



Discussion Notes:

Simple, Scientific, Effective Methods to Prepare Supported Metal Catalysts

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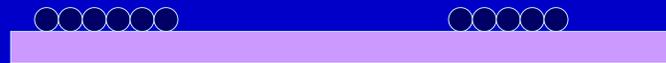
Motivation

- Preparing highly dispersed supported metal catalysts is relatively simple.
 - Biomass conversion
 - Exhaust emission
 - Pharmaceuticals
 - Commodity and Specialty chemicals
- Hypothesis: strong adsorption of metal precursor will lead to high dispersion of reduced (finished) catalyst:

1) adsorption of $[\text{PtCl}_6]^{-2}$ precursors

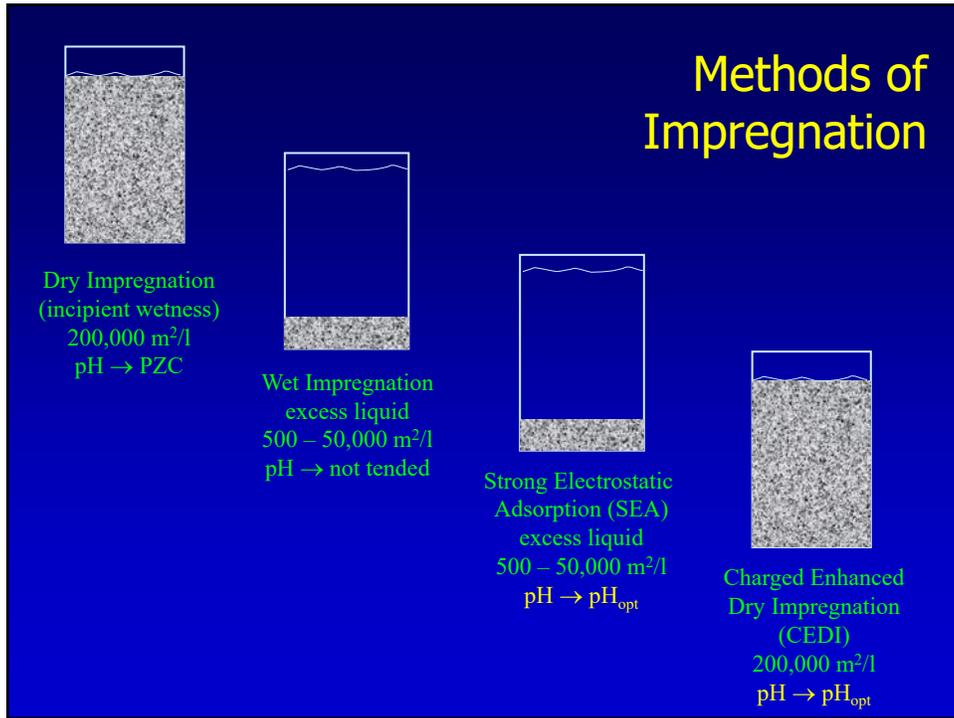


2) reduction of $[\text{PtCl}_6]^{-2}$ to Pt^0

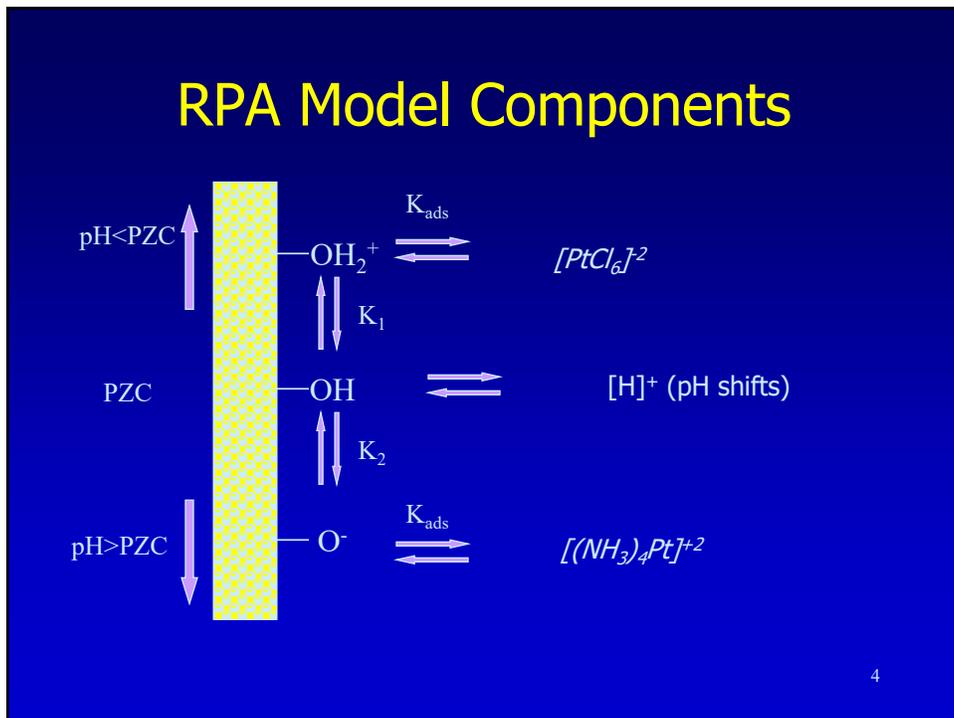


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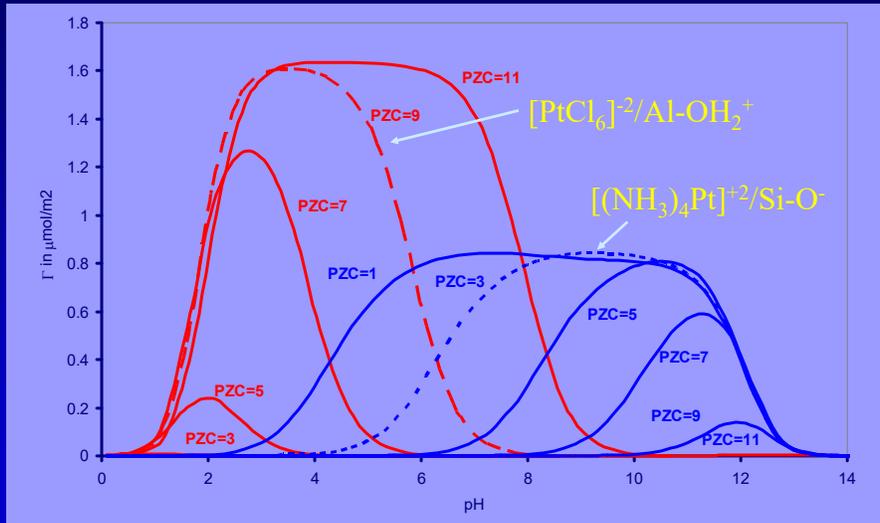


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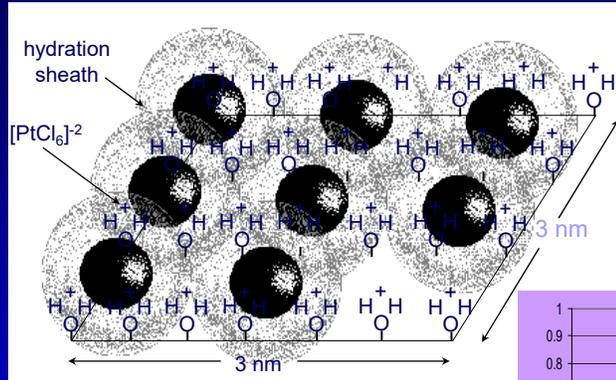
Simulation of CPA and PTA Adsorption Over Supports with Different PZC



X. Hao, W. A. Spieker, J. R. Regalbuto, *J. Colloid Interface Sci.*, 267 (2003) 259.

□5

An electrostatic view of impregnation

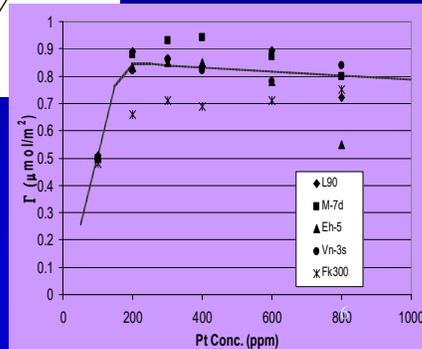


Santhanam et al., *Catal. Today* 1994

Schreier & JR, *J. Catal.* 2004

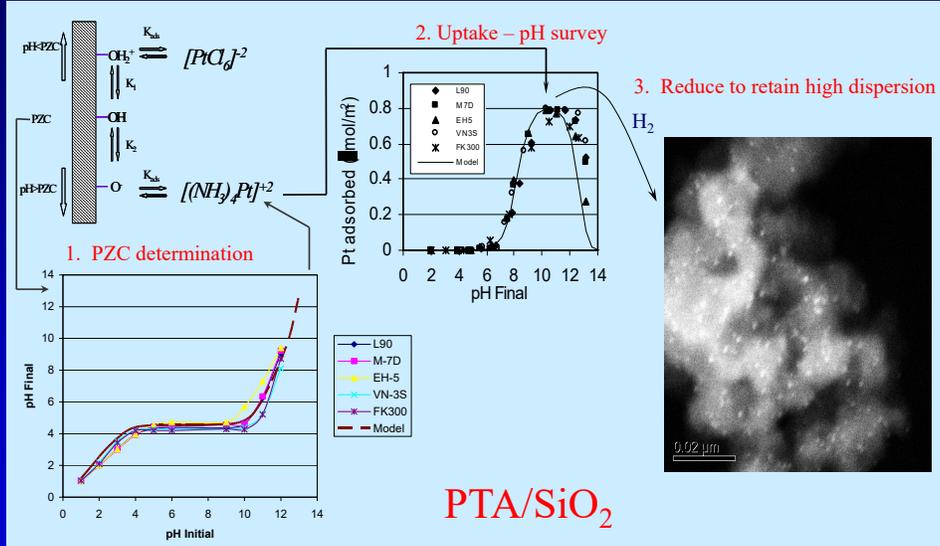
- CPA adsorbs with one hydration sheath

- PTA adsorbs with two



□6

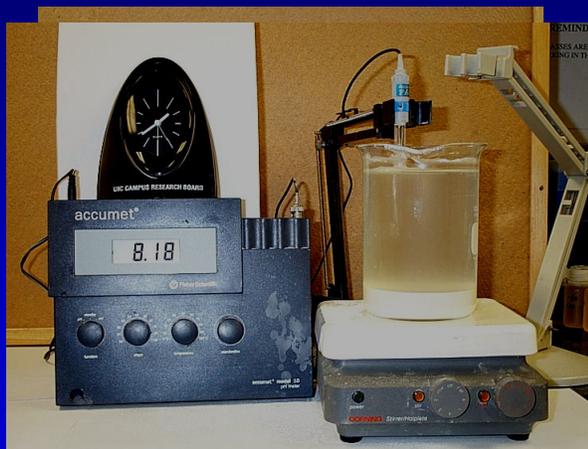
Method of "Strong Electrostatic Adsorption (SEA)"



M. Schreier, J. R. Regalbuto, *J. Catal.*, 225 (2004) 190.

□7

Oxide Buffering Demo



- 1 liter solution, KCl added to increase ionic strength
- initial pH 2.78
- add 50 g alumina (Versal GL, 250 m²/gm)

8

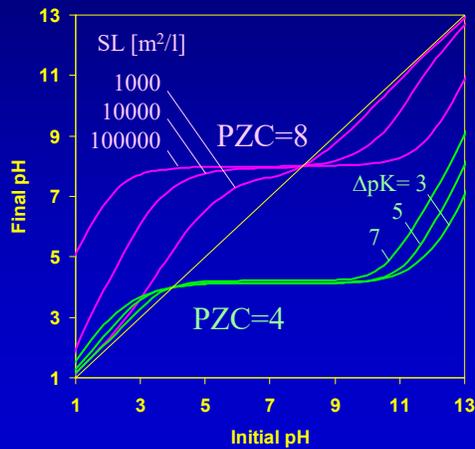
□8

□4

Quantification of Proton Balance

Prediction of pH shifts in oxide-water suspensions

(Park and Regalbuto, *JCIS* 175, 1995, 239)



1000 m²/l

100,000 m²/l



- Proton balance added to surface chemistry and EDL equations
- simulate pH shifts as function of
 - oxide material (PZC, ΔpK)
 - surface loading (m² oxide/l)
- Results:
 - pH shifts are usually large
 - pH plateau gives oxide PZC
- Use to measure PZC, or predict pH shifts

9

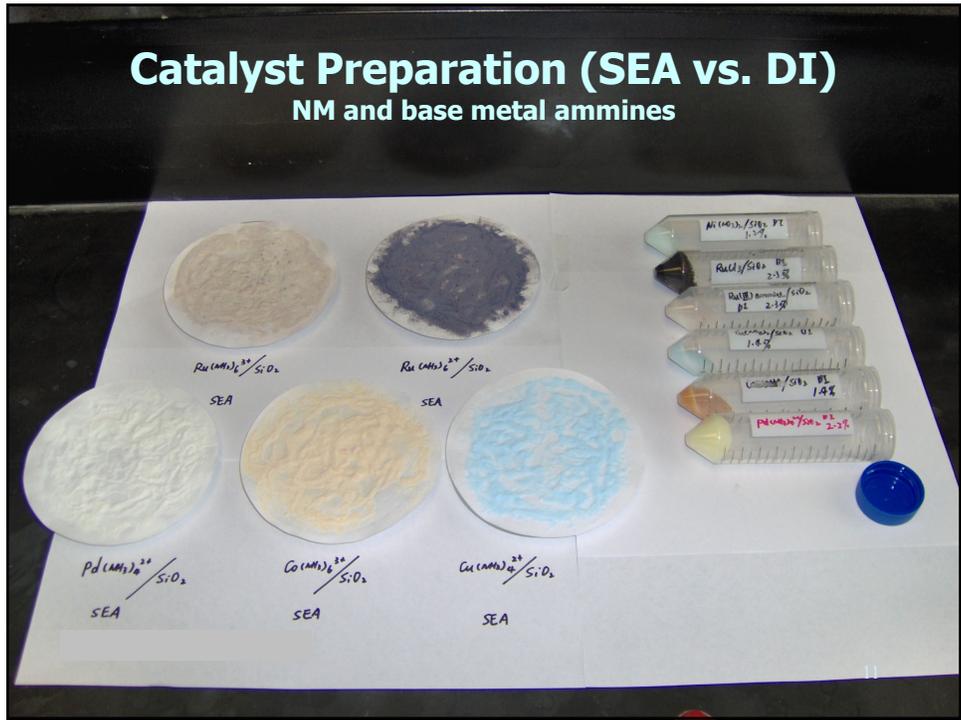
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Outline

