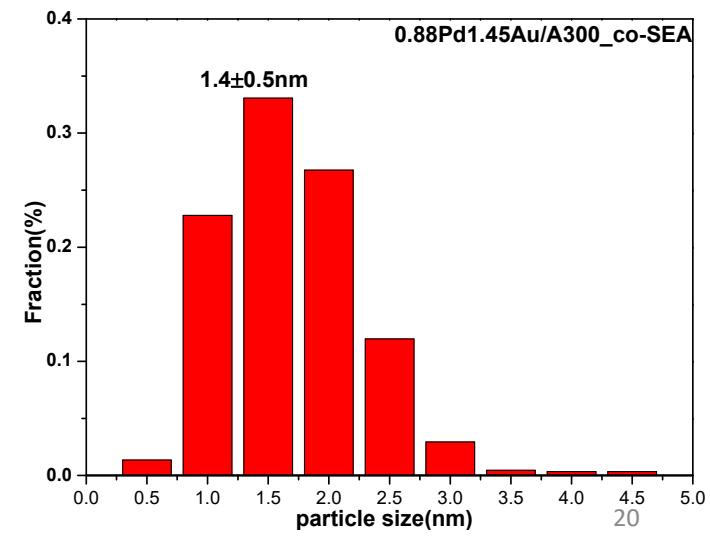
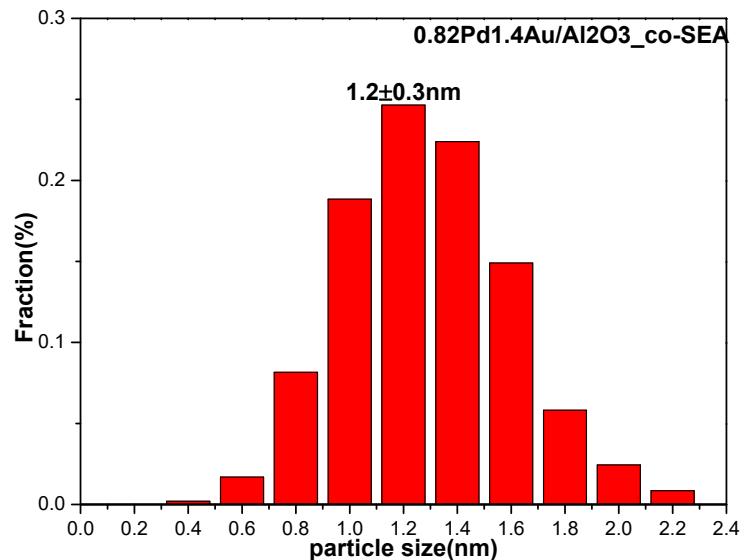
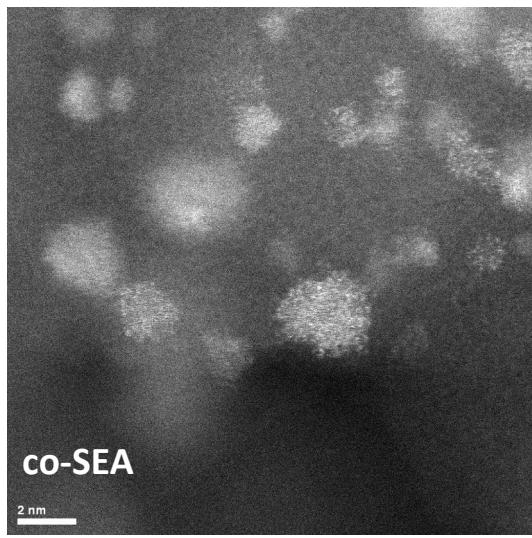
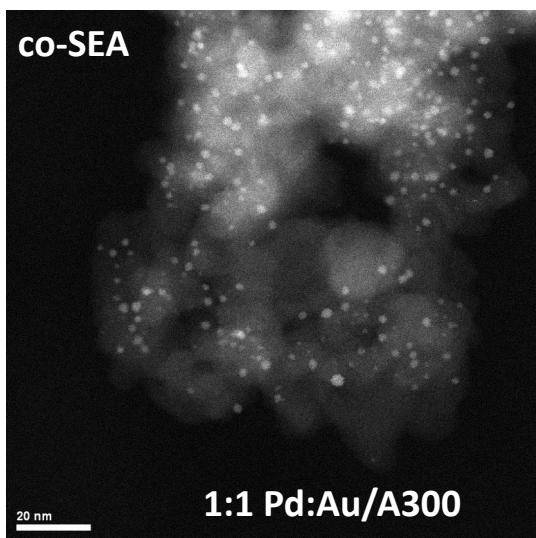
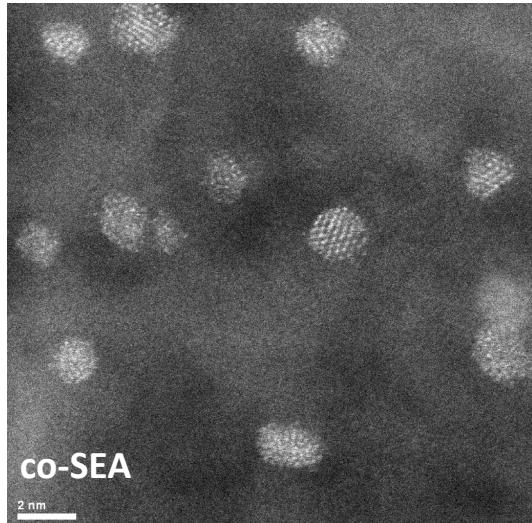
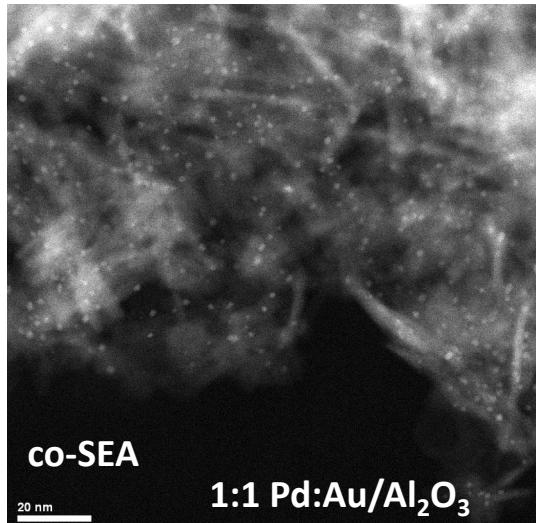
- This research was sponsored by The National Science Foundation, the University of South Carolina, and the Center of Catalysis for Renewable Fuels at USC.
- Regalbuto Group
- Dr. Monnier
- Vannucci Group



