

Strong Electrostatic Adsorption for the Facile Synthesis of Supported, Dilute Limit Alloy Nanoparticles

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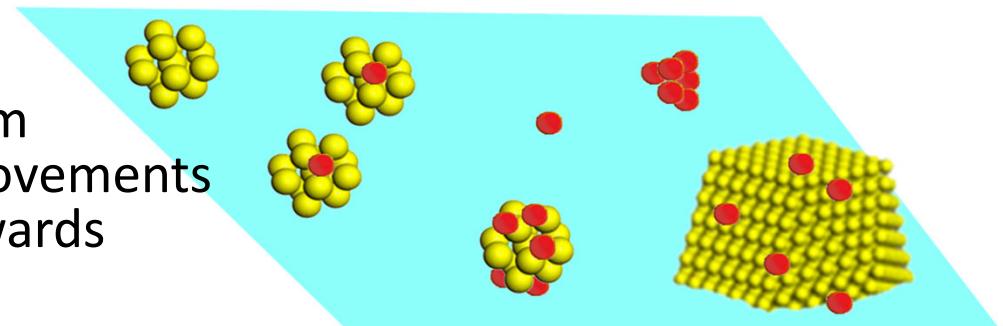
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Outline:

- Introduction
- Review of Literature
- Objective and Significance of the Study
- Methodology
- Results & Discussion
- Conclusions

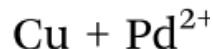
Introduction

- Recent synthesis of supported metal catalyst aims to not only maximize noble metal utilization but also to exploit the unique intrinsic electronic differences and binding capacities of catalyst arising from various forms ranging from **single atoms** to **clusters** and to **nanoparticles**.
- The addition of another metal to form **bimetallic catalyst** have shown improvements in catalyst activity and selectivity towards a specific type of reactions.
- In trying to achieve the desired catalyst characteristics, as predicted by computational techniques, various synthesis methods are being developed and applied.



Review of Literature – Synthesis

- Simultaneous strong electrostatic adsorption (co-SEA) have small ($<1\text{nm}$) with well dispersed base metals
- Deposition of nanoparticles is a common method to synthesize alloy.



- Sequential reduction was used to introduce (0.4%at) intermetallic nanoparticles