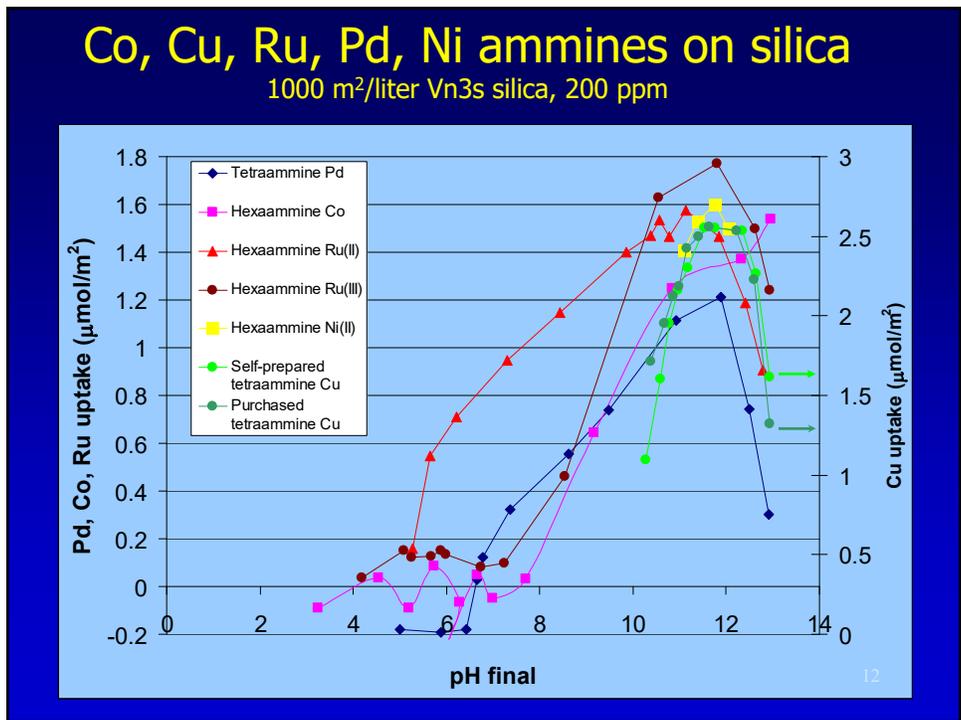
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 - amorphous silica, SBA-15, alumina, carbon, etc.
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10

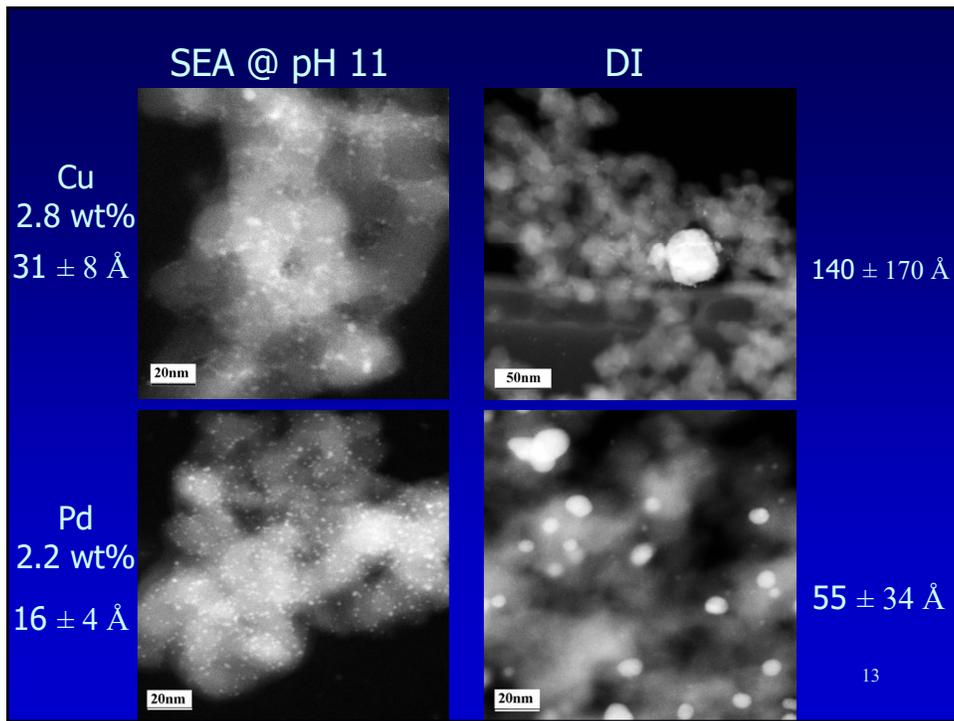
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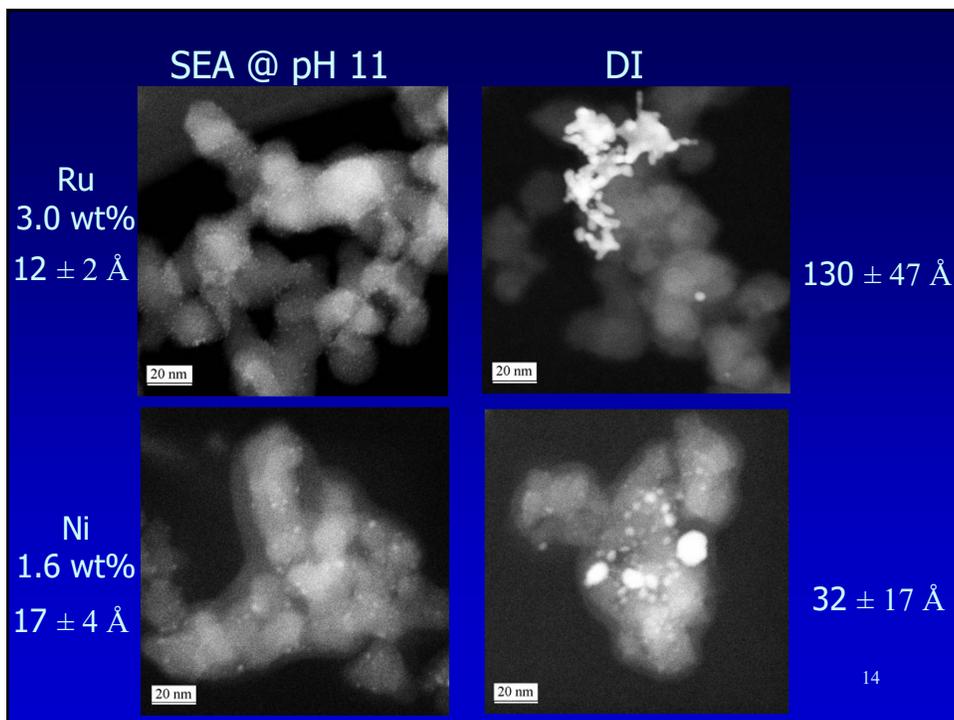
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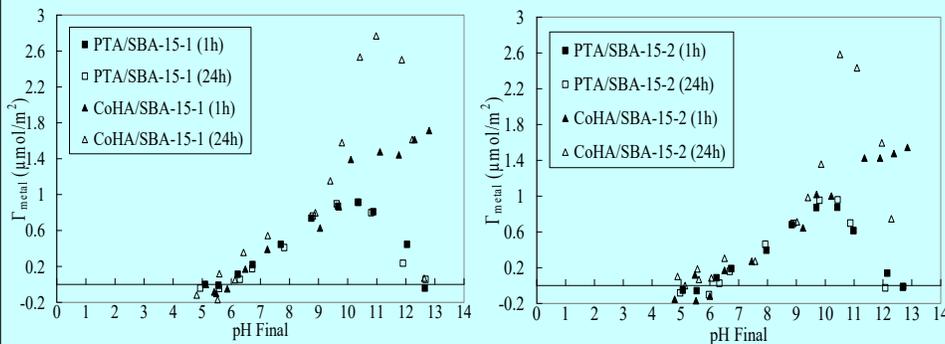
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□15

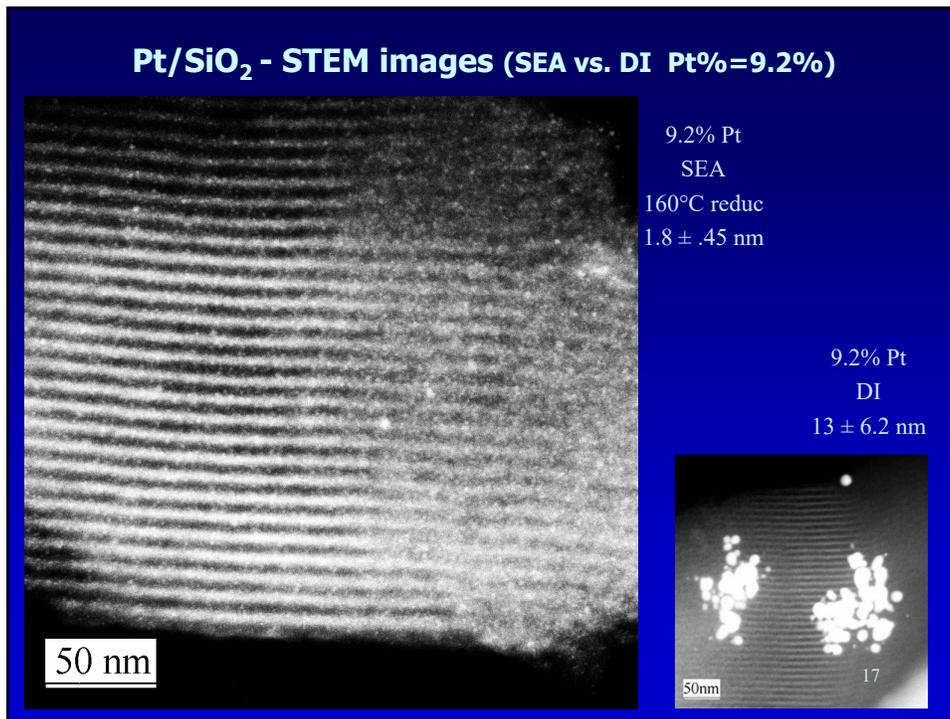
Pd, Cu, Co, Ru, Pd, Ni amines on SBA-15 1000 m²/liter SBA-15, 200 ppm, 1 and 24 hrs contact



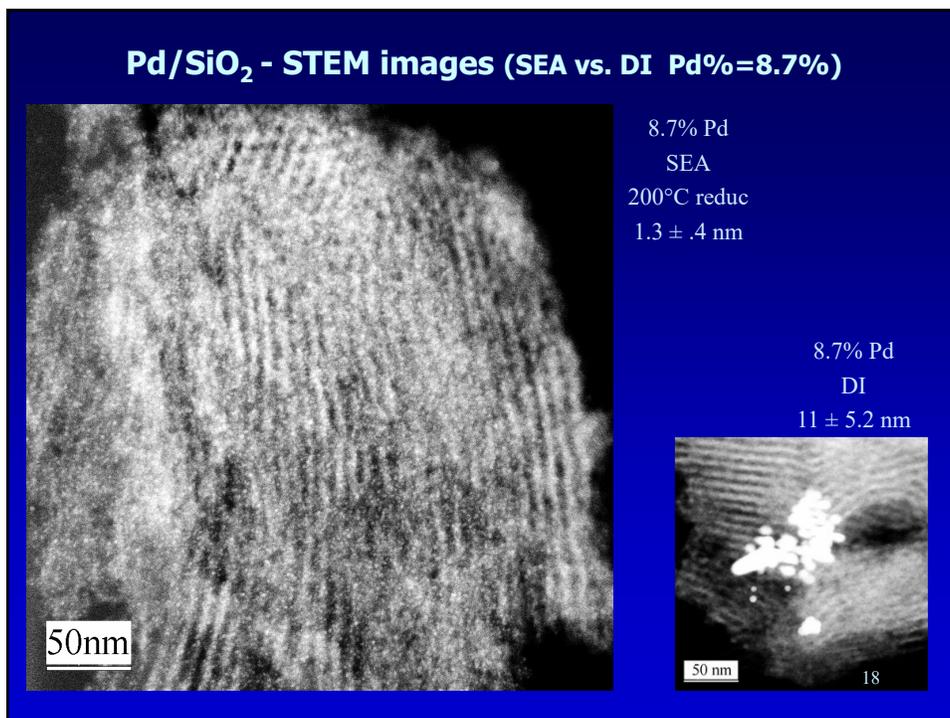
- high surface density implies access to internal pore volume
- Reactivity of Co - phyllosilicates

L. Jiao, J.R. Regalbuto,
J. Catal., 260 (2008) 342

□16

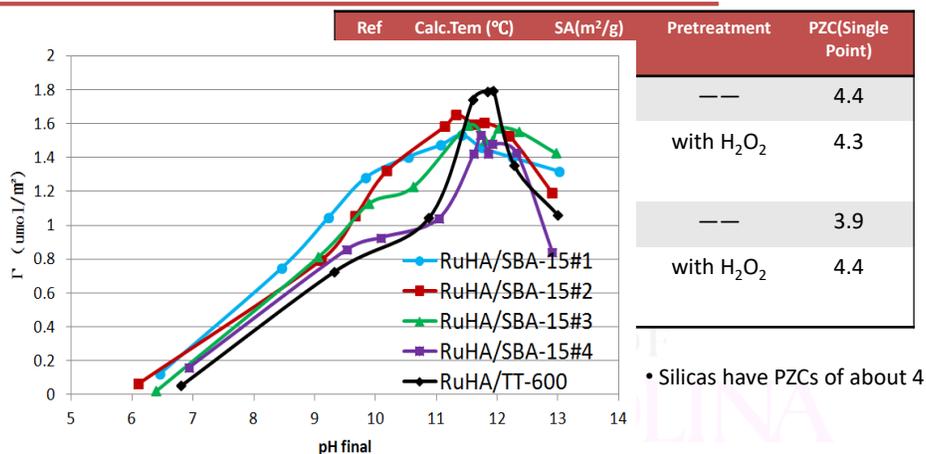


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RuHA on SBA-15

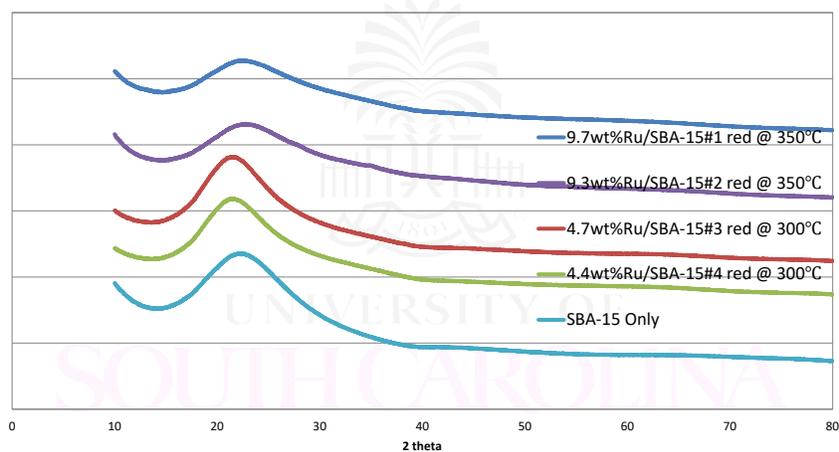


- with regards to metal adsorption, "silica is silica"
- optimal pH at 11.5

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□19

XRD: Ru on SBA-15s, mild reduction



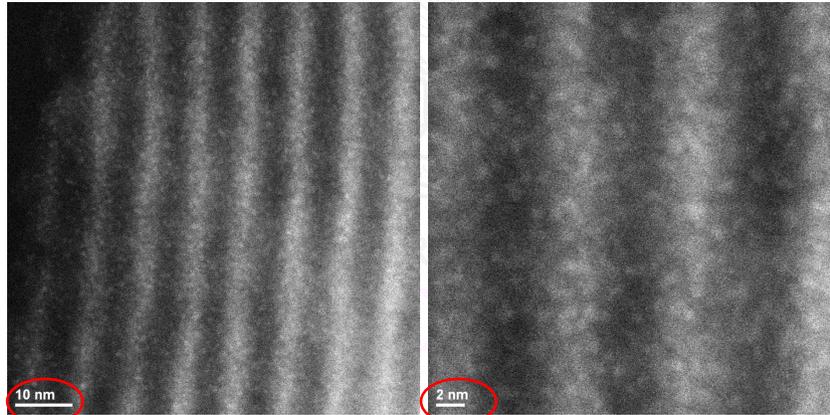
- Well dispersed nanoparticles (< about 1 nm) form