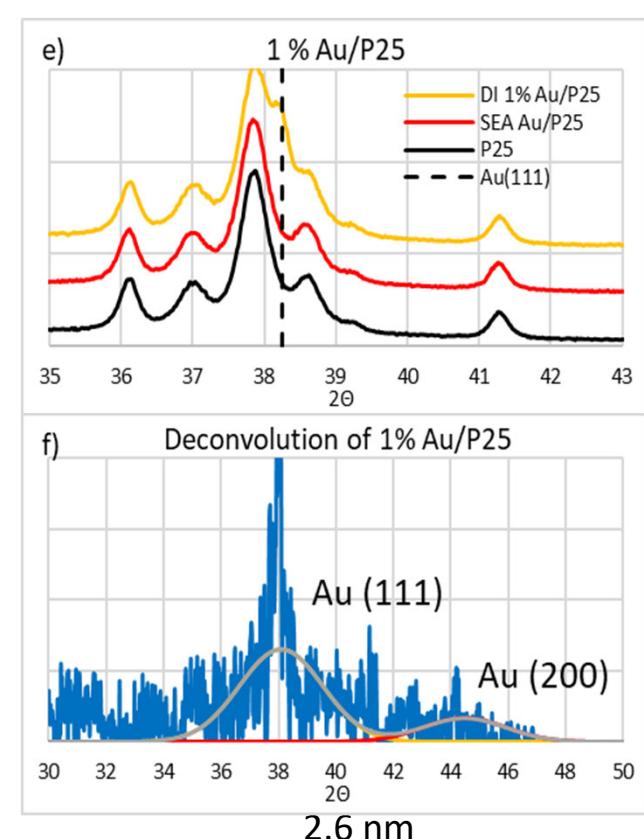
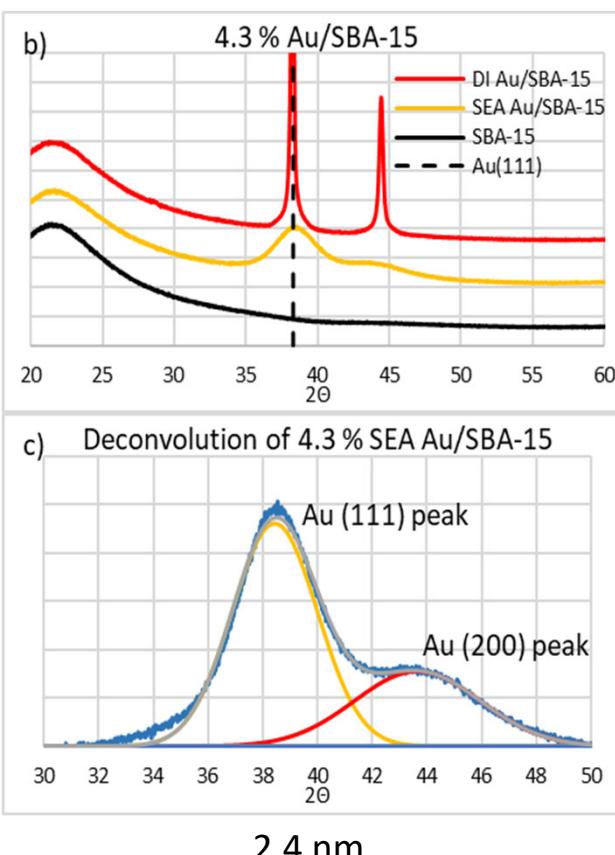
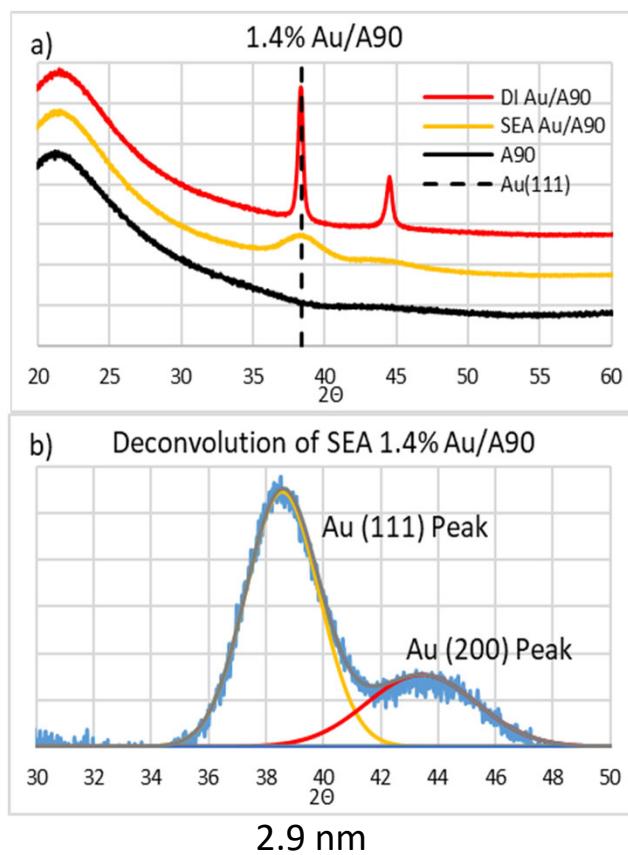
Questions?