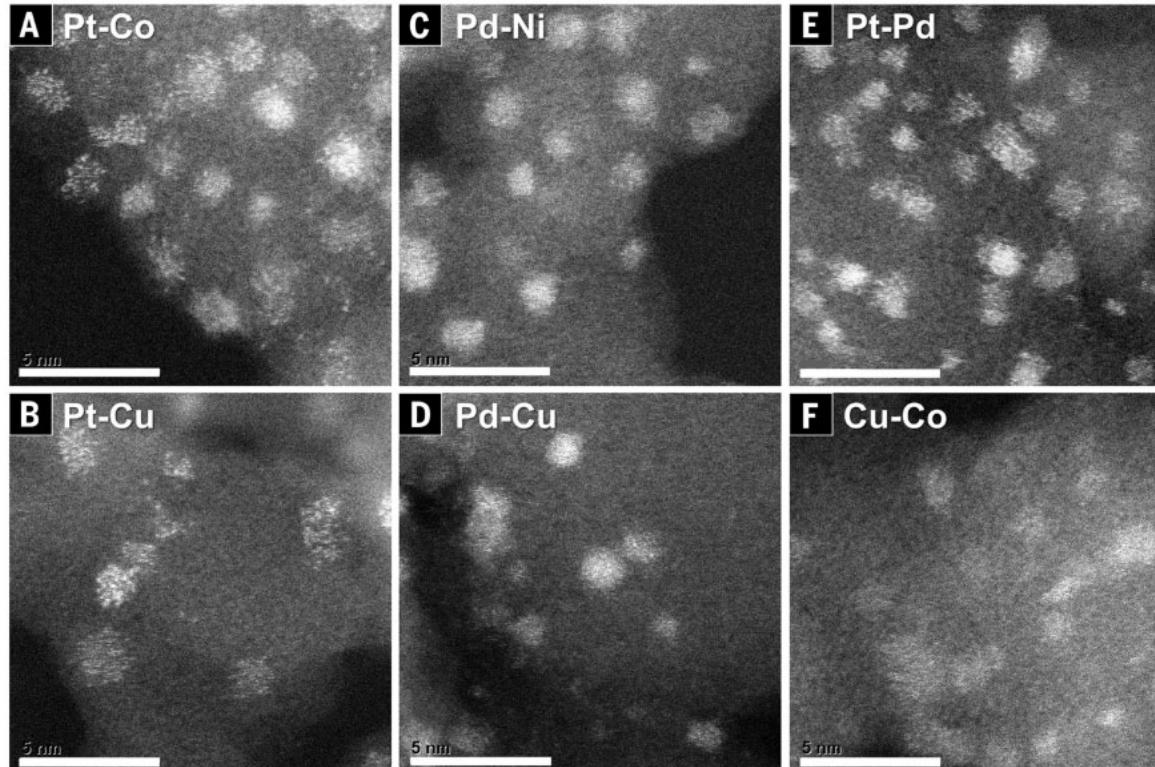


Fig. 3. Atomically resolved Z-contrast images showing NP speckling of alloys. (A and B) Pt-Co and Pt-Cu, separated by two rows in the table of elements. (C to E) Pd-Ni, Pd-Cu, and Pt-Pd, separated by one row. (F) Cu-Co, in the same row. Scale bars, 5 nm.

CATALYSIS

Synthesis of ultrasmall, homogeneously alloyed, bimetallic nanoparticles on silica supports

J. Regalbuto^{1*}

One metal have a variety of applications and synthesis techniques for this type of particles that lack the interactions between the different metals. We demonstrate a method to produce highly dispersed, well-alloyed bimetallic and base metals (platinum, palladium, copper) with average particle sizes from 0.9 to 1.5 nm resolution imaging and x-ray analysis of ultrasmall nanoparticles.

15 interactions

current,^a and

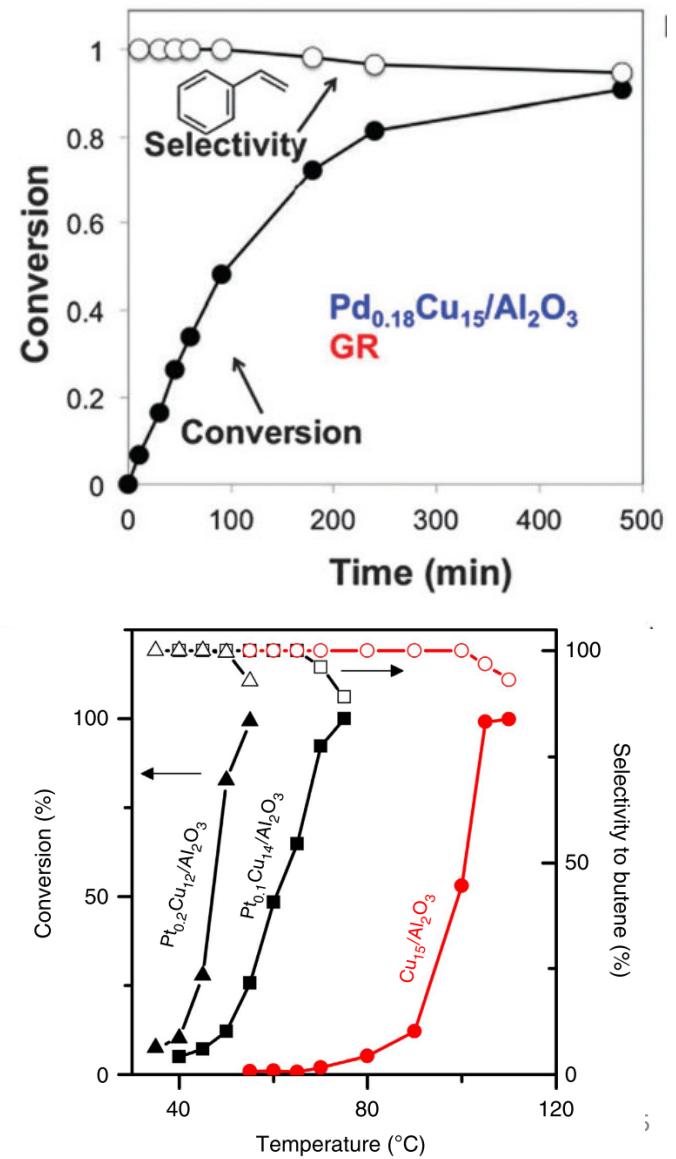
amounts of Pd, for model single atom uptake, dissociation, by addition of trace amounts of phenylpyridine or phenylpyridine pressure of hydrocarbons higher activity for catalysis while maintaining activity to styrene is found for Pd catalysts with XRD and UV-visible spectroscopy. Scanning tunnelling microscopy has been used to study the feasibility of a wide range of Pd