□20

□20

STEM Images

9.7wt% Ru/SBA-15#1 red @ 350°C

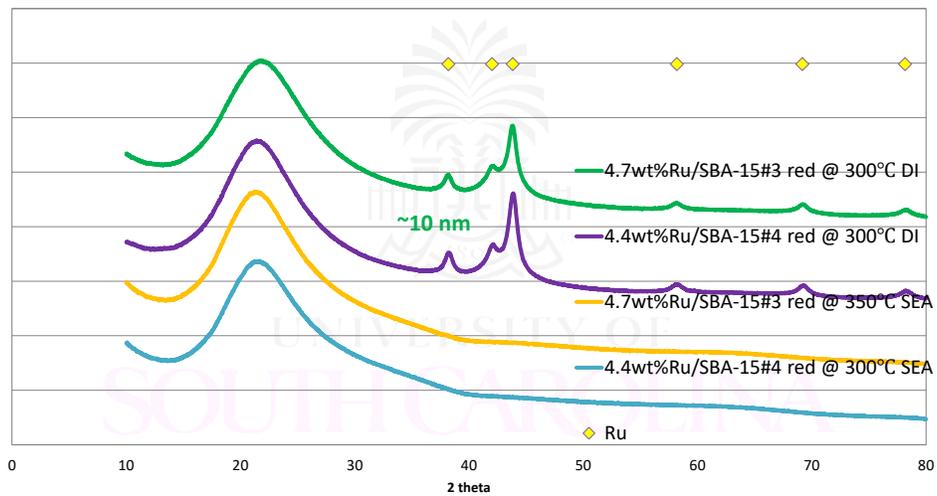


•Average Ru Particle Size 1.1 ± 0.2 nm

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□21

SEA VS DI (Ru)



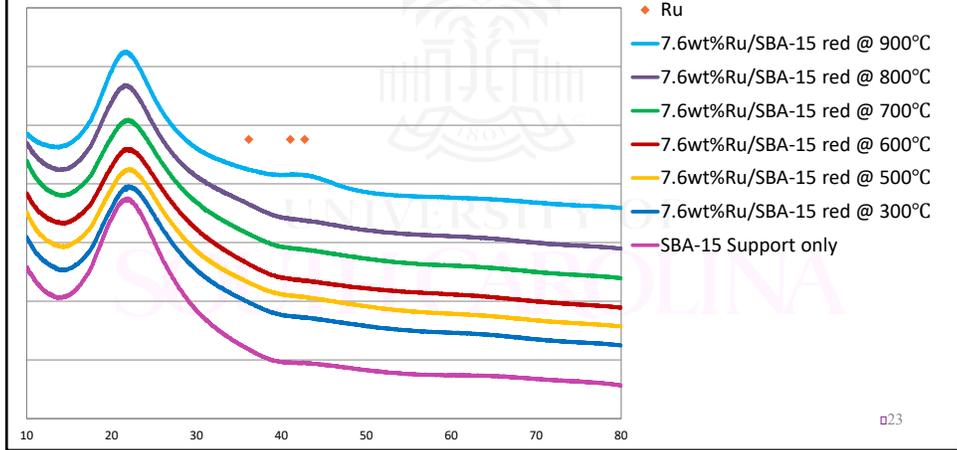
- Much smaller particle size can be obtained by SEA than DI
- DI likely results in exterior deposition

□22

□22

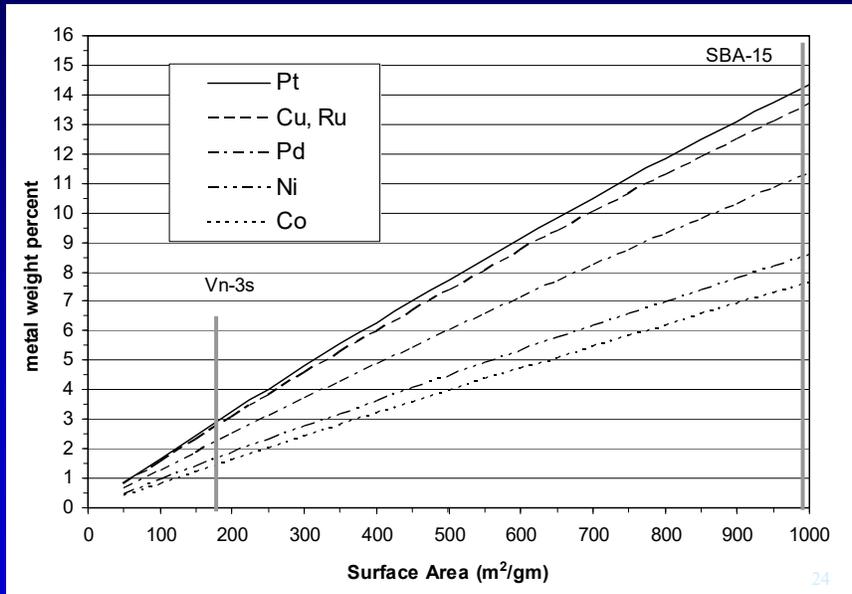
XRD Profiles

- 7.6wt% Ru/SBA-15 reduced @ 500°C, 600°C, 700°C, 800°C, 900°C.
- Particle Size from sample red @ 900°C is around 1.4 nm.



□23

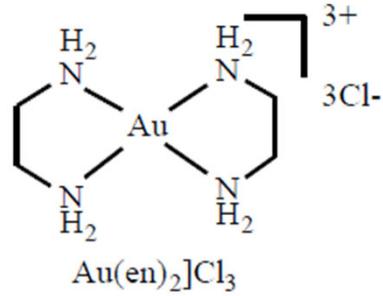
Maximum ammine loading obtainable in a single SEA step



□24

$[\text{Au}(\text{en})_2]^{3+} 3\text{Cl}^-$

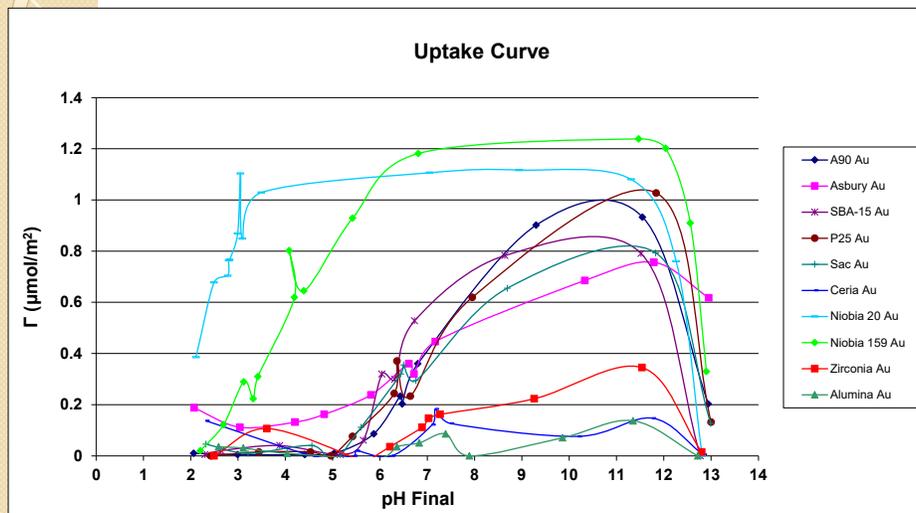
- First production
 - Block et. al 1951
- Current groups using Precursor
 - Catherine Louis
 - Titania
 - Other Groups
 - Silica/Carbon



□25

□25

Cation Adsorption Results

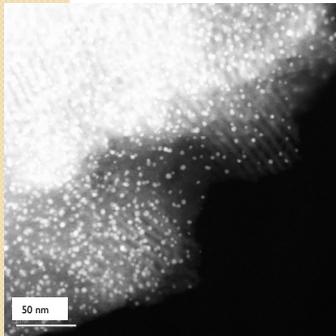


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Representative STEM Images

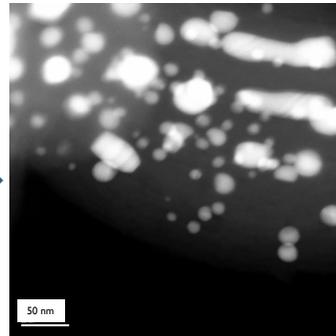
SBA-15 Mesoporous Silica



$D_{avg}: 2.3 \pm 0.6$ nm

← SEA

DI →



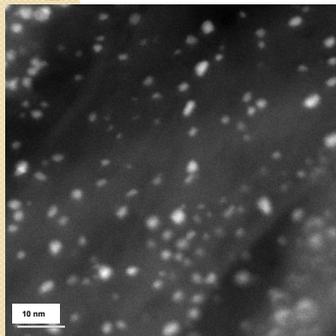
$D_{avg}: 6.7 \pm 1.4$ nm

□27

□27

Representative STEM Images

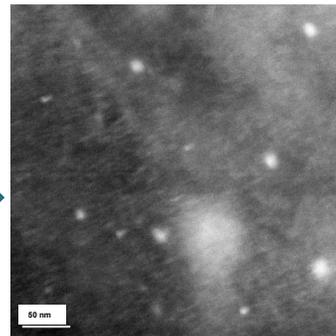
Asbury Graphite



$D_{avg}: 1.8 \pm 0.4$ nm

← SEA

DI →

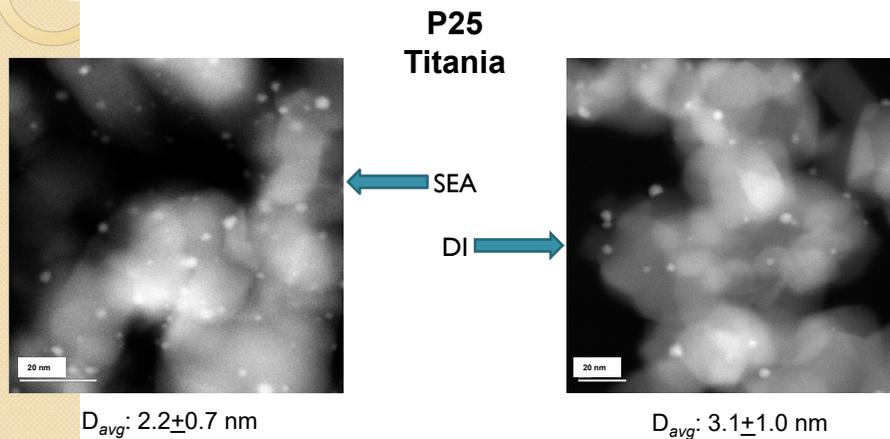


$D_{avg}: 8.2 \pm 1.4$ nm

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Representative STEM Images



□29

□29

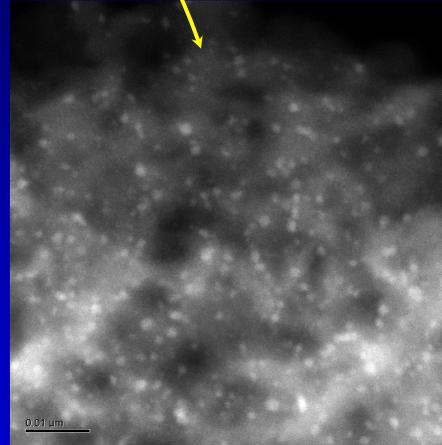
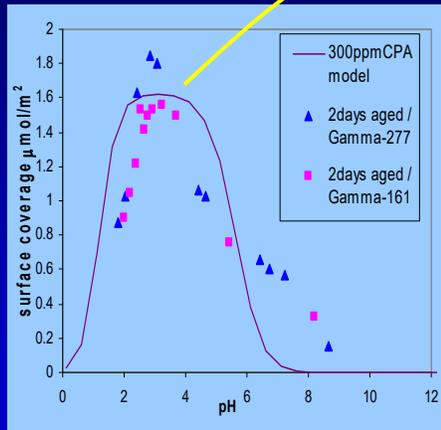
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□30

SEA: CPA/ Al_2O_3



3.1 wt% Pt/ Al_2O_3 ($277 \text{ m}^2/\text{gm}$), $d_{\text{av}} = 1.3 \text{ nm}$