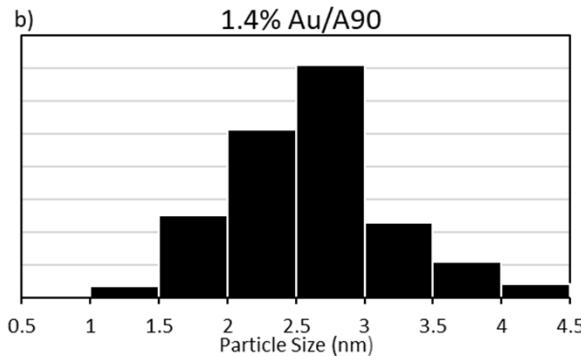
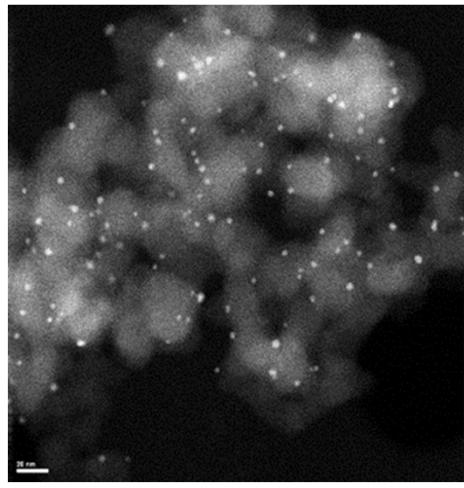
-STEM for PdAu bimetallic catalysts on A300 and alumina by co-SEA or co-DI