Alloy catalysts for the hydrogenation of 1-hexyne†

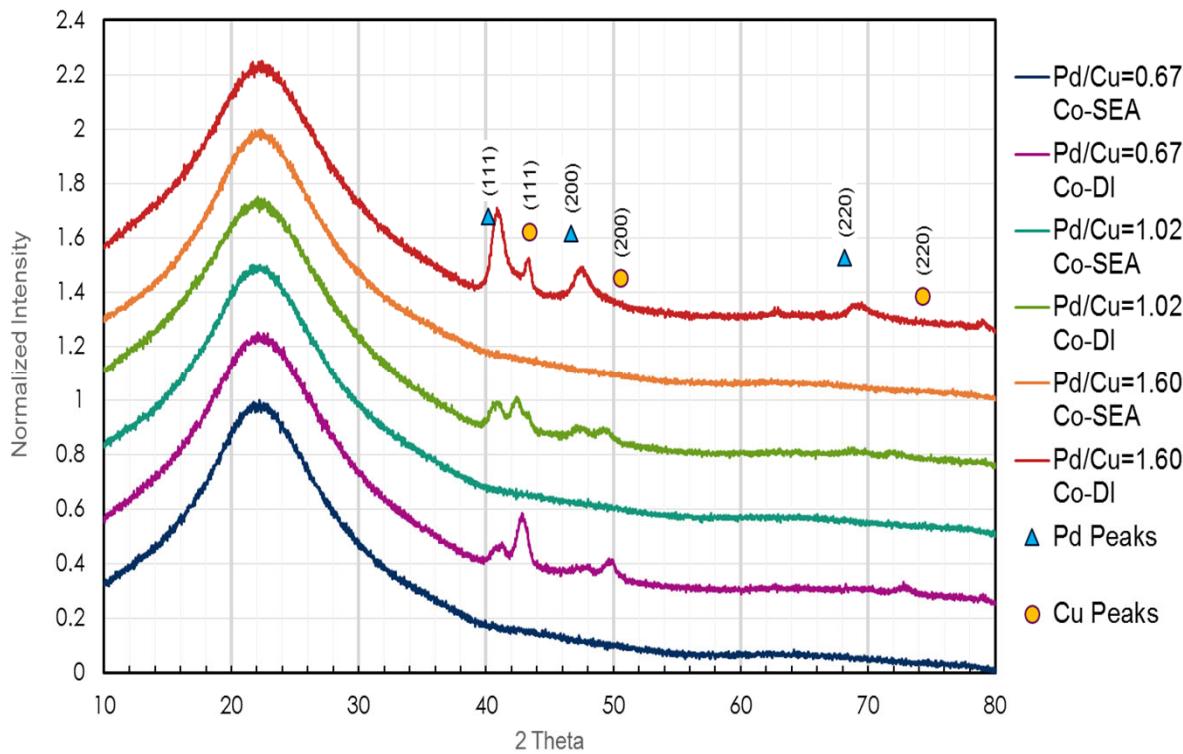
Jing Cao,^a Christos I. Manopoulos^{*a}

Review of Literature – Applications

- High selectivity of phenylacetylene hydrogenation to styrene using $Pd_{0.18}Cu_{15}/Al_2O_3$ than either monometallic catalyst at comparable conversion. (Boucher, M. B., Zugic, B., Cladaras, G., Kammert, J., Marcinkowski, M. D., Lawton, T. J., ... Flytzani-Stephanopoulos, M. (2013). *Phys.Chem.Chem.Phys.*, 2013, 15 12187-12196)
- $Ni_{0.01}Cu$ NPs lowers the barrier of C-H bond activation to improve catalytic activity of Cu for ethanol dehydrogenation.(Shan, J., Liu, J., Li, M., Lustig, S., Lee, S., & Flytzani-Stephanopoulos, M. (2018). *Applied Catalysis B: Environmental*, 226, 534–543)
- Selective partial hydrogenation of 1,3-butadiene using $Pt_{0.2}Cu_{12}/Al_2O_3$ to butene to increase the purity of alkenes feedstock used in polymerization.(Lucci, F. R., Liu, J., Marcinkowski, M. D., Yang, M., Allard, L. F., Flytzani-Stephanopoulos, M., & Sykes, E. C. H. (2015). *Nature Communications*, 6, 1–8.)



Why use Strong Electrostatic Adsorption?