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□31

Outline

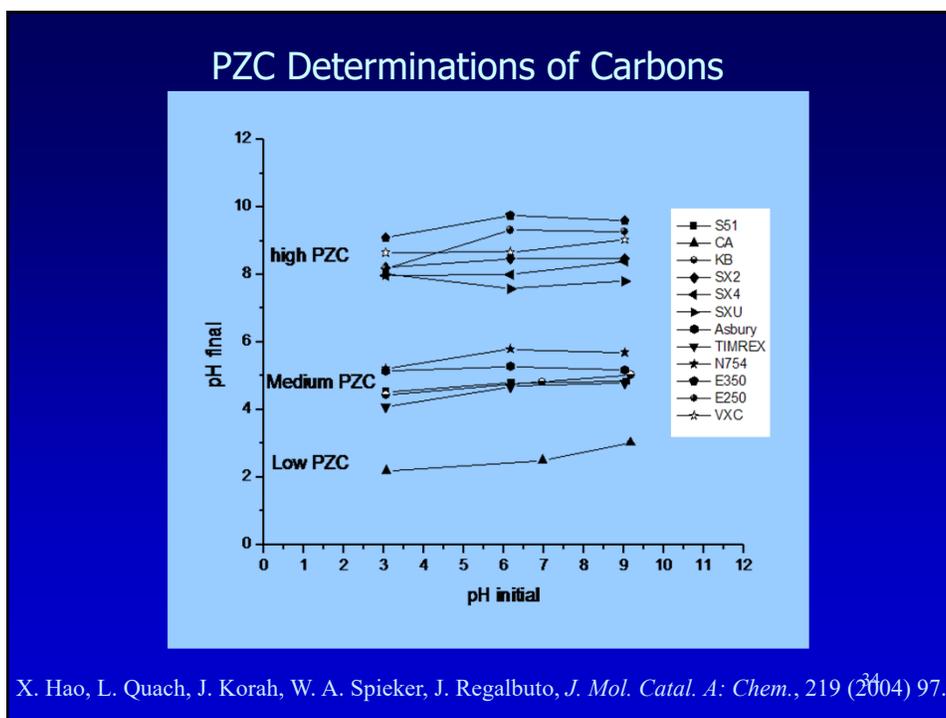
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□32

Carbon Name	Abbreviation	SA (m ² /g)	Pretreatment	Total Pore Volume (ml/g)	PZC
Activated carbon					
Darco s-51	S51	650	Acid washed, steam activation of lignite coal	1.0	4.7
Norit SX 2	SX2	800	Acid washed steam activated	1.36	8.4
Norit SX 4	SX4	650	Acid washed steam activated		7.9
Norit SX ULTRA	SXU	1200	Acid washed steam activated	2.16	7.8
Norit CA-1	CA	1400	Chemically activated by phosphoric acid	0.9	2.6
Darco KB-B	KB	1500	chemical activation of hardwood	1.8	4.8
Graphite					
Asbury Grade 4827	ASBURY	115	Heated, ground natural graphite	2.55	5.2
Timcal TIMREX HSAG 300	TIMREX	280	Heated, ground petroleum coke	1.64	4.5
Carbon Black					
Degussa A1-04088 N754	N754	25	pyrolysis	0.7	5.6
Ensaco 250 Powder	E250	62	pyrolysis	1.4	9.0
Ensaco 350 Powder	E350	770	pyrolysis	8.0	33 9.5
Vulcan XC 72	VXC	254	pyrolysis	3.46	8.9

□33

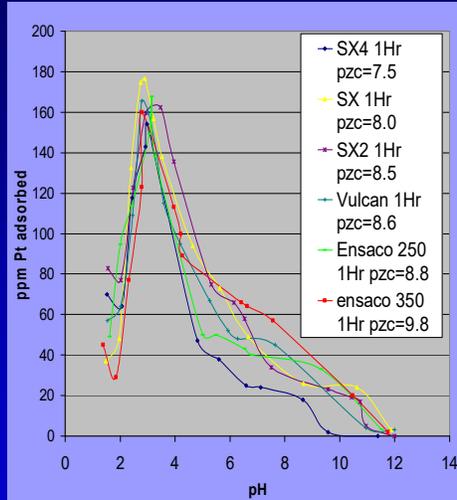


X. Hao, L. Quach, J. Korah, W. A. Spieker, J. Regalbuto, *J. Mol. Catal. A: Chem.*, 219 (2004) 97.

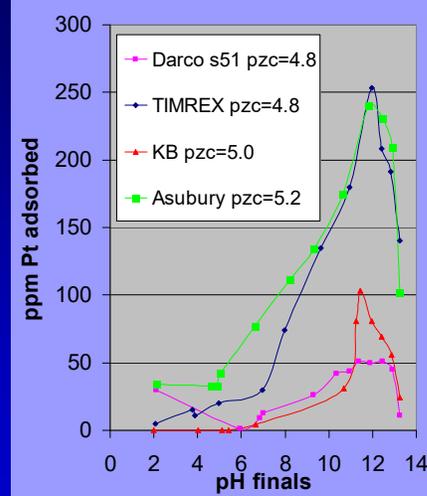
□34

CPA, PTA uptake vs. pH, varying carbon type

CPA/high PZC



PTA/mid PZC

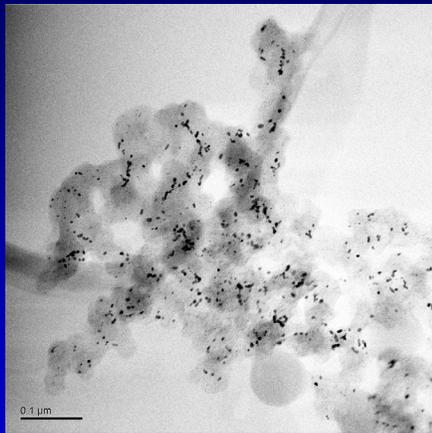


- narrower volcano curves w.r.t alumina, silica
- pore exclusion of PTA from small pore carbons at high pH

□35

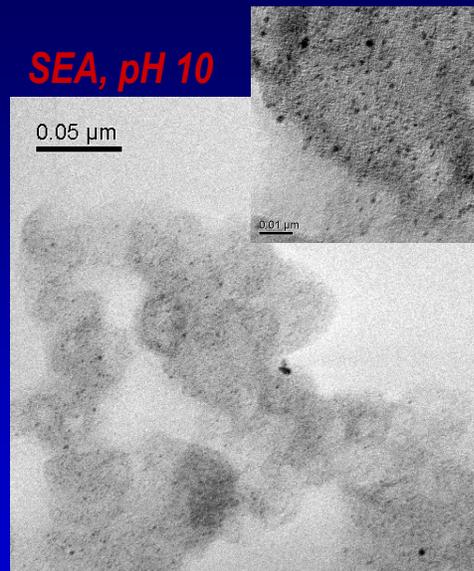
STEM of PTA/Timrex after 200°C Reduction

dry impregnation



- average size \cong 8-10 nm

SEA, pH 10

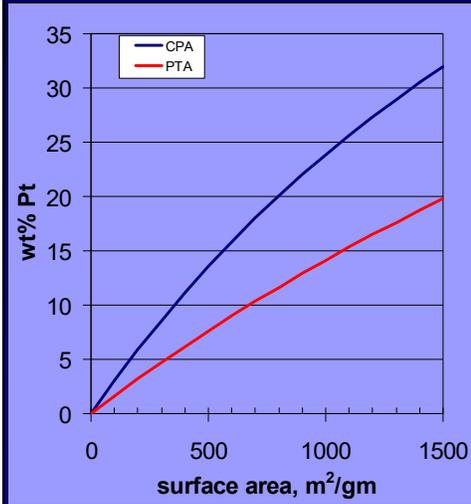


- average size \cong 1.5 nm

□36

Fuel Cell Electrocatalyst Synthesis

Max. loading via SEA



Carbon Black	Surface area (m ² /g)
Ketjen Black EC 300J	795
Ketjen Black EC 600J	1415
Black Pearls 2000	1475
Enasco 350	795

□ CPA limit: 1.6 μmol/m²

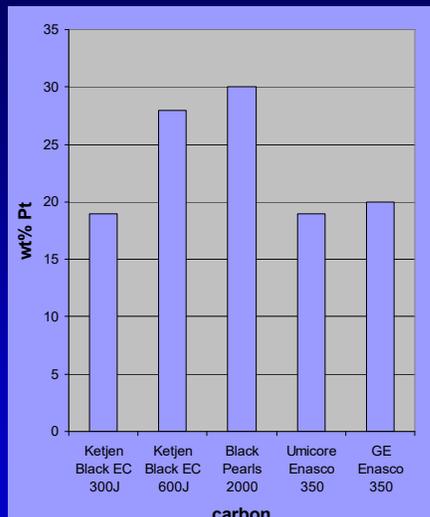
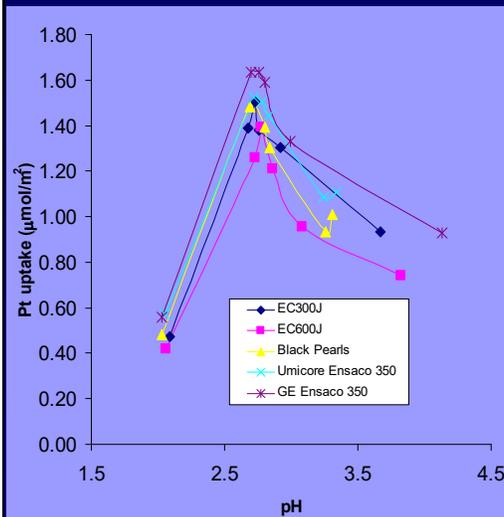
□ PTA limit: 0.84 μmol/m²

(Santhanam et al., Catal Today 1994)

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□37

CPA uptake vs. pH, carbon blacks



- optimal pH = 2.9

- max loading achieved = 30 wt% Pt

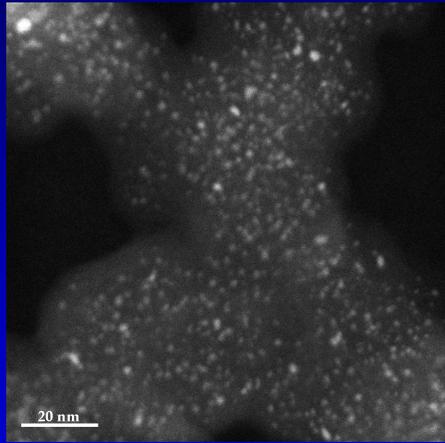
M. Castorano and J. 38
Regalbuto, in preparation

□38

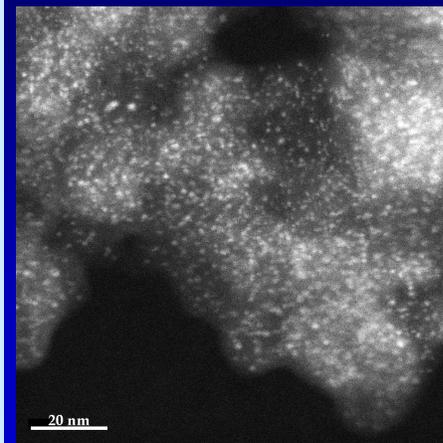
Comparison of Platinum Particle size on High Surface Area Carbon Black (BP2000, 1500 m²/gm)

SEA, 500 m²/l, pH 2.9, 200°C reduc.

DI (pore filling, pH_{init} 0.5), 200°C reduc.



○ Good dispersion and small particle size (1-2 nm)



○ Also good dispersion and small(er?) particle size (1-2³⁹ nm)

□39

Outline

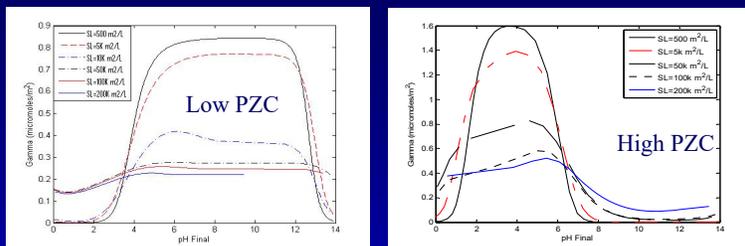
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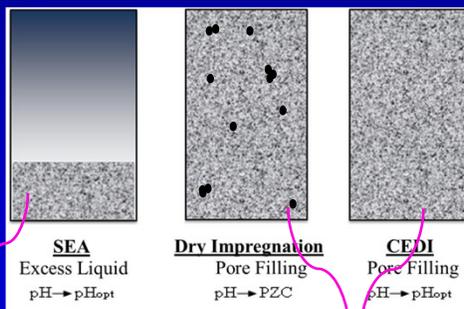
□40

Supported Pt Catalysts Prepared by Charge-Enhanced DI

Zhu, Cho, Regalbuto, ACS Catalysis 2013



500m²/L



100,000m²/L

□41

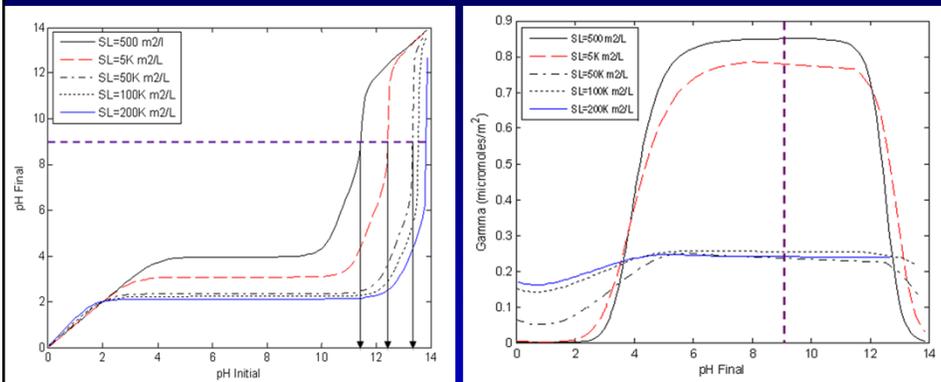
Result - STEM

	Pt/oxCarbon	Pt/Silica	Pt/Alumina
DI			
CEDI			

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□42

Example (PZC = 2)



Surface Loading	Target final pH	Initial pH
500 m ² /L	9	11.5
5,000 m ² /L	9	12.5
50,000 m ² /L	9	13.4

- Use pH shift plot to pick off appropriate pH_{initial}

□43

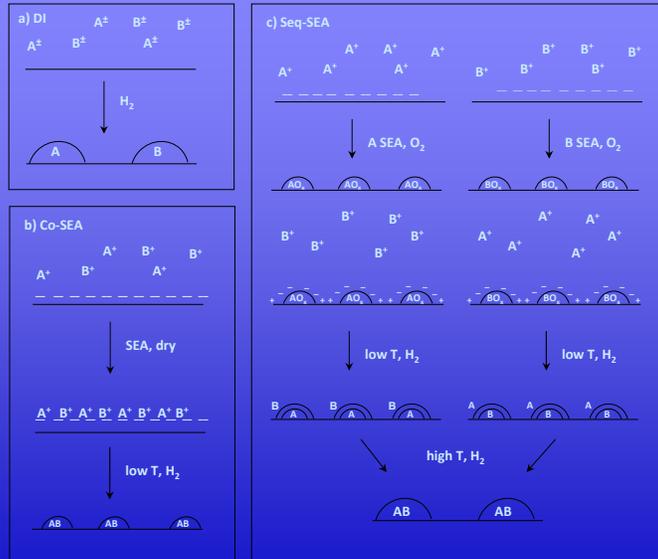
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Extension of SEA for bimetallic nanoparticle synthesis



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□45

Individual Metal Adsorption on SiO_2 , C_{ox} , Al_2O_3 , C

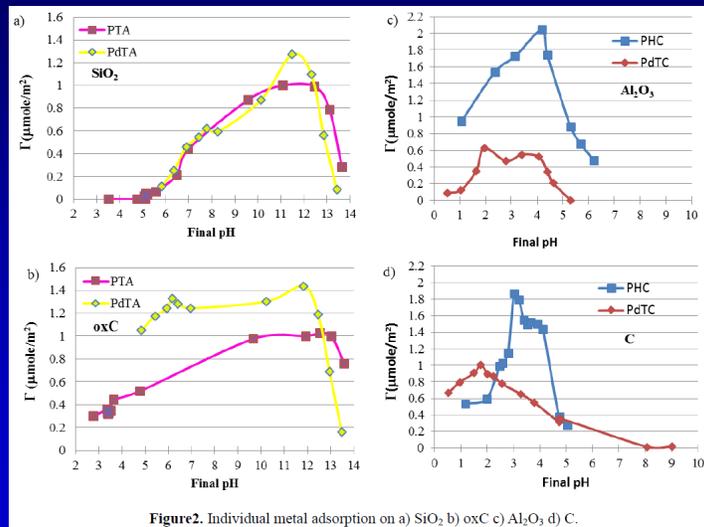


Figure 2. Individual metal adsorption on a) SiO_2 b) oxC c) Al_2O_3 d) C.