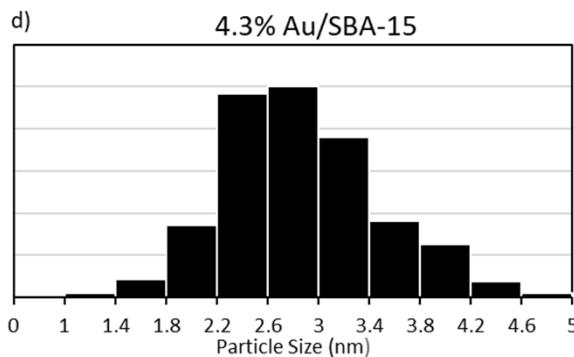
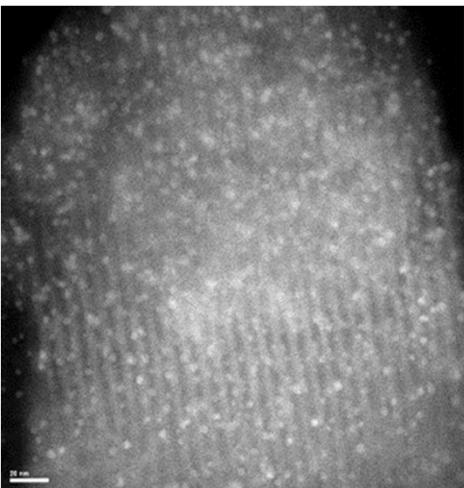
Au Pd XRD Deconvolution



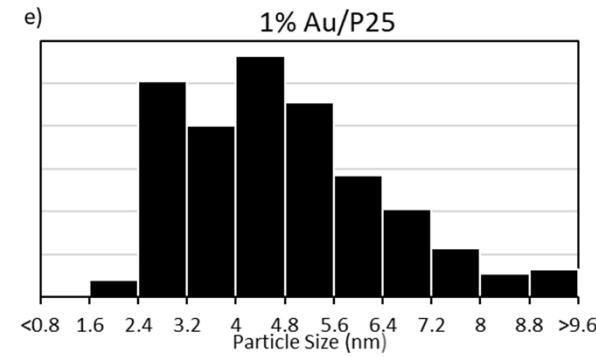
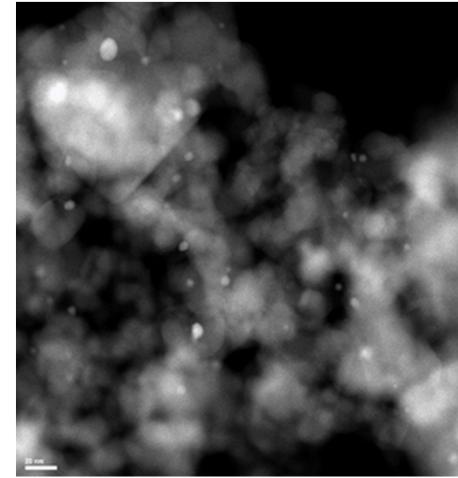
What do the STEM images look like?



2.6 ± 0.7 nm



2.7 ± 0.6 nm



4.7 ± 1.7 nm

Why do we use $\text{Au}(\text{en})_2\text{Cl}_3$?