XRD Plot of Silica-Supported Bimetallic Pd and Cu with varying molar ratios using co-Dry Impregnation and co-SEA Synthesis method

Advantages of SEA:

- Deposition thru adsorption of metal complex with strong attraction to the support prevents the formation of larger particle size during the reduction process.
- Simple method which could be extended to Charged Enhanced Dry Impregnation

Challenges in using co-SEA

- Stability of metal complex on surface during co-adsorption
(Ammonia Environment for ammine complex stability)
- Predictability of bimetallic ratio of final supported metal catalyst.
(Metal Complex precursor concentration within one monolayer of maximum surface density)

Objective & Significance of the work:

- Objective:

To synthesize and characterize supported bimetallic alloy at dilute limit prepared by the method of simultaneous strong electrostatic adsorption.

To evaluate catalyst activity and selectivity on promising catalytic reactions involving Dilute Limit Alloy.

- Significance:

A generalizable method of preparing dilute limit alloy of one metal (precious) in another metal that is simpler without the limitation of reduction potential compatibility.

Question: Can we make a dilute limit alloy via co-SEA method?

- Limitations

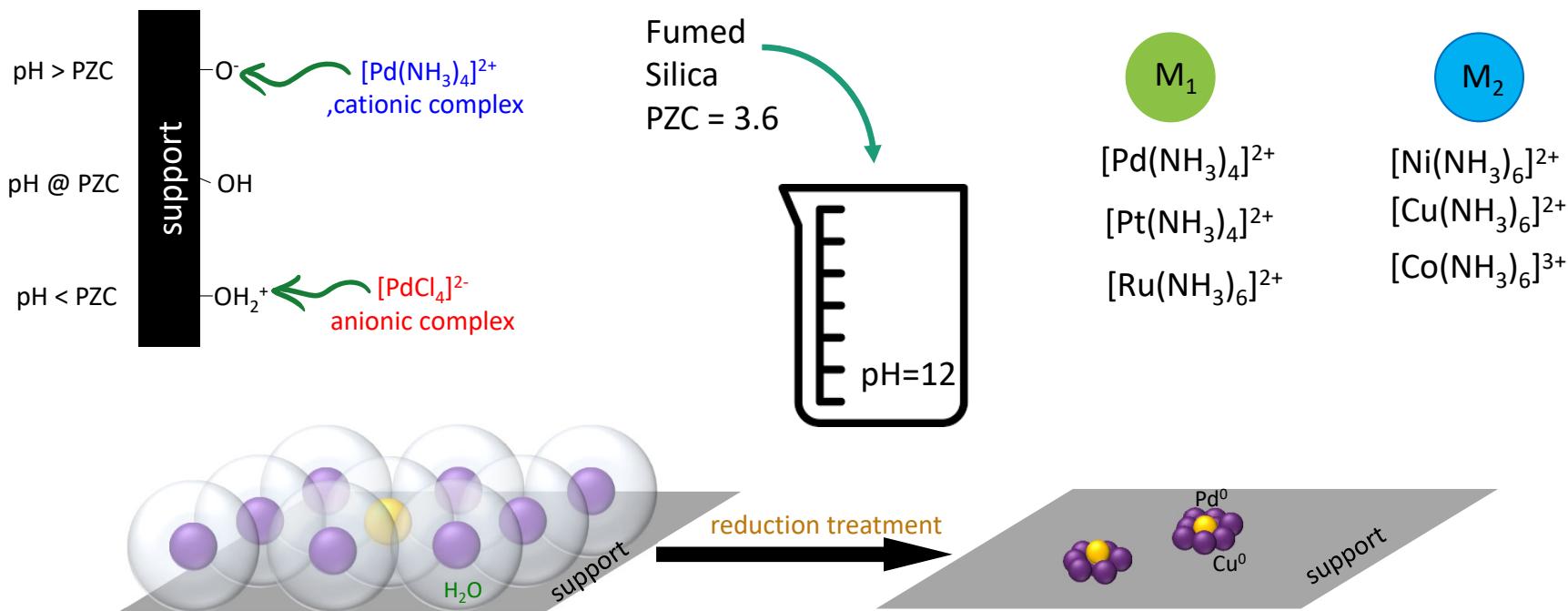
Maximum metal loading is dependent on the available surface density of the support for strong electrostatic adsorption.