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Co-SEA on SiO₂, C_{ox}, Al₂O₃, C

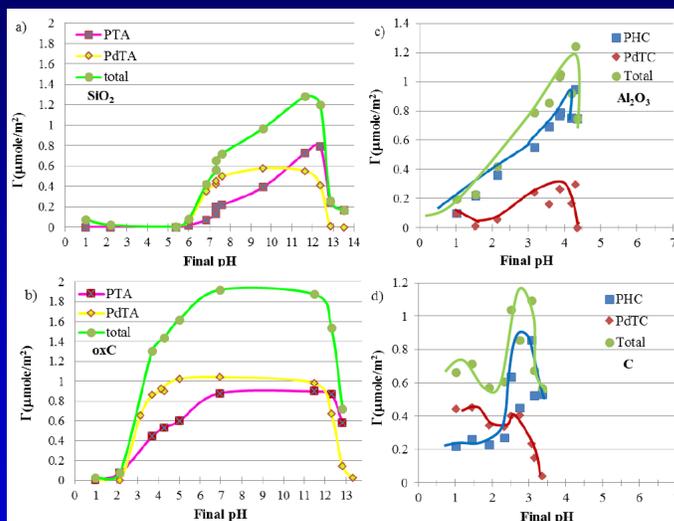


Figure 3. Individual and total metal uptake via co-SEA adsorption on a) SiO₂ b) oxC c) Al₂O₃ d) C

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□47

Table 2 Metal wt% of each catalyst by ICP result

Support	Type	Pt wt%	Pd wt%
silica	Single Pt SEA	5.0	-
	Single Pd SEA	-	4.0
	Pt-Pd co-SEA	4.5	2.0
oxC	Single Pt SEA	3.0	-
	Single Pd SEA	-	2.5
	Pt-Pd co-SEA	3.0	1.8
alumina	Single Pt SEA	11	-
	Single Pd SEA	-	2.1
	Pt-Pd co-SEA	5.3	1.6
C	Single Pt SEA	8.3	-
	Single Pd SEA	-	2.7
	Pt-Pd co-SEA	4.0	1.0

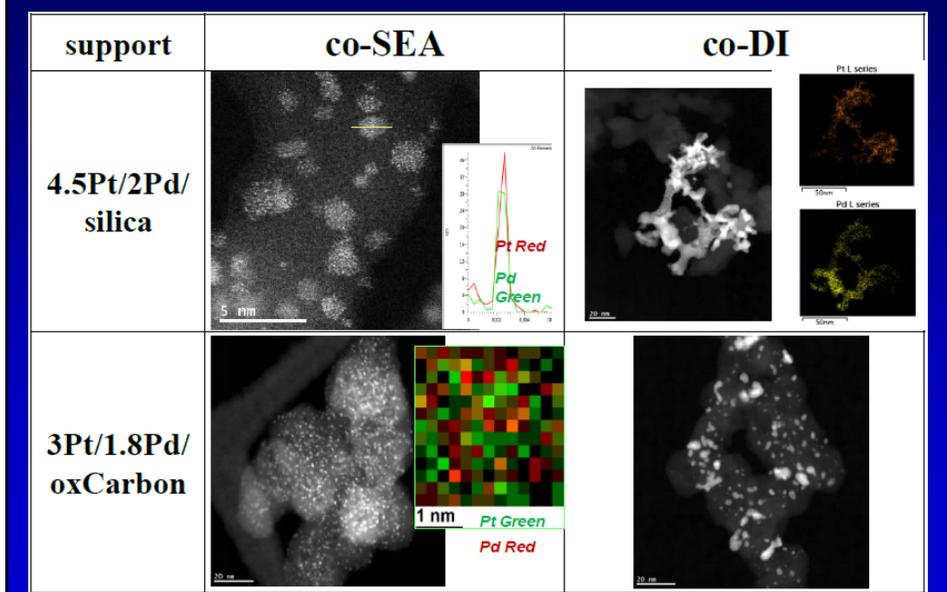
Total metal loading can be increased with co-SEA over low PZC supports: more closely packed monolayer via shared hydration sheaths.

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□48

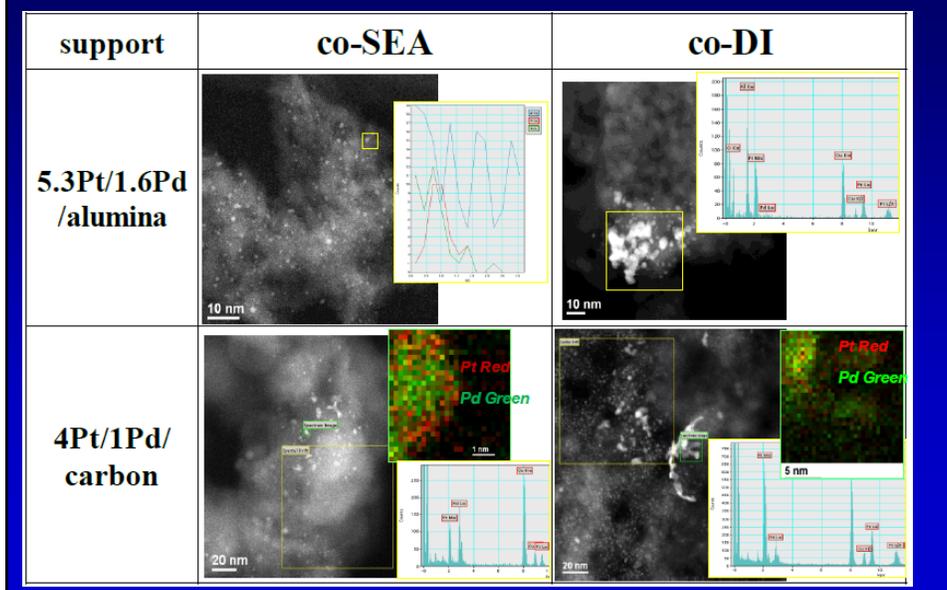
□24

STEM analysis of co-SEA on SiO_2 , C_{ox}

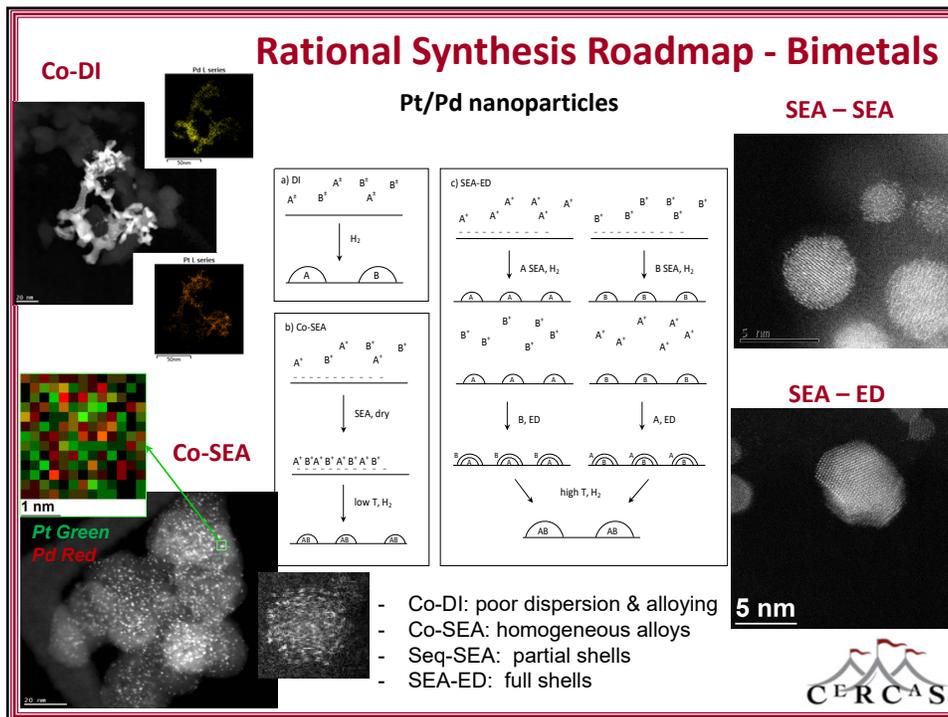


□49

STEM analysis of co-SEA on Al_2O_3 , C



□50



□51

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□52

Surface free energy stabilization of Au shells over noble metal cores for the hydrochlorination of acetylene

Kerry C. O'Connell, J.R. Regalbuto and John Monnier

I&EC Symposium in honor of Bala Subramaniam

ACS Spring Meeting, San Diego, CA

March 13, 2016



UNIVERSITY OF
SOUTH CAROLINA

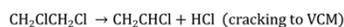
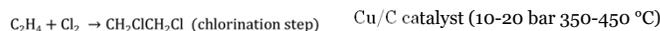


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VINYL CHLORIDE MONOMER SYNTHESIS

- The main use of Vinyl Chloride monomer (VCM) is for PVC production
 - Worldwide demand to exceed **40 million tons in 2016**
 - Understudied reaction, opportunities for fundamental and applied research
- Industrial methods of VCM production

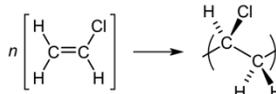
Oxychlorination "balanced" VCM process



Direct hydrochlorination VCM process



- Current issues with the acetylene process
 - China is largest producer of VCM and 70% produced from $\text{HC}\equiv\text{CH}$
 - Current catalysts undergoes deactivation from reduction of Hg^{2+} to Hg^0
 - **Between 300-450 tons of Hg^0 estimated to be lost annually by volatilization into atmosphere**

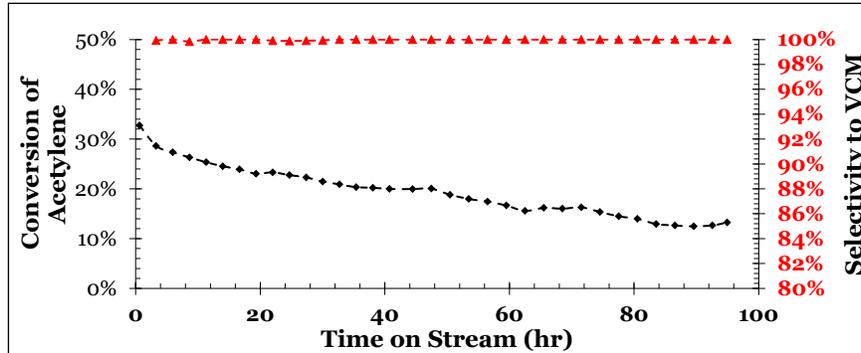


Phase I Final Report - PVC Project Report for China-UNEP 2010
J. Zhang Front. Chem. Sci. Eng., 2011, 5, 514-520

□54

□54

THE PROBLEM: LONG TIME DEACTIVATION OF Au/C



Goal: Understand and overcome deactivation of Au

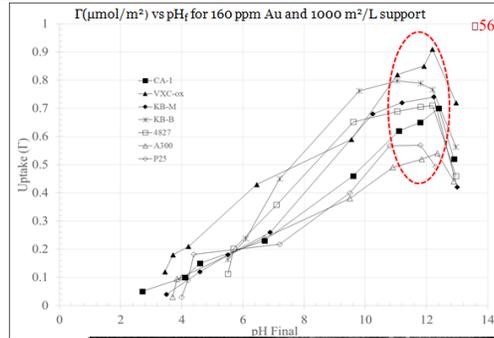
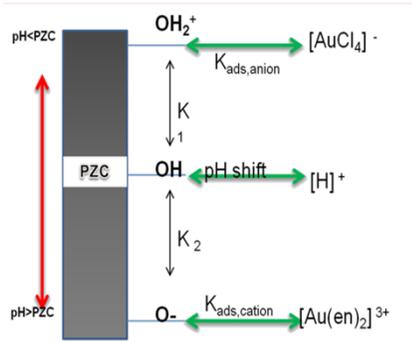
Outline:

- o Begin with identical well dispersed Au on a series of carbon and oxide supports
- o Relate deactivation to sintering and support
- o Anchor shells of Au with high SFE cores

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Strong Electrostatic Adsorption (SEA)



1% Au /C via SEA
Particle Size-1.2 nm

Support		Surface Area (m ² /g)	Pore Volume (ml/g)	(PZC)
HNO ₃ Oxidized Vulcan XC-72 (Cabot)	VXC-ox	180	1.9	3.7
Vulcan XC-72 (Cabot Corporation)	VXC	254	2.3	8.5
Norit CA-1 (Norit Americas Inc.)	CA-1	1400	1.7	2.6
Darco KB-M (Norit Americas Inc.)	KB-M	1200	3.2	3.5
Darco KB-B (Norit Americas Inc.)	KB-B	1500	4	4.8
Asbury grade 4827 (Asbury)	4827	115	0.4	4.7
Aersoil 300 fumed silica (Evonik)	A300	330	0.8	3.7
Aeroxide P25 (Evonik)	P25	35	0.7	4