- Au^{3+} fraction decreases at high pH
- Coordination number decreases with increasing pH

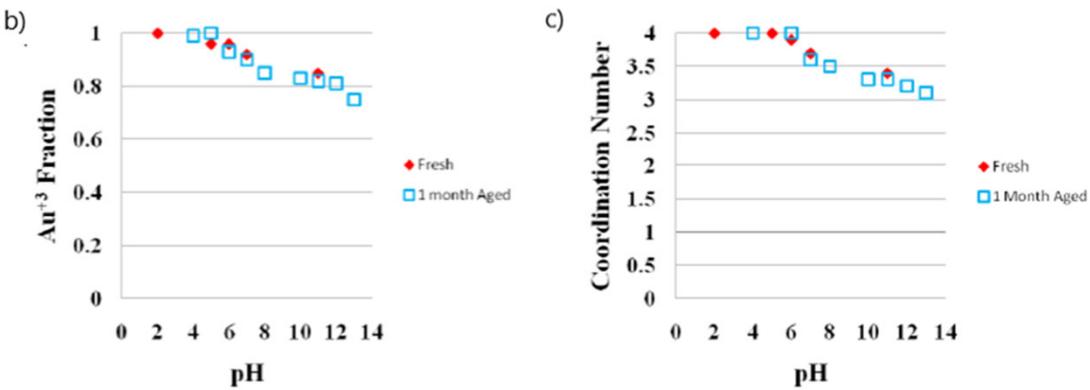


Figure 1b) Au^{3+} fraction trend from XANES spectra of both fresh and aged samples with increasing pH, c) Coordination number trend from EXAFS fittings of both fresh and aged samples with increasing pH

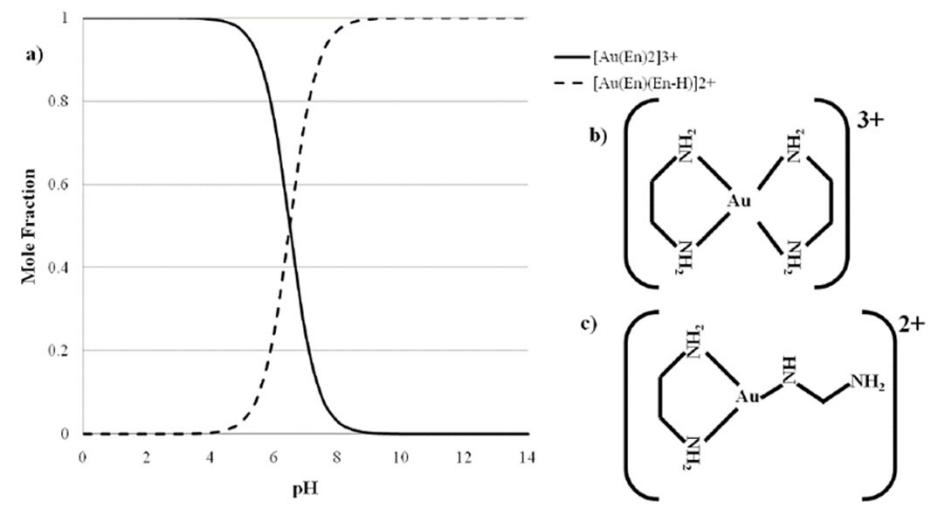


Figure 2: a) Speciation curves of ethylenediamine in aqueous solution

Can we do co-SEA with Au and Pd?

CO-SEA or SEA catalysts preparation conditions:

Metal precursor: $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$, $\text{Au}(\text{en})_2\text{Cl}_3$; SL=1000m²/l; SA=280m²/g, pH=12 by NaOH; shake at 120 rpm for 1 hr.

Dry at room temperature for one day then in vacuum at room temperature for two days.