Requires an oppositely charged and stable metal complex precursors from that of the support

Methodology:

- Extending the method of co-SEA to dilution limit of one or two atoms in a crystallite of 30 or 40 atoms. The synthesis of various combinations of representative metals (Ru, Pd, Pt, Ni, Co, and Cu) on high surface area amorphous silica were made
- Catalyst characterization includes using high sensitivity powder x-ray diffraction, aberration-corrected electron microscopy, temperature programmed reduction, X- ray photoelectron spectroscopy and FTIR spectroscopy. Catalyst activity will be tested on reactions requiring enhanced selectivity

Methodology: Charged metal precursors are strongly adsorbed onto oppositely charged oxide or carbon surfaces by controlling the pH relative to the surface point of zero charge (PZC)



- resulting close packed monolayer of ionic complex (retaining hydration sheaths) with **strong interaction** with support

- decreased mobility of metal atoms result in smaller catalyst particles (compared to simple impregnation)

Methodology: co-SEA Synthesis Condition

Parameter	Values
High Surface Area Support	Amorphous Silica (Aerosil® 300)
Support Surface Area	~315 m ² /g
Surface Loading for SEA	1000 m ² /L
Initial pH	12
Adsorption time	15 mins
Shaking speed	120 rpm
Metal Precursors	Metal Ammine Complexes
Metal Complex Total Concentration	~ 1 µmole/m ²
Desired Metal Molar Ratios	1:30 (typical)
Drying Conditions	Overnight RT drying + 4 hrs @120°C in muffle furnace
Reduction condition	1 hr at 400°C, 5C/min Ramp Rate under 20%H ₂ /80%N ₂ Gas

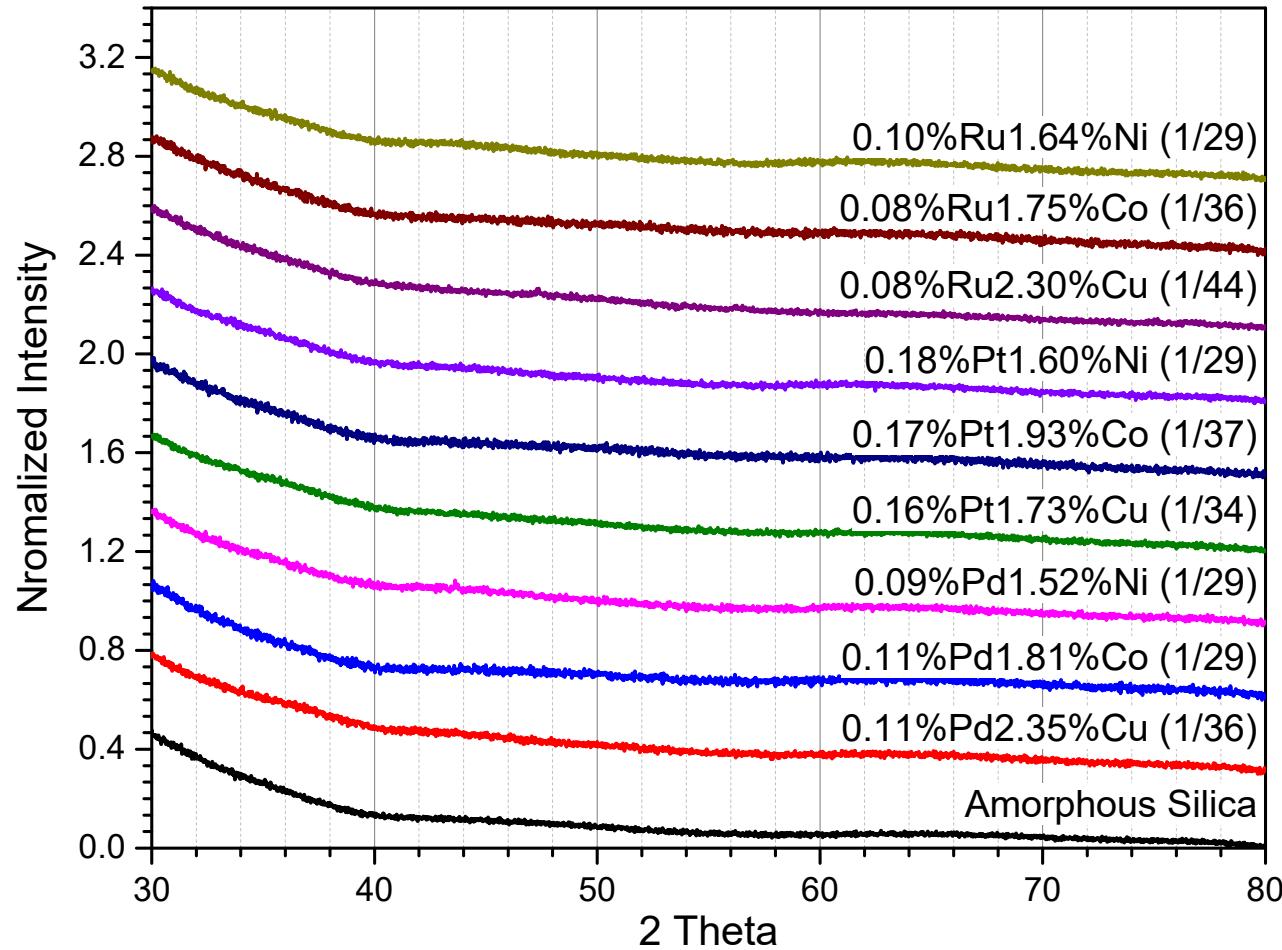
Results:

As Synthesized Dilute Limit Alloy Catalyst

Metal 1	Metal 2	As Synthesized Catalyst (wt%)	Molar Ratio (M2/M1)	Total Surface Density ($\mu\text{mole}/\text{m}^2$)
Palladium	Copper	0.11%Pd2.35%Cu/SiO ₂	36	1.2
	Cobalt	0.11%Pd1.81%Co/SiO ₂	29	1.0
	Nickel	0.09%Pd1.52%Ni/SiO ₂	29	0.9
Platinum	Copper	0.16%Pt1.73%Cu/SiO ₂	34	1.0
	Cobalt	0.17%Pt1.93%Co/SiO ₂	37	1.1
	Nickel	0.18%Pt1.60%Ni/SiO ₂	29	0.9
Ruthenium	Copper	0.08%Ru2.30%Cu/SiO ₂	44	1.2
	Cobalt	0.08%Ru1.75%Co/SiO ₂	36	1.0
	Nickel	0.10%Ru1.64%Ni/SiO ₂	29	0.9

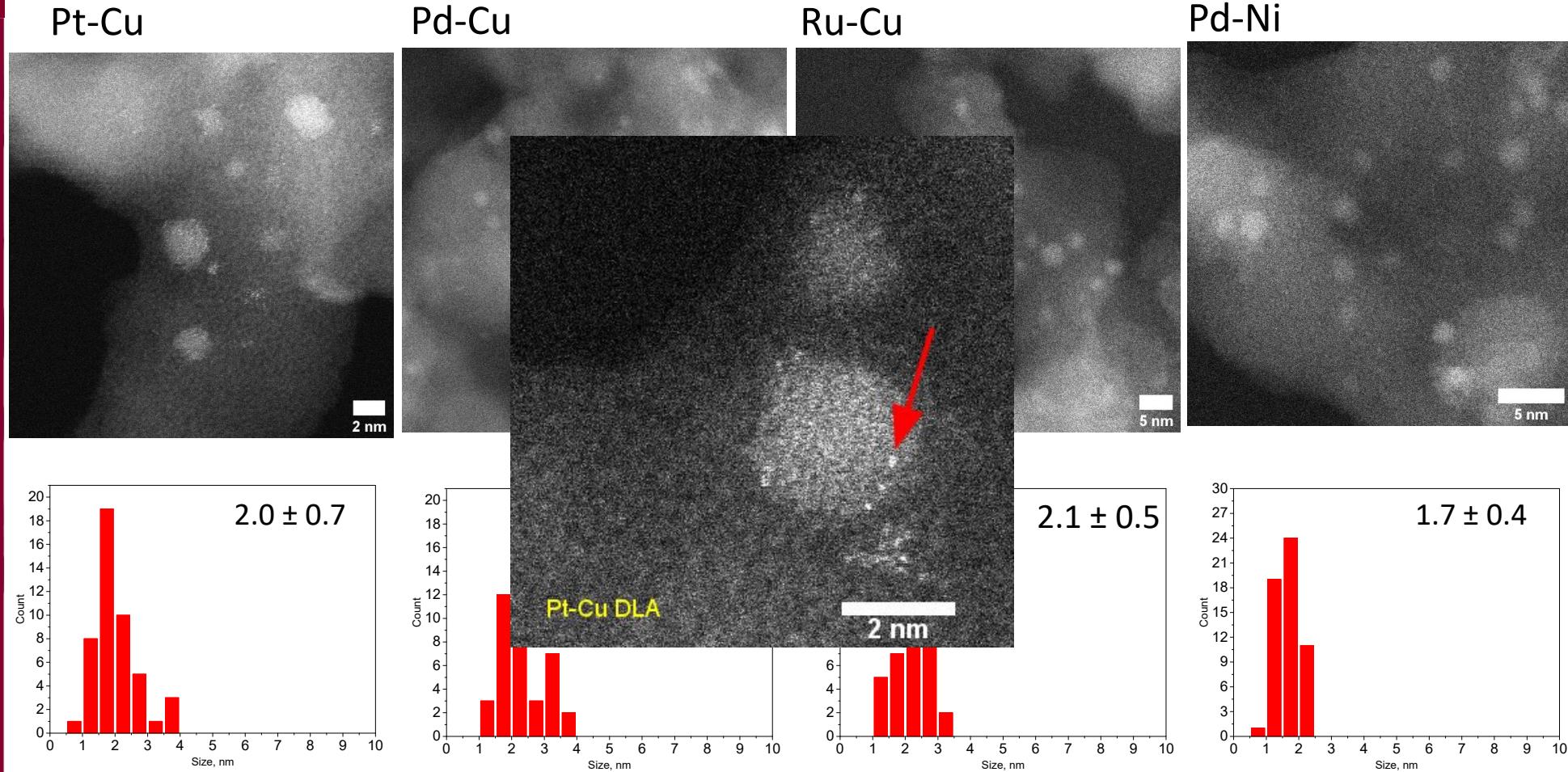
Results:

XRD Pattern for Dilute Limit Alloy Bimetallic Catalyst

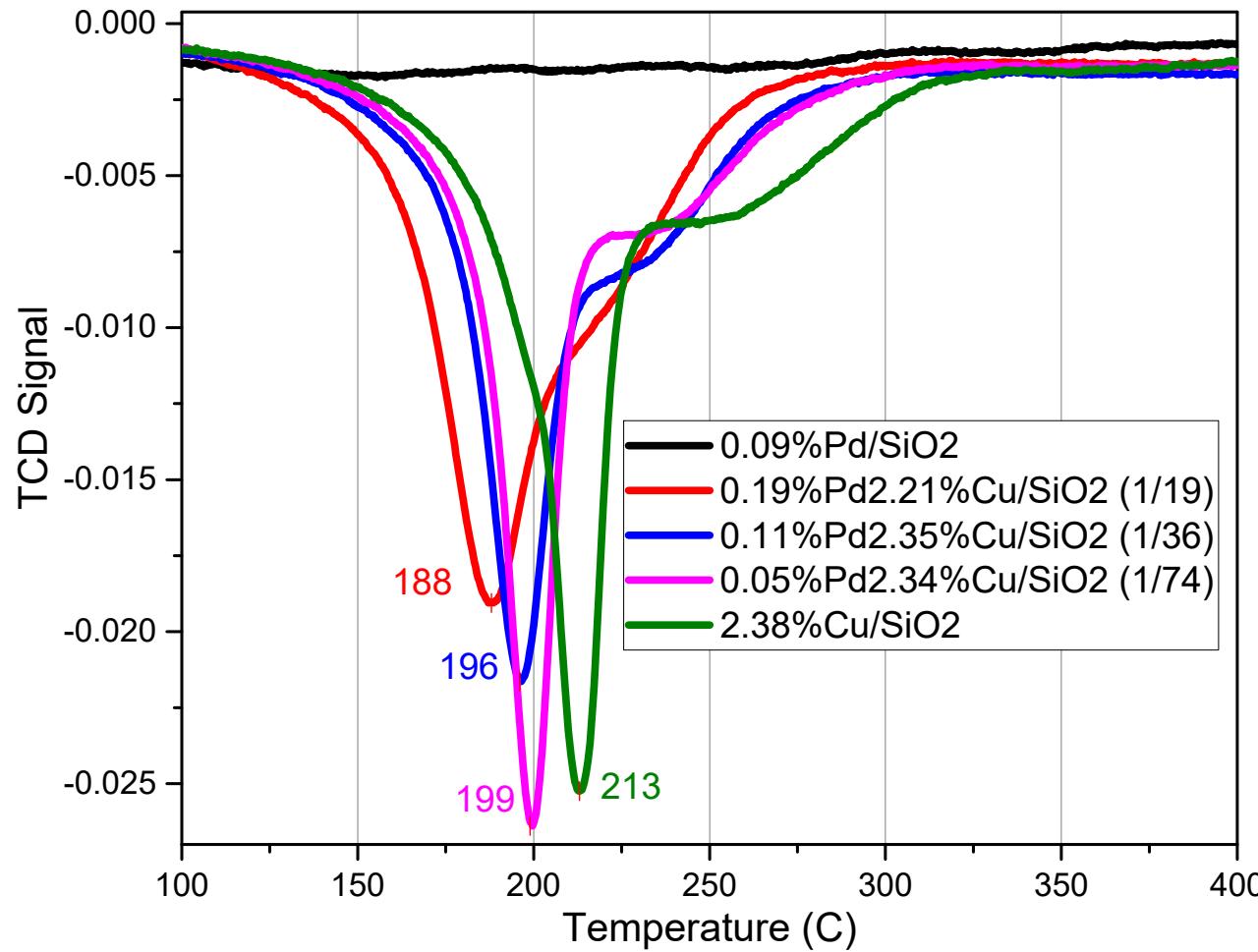


No visible sharp peak for large nanoparticles.