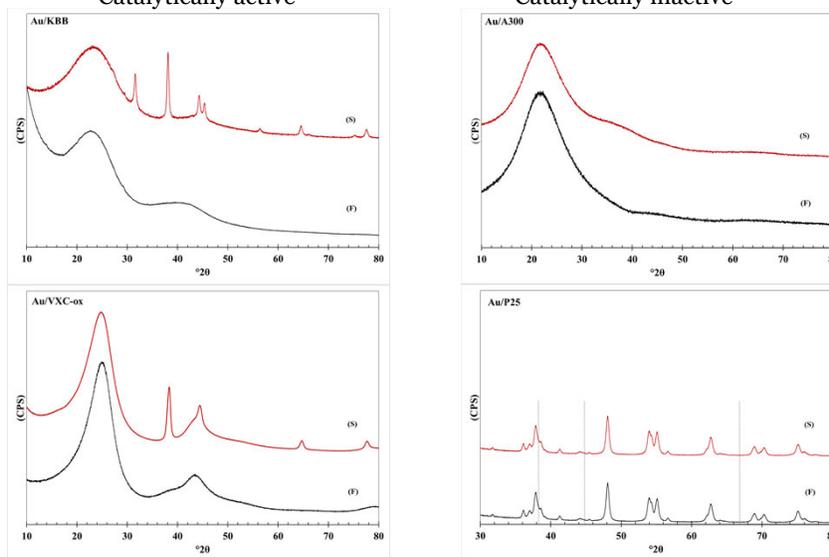
10 nm

□56

PARTICLE GROWTH AND ACTIVITY RELATIONSHIP

Catalytically active

Catalytically inactive

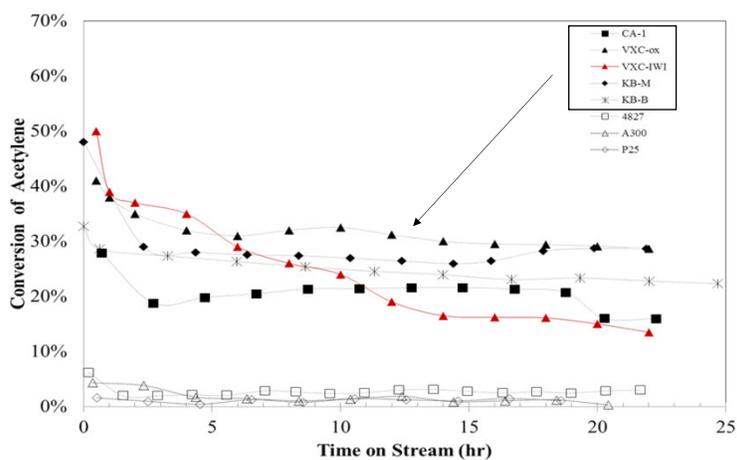


- Fresh (F) Au nanoparticles are XRD transparent (<1.5 nm) on all supports
- Confirms STEM

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□57

SUPPORT EFFECT FOR CONVERSION AND PARTICLE GROWTH

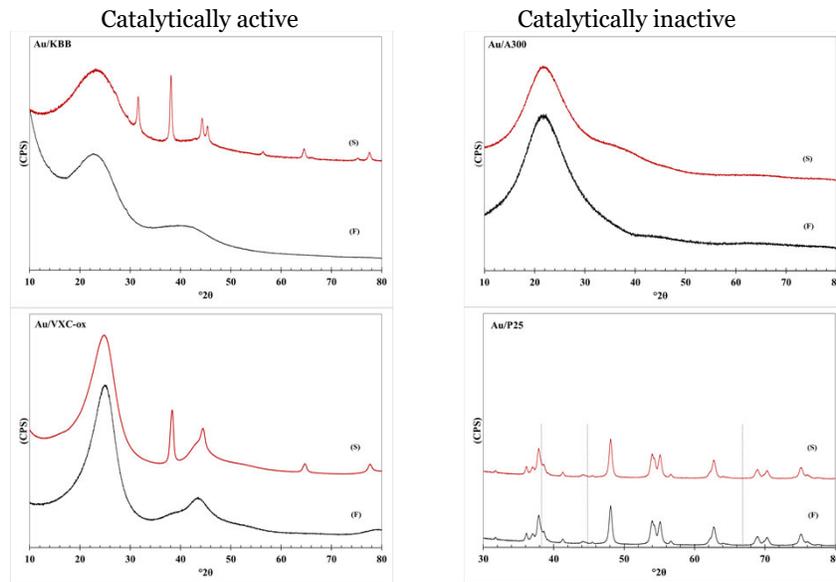


- Activated carbon shows typical activity profile(GHSV: 4500 hr⁻¹)
- Effect of surface oxygen seen in VXC-ox vs. VXC-IW
- Trends with surface O content agree with Netskina et al.. Appl. Catal., A 2013, 467, 386
- Metal oxide and graphitic carbon catalysts are inactive

□58

□58

PARTICLE GROWTH AND ACTIVITY RELATIONSHIP

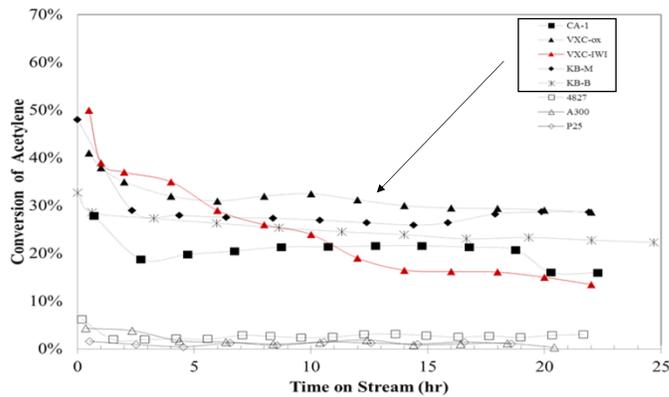


- Gold supported on metal oxides was inactive and no sintering was observed.
- Active species appears to involve mobile intermediate

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□59

SUPPORT EFFECT FOR CONVERSION AND PARTICLE GROWTH



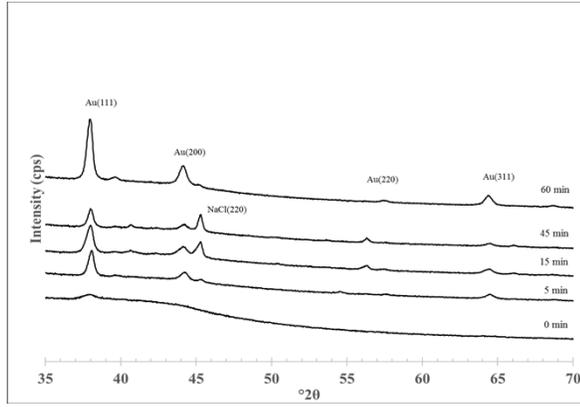
Catalyst	Notation	Fresh Particle Size (nm)	Spent Particle Size (nm) 4500 hr ⁻¹
1 wt. % Au/ VXC-ox	VXC-ox	<1.5	12.3
1wt. % Au/VXC (IWI)	VXC-IWI	<1.5	16.4
1 wt. % Au/CA-1	CA-1	2	20.1
1 wt. % Au/KB-M	KB-M	3	17.5
1 wt. % Au/KB-B	KB-B	2.1	22.2
1 wt. % Au/4827	4827	<1.5	3.7
1 wt. % Au/A300	A300	<1.5	<1.5
1 wt. % Au/P25	P25	<1.5	<1.5

- Activity proportional to sintering
- How fast does sintering occur?

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□60

PARTICLE AGGLOMERATION DURING PRETREATMENT



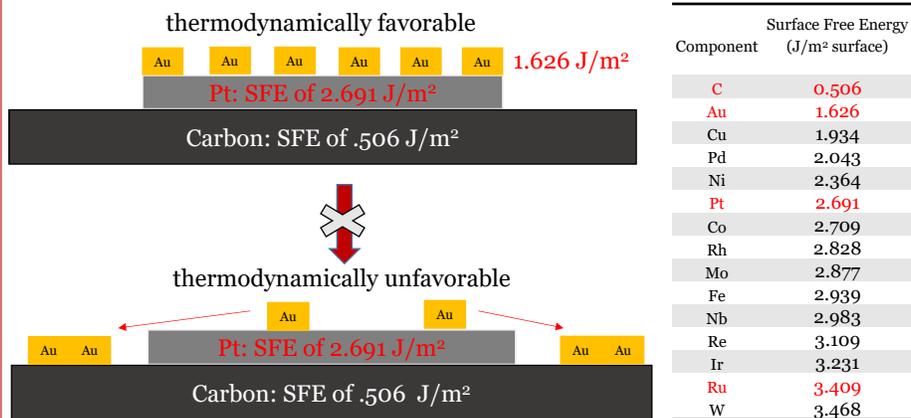
Time (min)	Particle size (nm)
60	20.7
45	20.4
15	18.8
5	20.6
0*	2.1

- XRD patterns for Au/C samples exposed to 50% HCl at 180°C up to 60 minutes
- Flowrate of 10 SCCM after drying for 180°C in He for 1 hour*.
- **Particles have fully sintered before reaction testing even begins!**

□61

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EXPLOITING DIFFERENCES IN SFE TO STABILIZE AU SHELLS



- To minimize surface area of the multicomponent system with Au@Pt/C, Au will want to remain covering the higher SFE Pt
- Maximize difference in SFE to test proof of principal

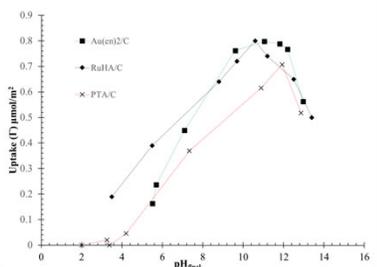
□62

□62

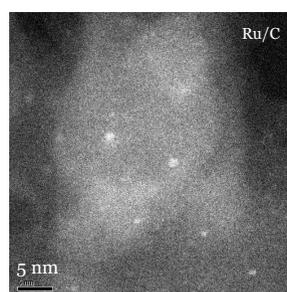
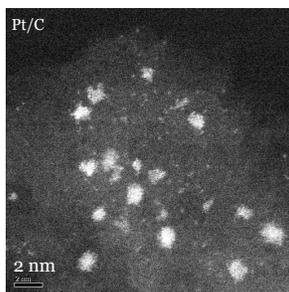
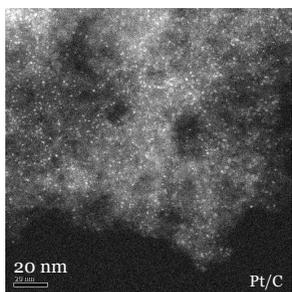
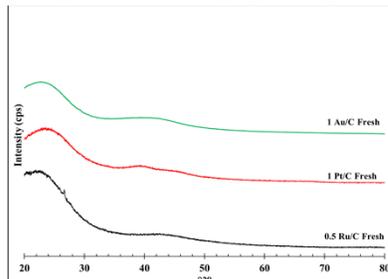
STABILITY OF METAL CORES FOR ED

□63

Γ(160 ppm) vs. pH survey at 1000 m²/L carbon

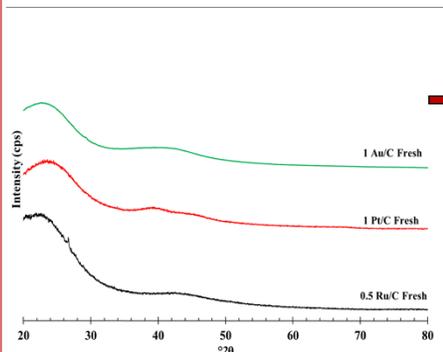


XRD profile of reduced catalysts pre HCl exposure

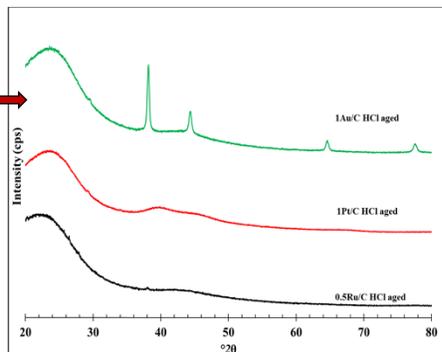


□63

STABILITY OF METAL CORES FOR ED



XRD profile of reduced catalysts pre HCl exposure
weight loading chosen to ensure similar atomic ratios



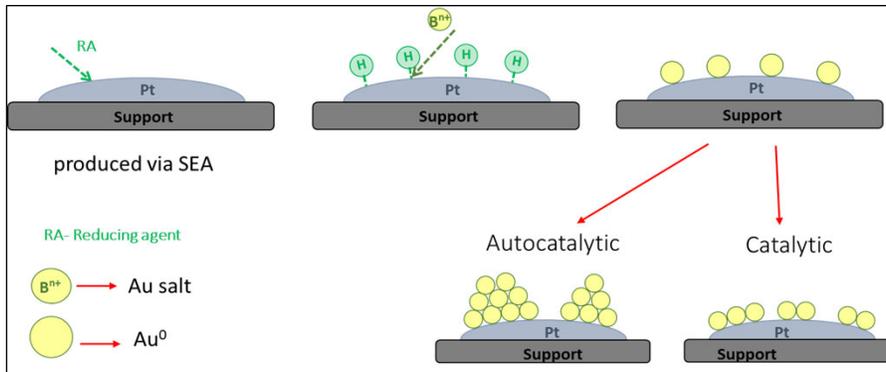
XRD profile of reduced catalysts after 60 min at
50% HCl at 180 °C

- Metals such as Pt, Ru, **Cu***, and **Pd** are more resistant to sintering in acidic environment than Au

□64

□64

ELECTROLESS DEPOSITION OF AU ONTO Pt (Pt@Au)



RA : Reducing agent
HCHO, N_2H_4 , DMAB, $H_2PO_2^-$, HCOOH

A : Primary metal
Pt, Pd, Co, Ru, Rh, Ag, Au, etc.

B : Secondary metal
Ag, Au, Pt, Cu, Re, Pd, Ru, etc.

Aqueous Developer Bath Conditions

Base catalyst: 0.5 g of 1 wt. % Pt/C

Metal Ion Source: $KAu(CN)_2$

Reducing Agent: N_2H_4

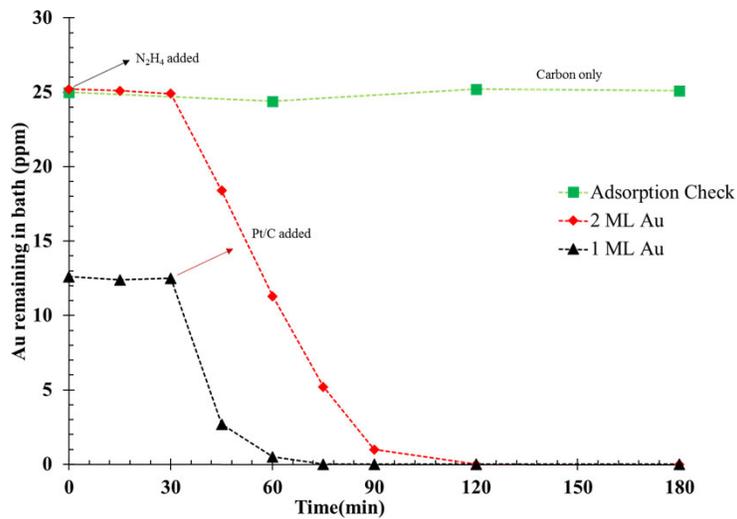
RA/Au ratio: 10/1

Temperature: 40°C pH:10

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□65

ED OF 1&2 ML OF AU ONTO 1.0 WT. % Pt/C



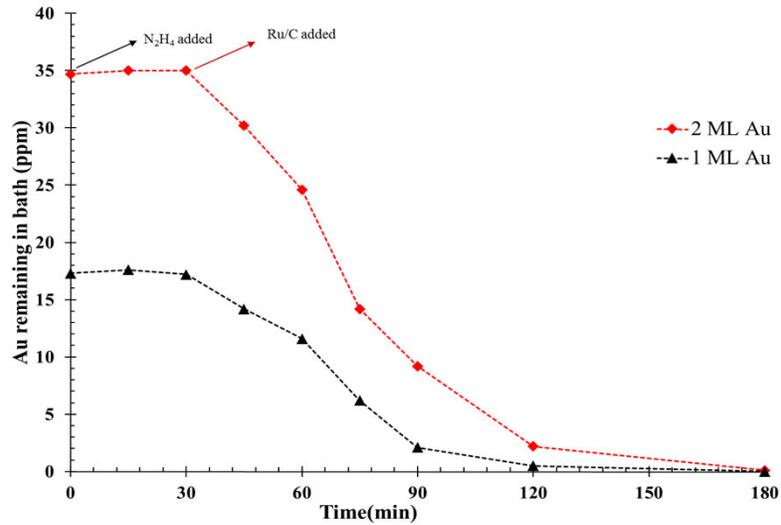
○ Complete deposition of 1 and 2 ML by 120 min, Au stable in solution

Rebelli, Jayakiran, et al. "Synthesis and characterization of Au-Pd/SiO₂ bimetallic catalysts prepared by electroless deposition." *Journal of Catalysis* 270.2 (2010): 224-233.