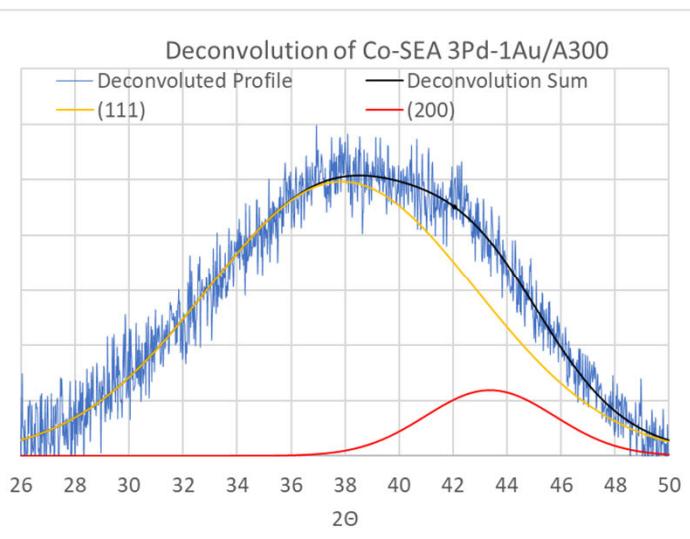
Bimetallic Pd-Au/A300 by CO-SEA method

	Molar ratio (plan)	Surface density (plan)	Molar ratio (actual)	Surface density (actual)	mass loading(%) (actual)	
samples	Pd:Au	(umol/m ²)	Pd:Au	(umol/m ²)	Pd	Au
1.0Pd-3.0Au	1:3	0.7	1:2.87	0.577	0.4325	2.295
1.0Pd-1.0Au	1:1	0.7	1:0.87	0.573	0.8849	1.451
3.0Pd-1.0Au	3:1	0.7	3.55:1	0.582	1.3245	0.691

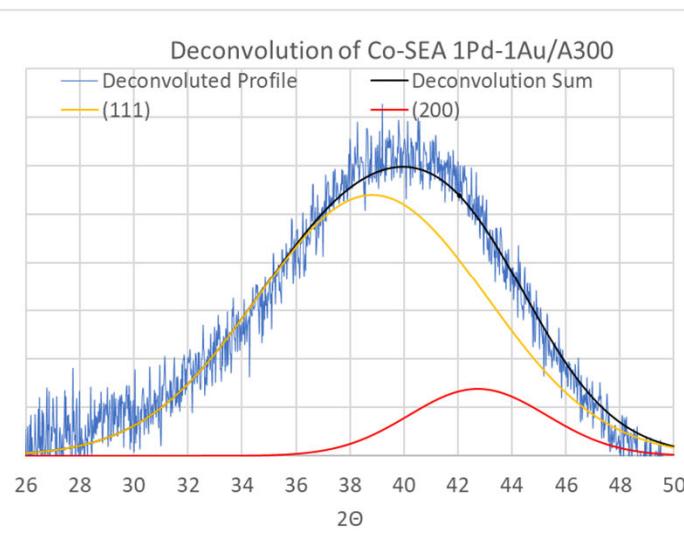
Single metal Pd or Au/A300 by SEA method

sample	mass loading (plan)	Mass loading(%) (actual)
1%Pd/Aerosil 300	1%	Waiting for ICP
1%Au/Aerosil 300	1%	Waiting for ICP

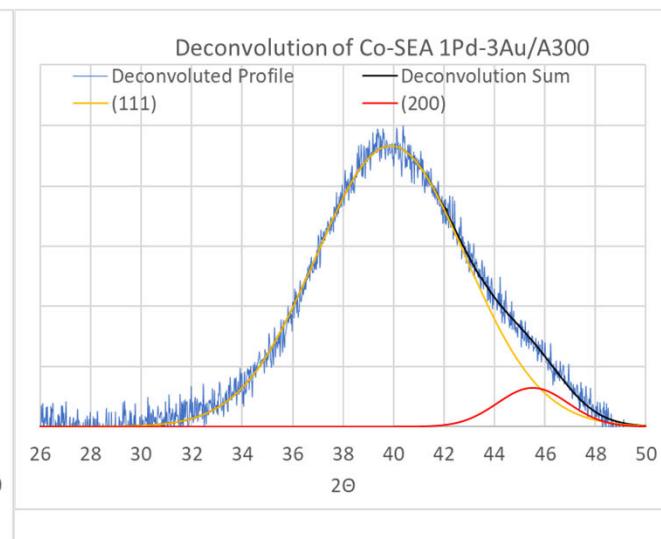
Au Pd XRD Deconvolution



0.76 nm



0.88 nm



1.26 nm

Can we do CO-SEA?

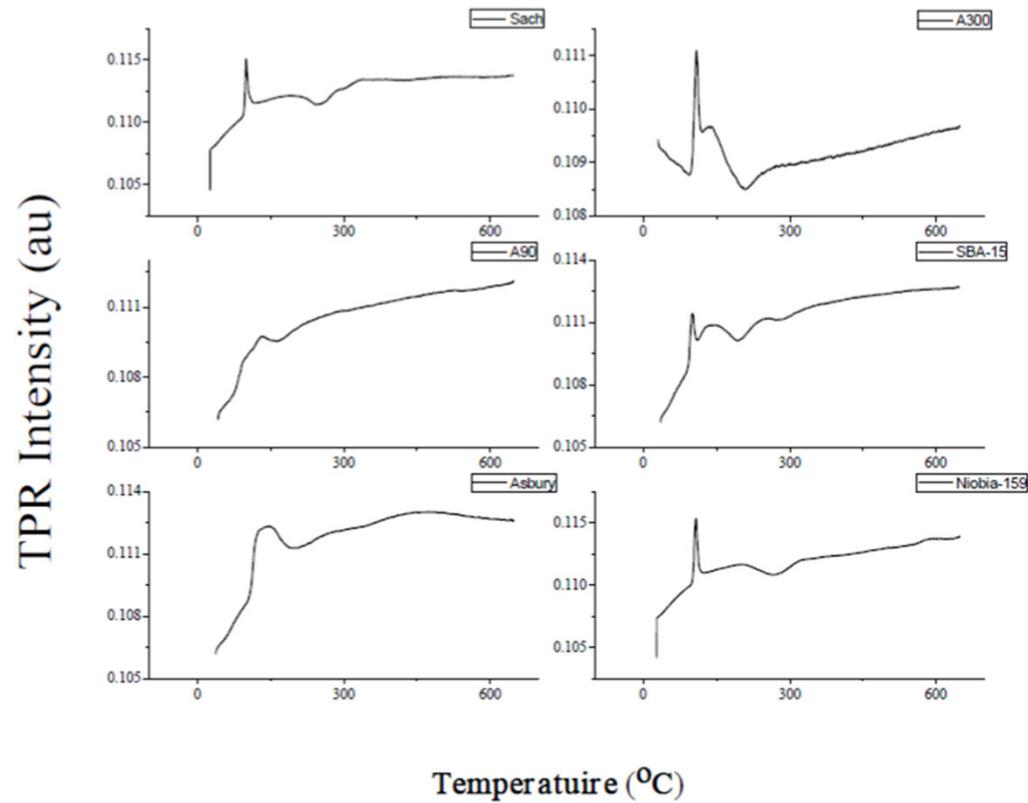
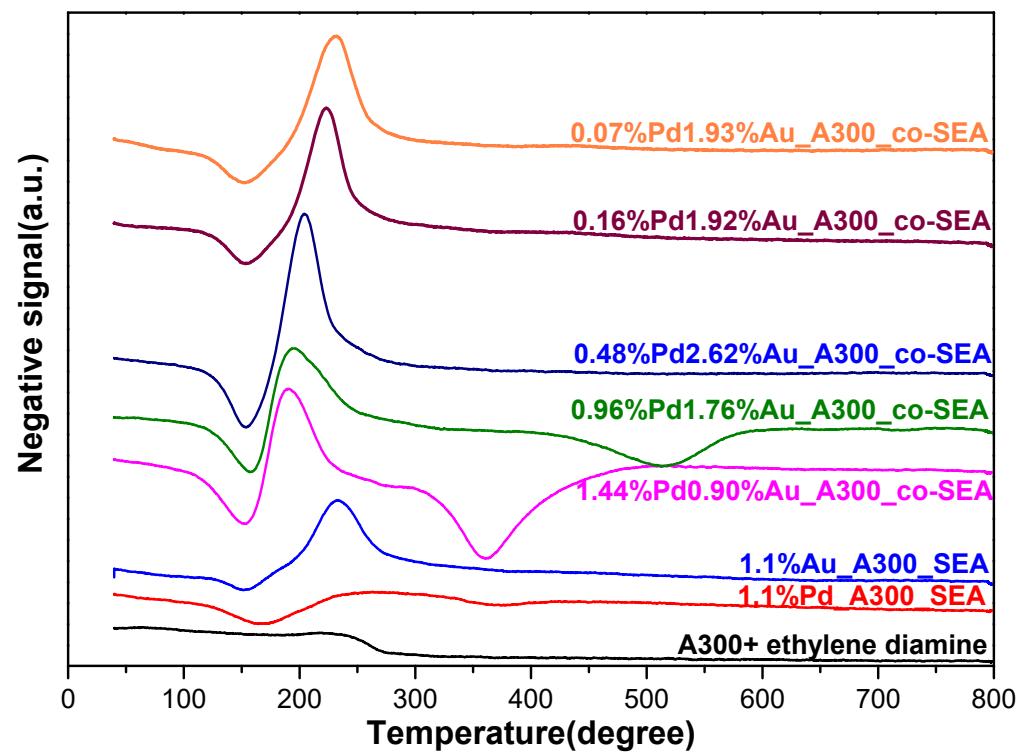