□66

□66

ED OF 1&2 ML OF AU ONTO 0.5 WT.% RU/C



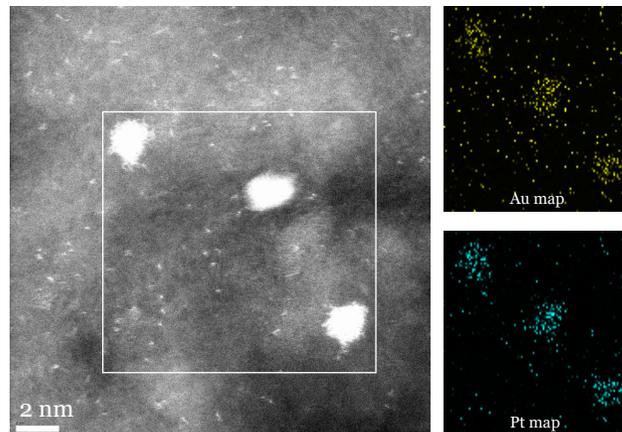
- Deposition slower over Ru, for further coverage increase bath temp or add N_2H_4

□67

□67

STABILIZED Pt@Au/C PARTICLES: STEM & EDXS

Spent 2ML Pt@Au catalyst



- Spent particles retain high dispersion (often atomic), Au and Pt in close contact
- No large particles observed (> 2 nm) from spent samples i.e. Au was stabilized on Pt surface

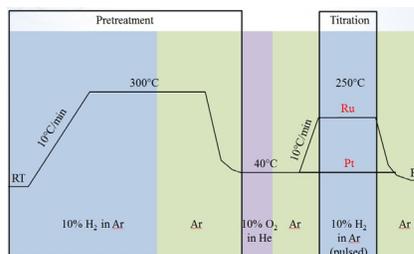
□68

□68

CONFIRMING COVERAGE OF CORE METALS: CHEMISORPTION

Chemisorption (H₂ titration) procedure

- Reduce sample with 10% H₂ at 300°C.
- Cool to room temperature in Ar.
- Expose to O₂ at room temperature for 30 mins.
- Flow Ar for 30 mins to purge residual gas phase O₂.
- Do H₂ titration at two different temperatures.
- Au not active for chemisorption at these conditions*



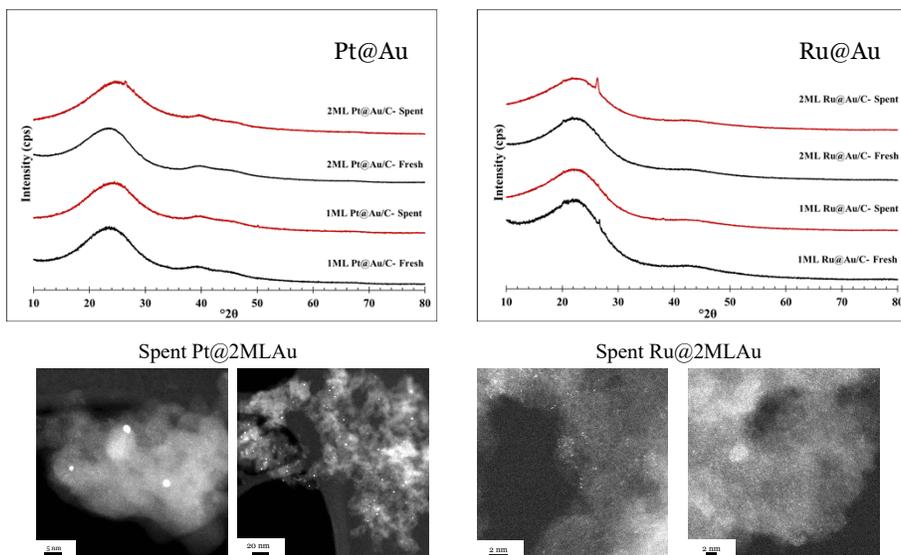
Theoretical coverage (ML)	Hydrogen Uptake (cm ³ /g)	Fractional coverage	Total Au (wt. %)
1% Pt/C	0.485	0	0
1 ML Au	0.217	0.55	0.47
2 ML Au	0.073	0.85	0.95
2 ML Au Spent	.020	0.96	
0.5% Ru/C	6.48	0	0
1 ML Au	3.04	0.25	0.51
2 ML Au	2.72	0.53	1.02
2 ML Au Spent	0.164	0.96	

A.G. Sault, R.J. Madix, C.T. Campbell, Adsorption of oxygen and hydrogen on Au(110)-(1 × 2), Surface Science, 160 (1986) 347-356

□69

□69

STABILIZED AU PARTICLES: A SUCCESS

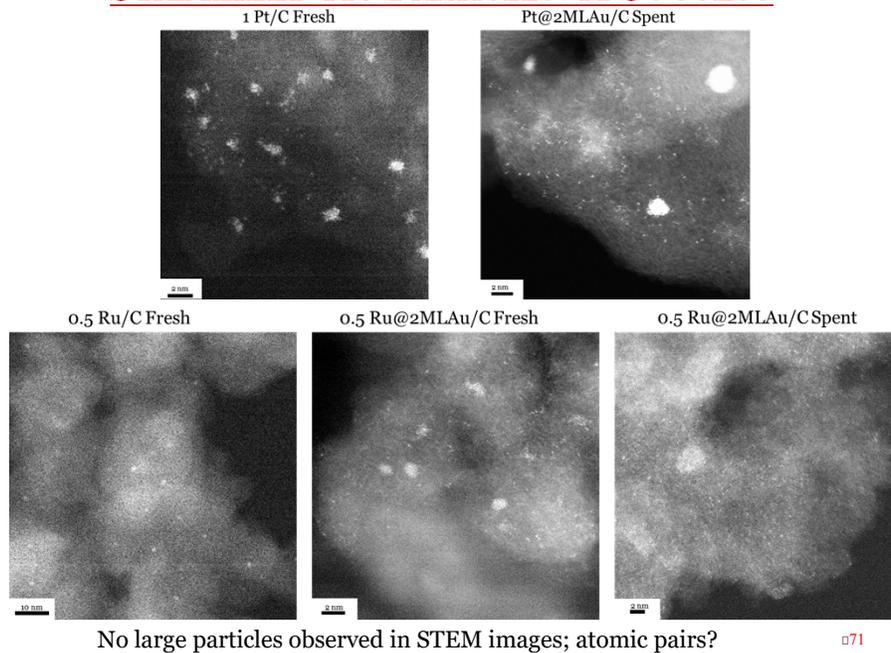


- XRD: Au unobservable, monolayer shells give about 20 times the Au area of sintered Au
- STEM: confirms stability, much material remains atomically dispersed

□70

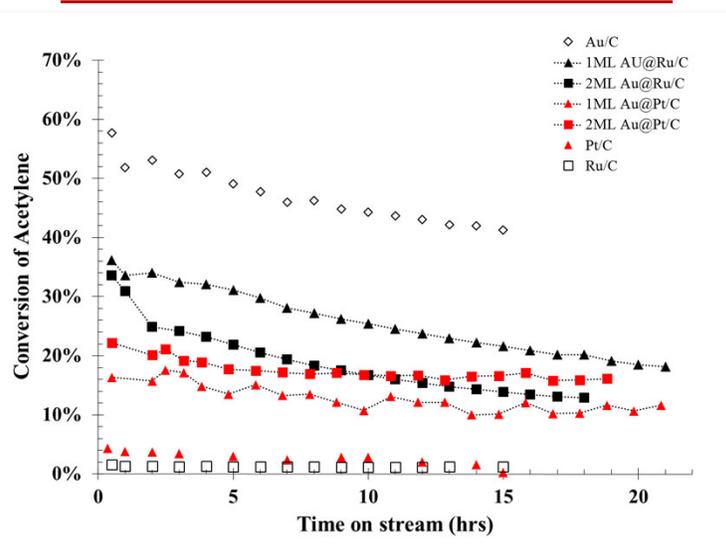
□70

STABILIZED AU PARTICLES: A SUCCESS



□71

ACTIVITY OF BIMETALLIC SYSTEMS

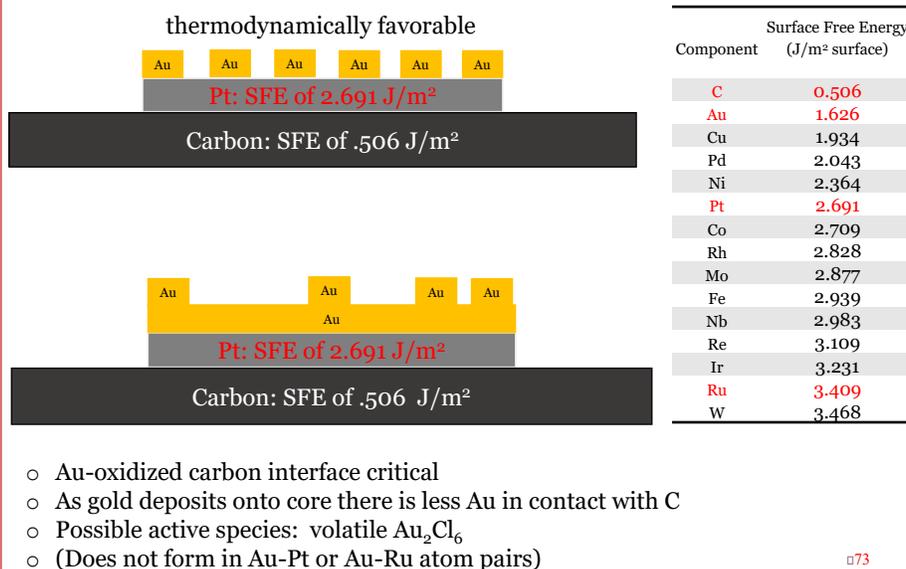


- Addition of secondary metal core retards activity, even though Au area has increased by 20x
- Active site not related to Au surface area

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□72

EXPLOITING DIFFERENCES IN SFE TO STABILIZE AU SHELLS



□73

CONCLUSIONS AND FUTURE WORK

- Rapid sintering of Au occurs in the presence of HCl, conversion continues to decay with time
- The support and surface groups play an important role in the anchoring of the active species (Au₂Cl₆?)
- Gold shells were stabilized via high SFE anchoring on stable metal cores
- Increase in Au surface area did not increase acetylene hydrochlorination activity
 - Other applications for Au that are size and structure sensitive (WGS/RWGS/CO oxidation)
- See John Monnier's talk (ENFL 128, Monday 4:30, Honor of Stu Soled) for a more detailed discussion of SFE anchoring



□74

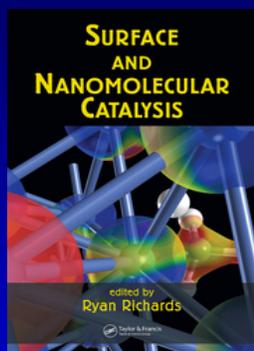
Conclusions

- SEA method is simple to apply; PZC is easy to measure
- An electrostatic mechanism is a good starting point for optimizing metal dispersion in many NM and BM systems
- Other mechanisms accompany SEA:
 - IE over zeolites
 - DP in mid pH with hydrolyzable metals
 - Surface reaction over carbon (others)
- The electrostatic model can be extended to the synthesis of promoted and bimetallic catalysts

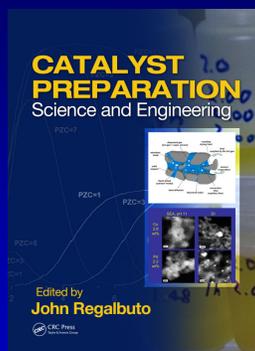
75

□75

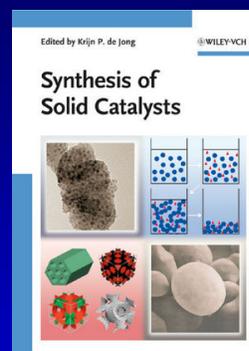
Book Chapters on SEA



Historical development and experimental underpinnings



"How To"
Do It Yourself
Manual



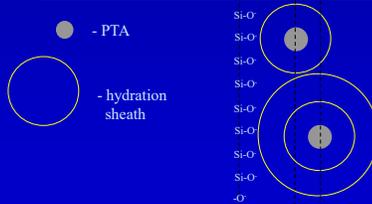
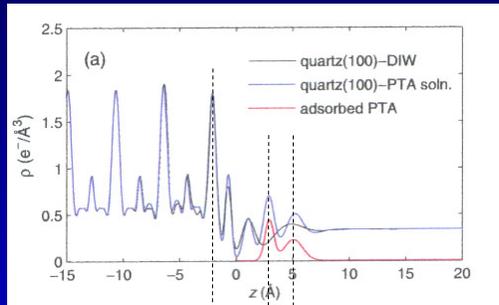
SEA in the
context of other
mechanisms

76

□76

X-ray reflectivity analysis of PTA/quartz

C. Park, P. A. Fenter, N. C. Sturchio, J. R. Regalbuto, *Phys. Rev. Lett.*, 94 (2005) 076104



77

□77

Quartz Crystal Microgravimetry

Boujday et al., *ChemComm* 50 (2014) 2049

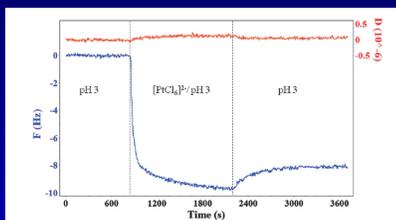
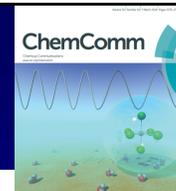


Fig. 1 Frequency changes (F) and dissipation measurements (D) upon adsorption of $[PtCl_6]^{2-}$ on alumina at pH 3.