Figure 10: Comprehensive TPR profiles obtained for freshly prepared Au catalysts

--TPR for PdAu bimetallic catalysts on A300 by co-SEA



What is the maximum surface coverage?

- Linear dependence of uptake at 500 m^2/L at concentrations below 300 ppm
- Increased surface loadings require higher metal concentration to saturate support
- 1 monolayer is 1.2 $\mu\text{mol}/\text{m}^2$
- 0.74 complex/ nm^2
- 13.2 Å complex size
- Similar results to Pt [6,7]

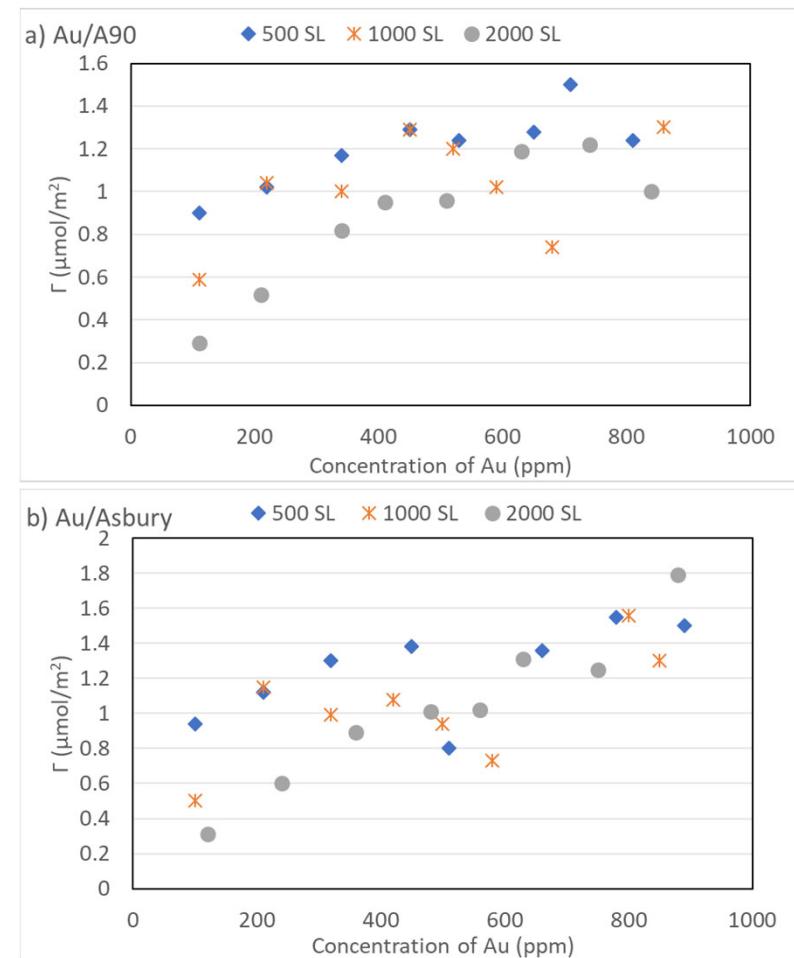


Figure 5: Maximum surface coverage determinations: a) A90 amorphous silica, b) Asbury graphitic carbon