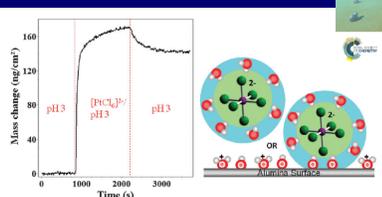


Fig. 2 Changes in adsorbed mass calculated from the Sauerbrey model upon $[PtCl_6]^{2-}$ adsorption on alumina at pH 3, along with the proposed adsorption model.

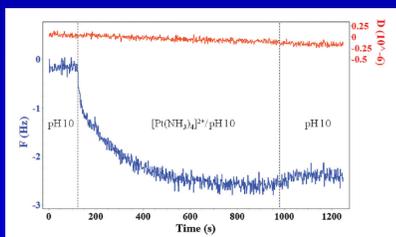


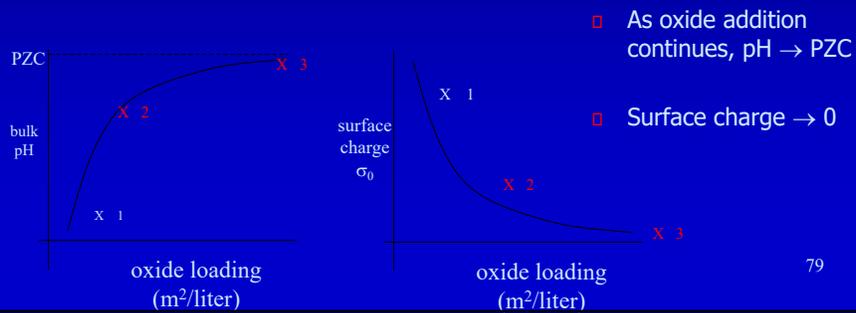
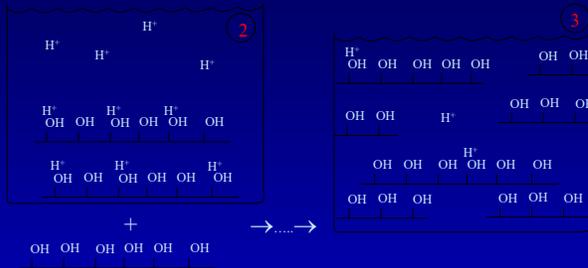
Fig. 4 Frequency changes and dissipation measurements upon $[(NH_3)_4Pt]^{2+}$ (PTA) adsorption on silica at pH 10.

- QCM results: weight increase corresponds to close packed layer of $[PtCl_6]^{2-}$ with one hydration sheath
- $[(NH_3)_4Pt]^{2+}$ adsorbs with 2 hydration sheaths

78

□78

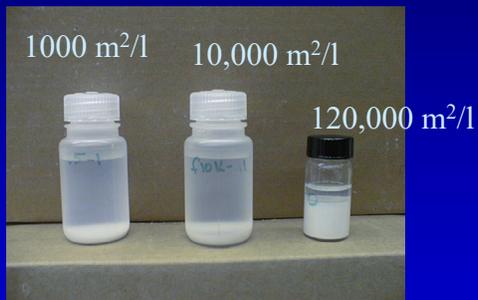
The Oxide Buffering Effect: Al₂O₃ (PZC = 8.5) added to acidic solution



□79

Various Surface Loadings of Alumina

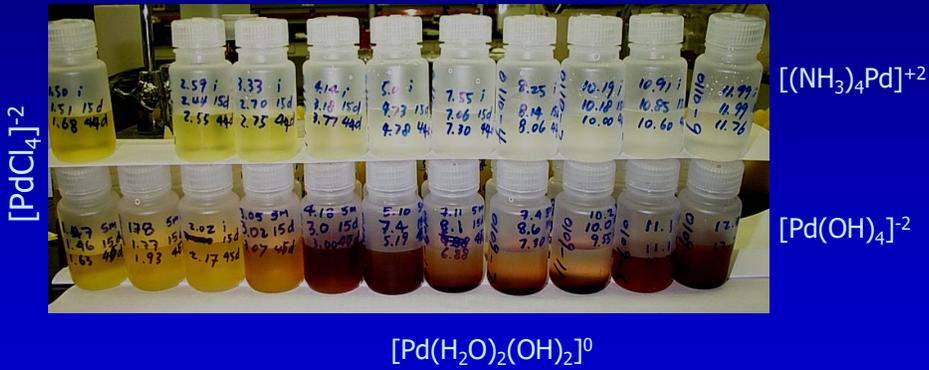
γ-Al₂O₃, 105 m²/gm



- 1000: .476 gm in 50 ml
- 10,000: 4.76 gm in 50 ml
- 120,000: 11.43 gm in 10 ml

□80

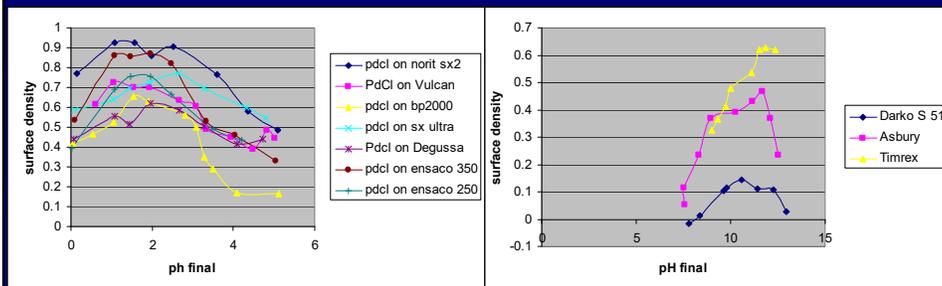
Top row: 300 ppm Pd(II)Cl₄ + NH₄OH,
 Bottom row: 300 ppm Pd(II)Cl₄ + NaOH,



81

□81

Pd(II) uptake on carbon

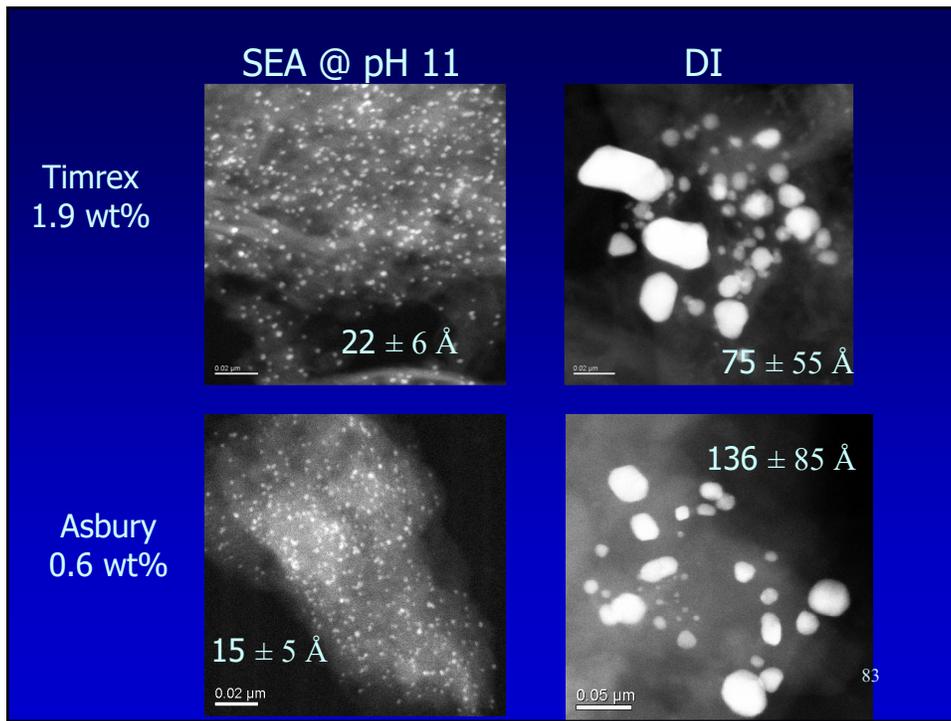


□ [PdCl₄]²⁻ dissolved in 5.6 times excess Cl⁻; basified with NH₄OH

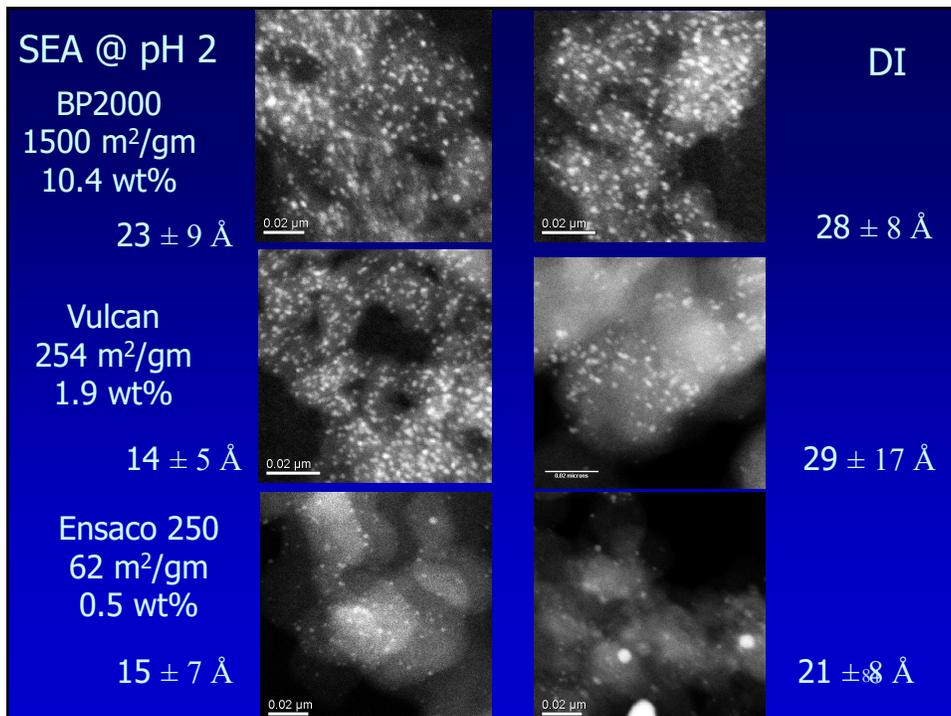
□ [(NH₃)₄Pd]⁺² starting solution, basified with NaOH

E. Kratzer and J. Regalbuto,
 in preparation

□82



□83



□84

Sequential SEA

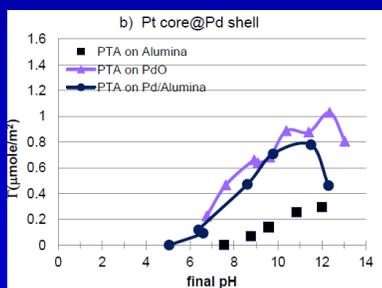
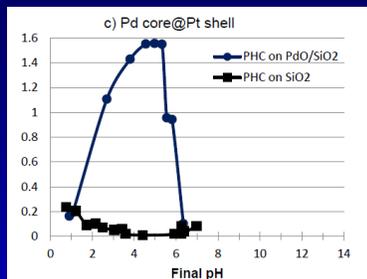
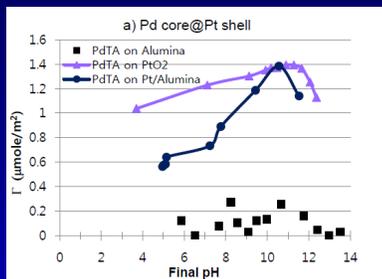


Table 4. Metal wt% of PT/Pd core shell catalysts

Support	Type	Pt wt%	Pd wt%
Silica	1 st seq-SEA	0.44	4
	2 nd seq-SEA	0.8	
	3 rd seq-SEA	1.0	
Alumina	1 st seq-SEA	6	0.55
	2 nd seq-SEA		1.0
	3 rd seq-SEA		1.28
	1 st seq-SEA	0.1	2
	2 nd seq-SEA	0.21	
	3 rd seq-SEA	0.33	

□85

Pd@Pt/SiO₂

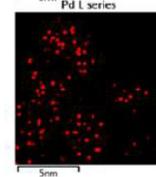
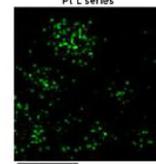
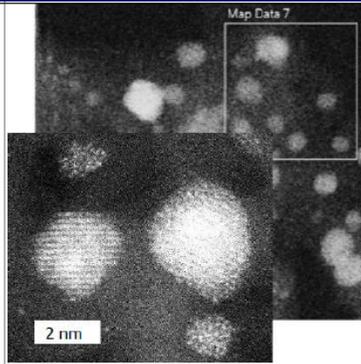
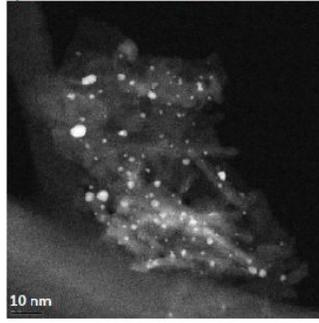
Catalyst	STEM images	Mapping of Pt & Pd
a) 1Pt/4Pd/silica		

86

□86

Pt@Pd/Al₂O₃

b) 1.28Pd/6Pt/alumina

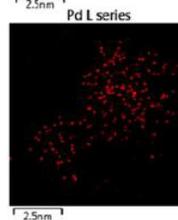
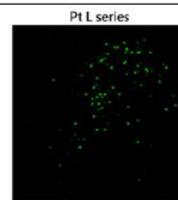
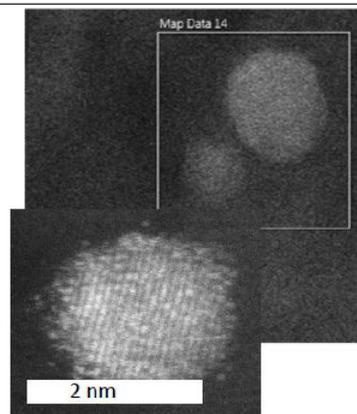
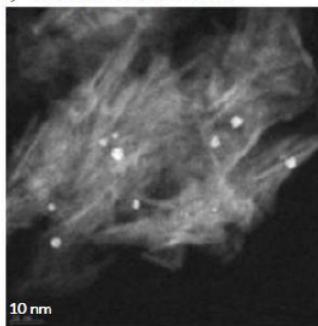


87

□87

Pd@Pt/Al₂O₃

c) 0.33Pt/2Pd/alumina



88

□88