Results: STEM Images of Dilute Limit Alloy

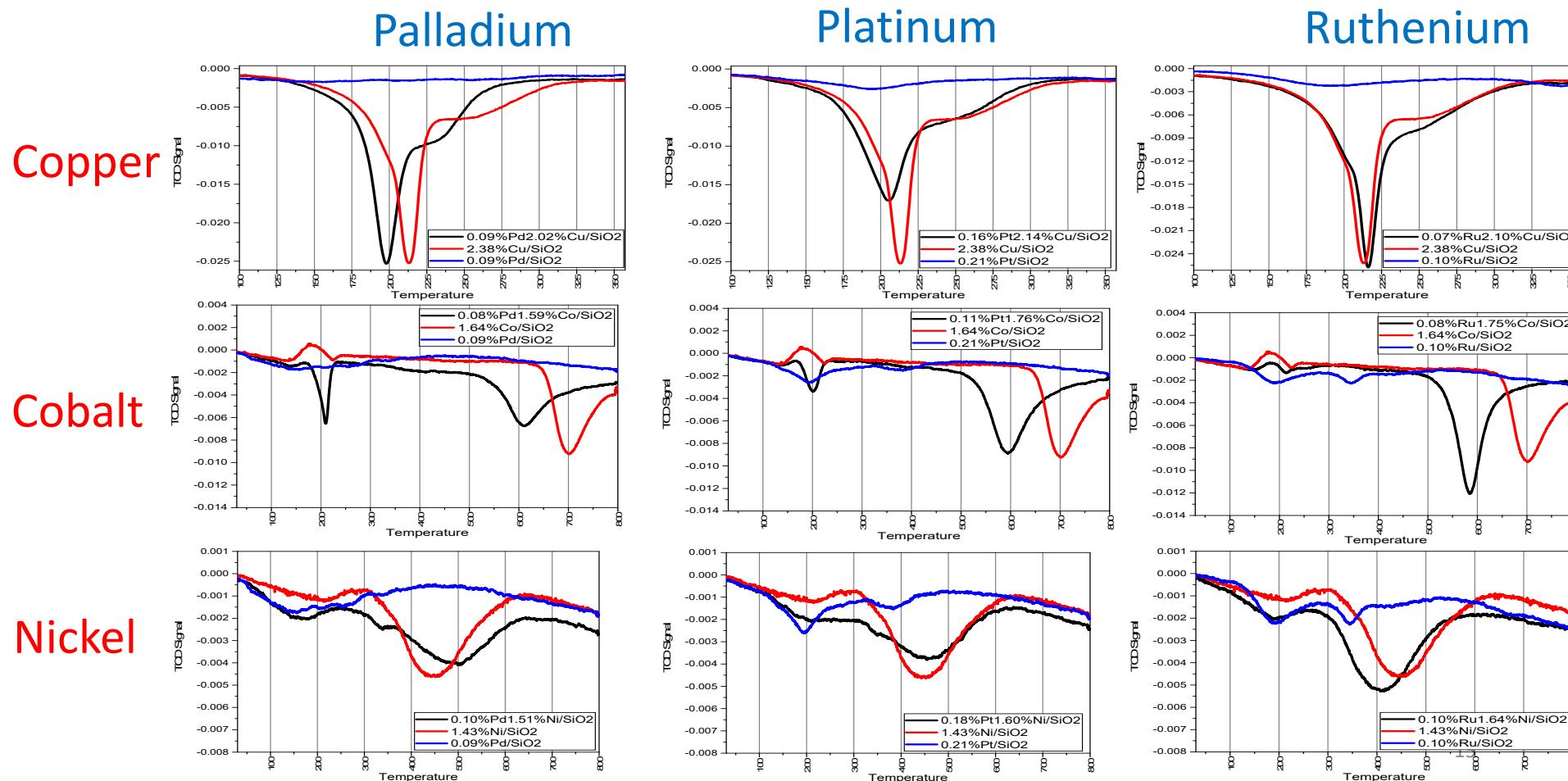


Results: TPR Profile of Dried SEA samples of Pd, Cu, and PdCu on Amorphous Silica Support



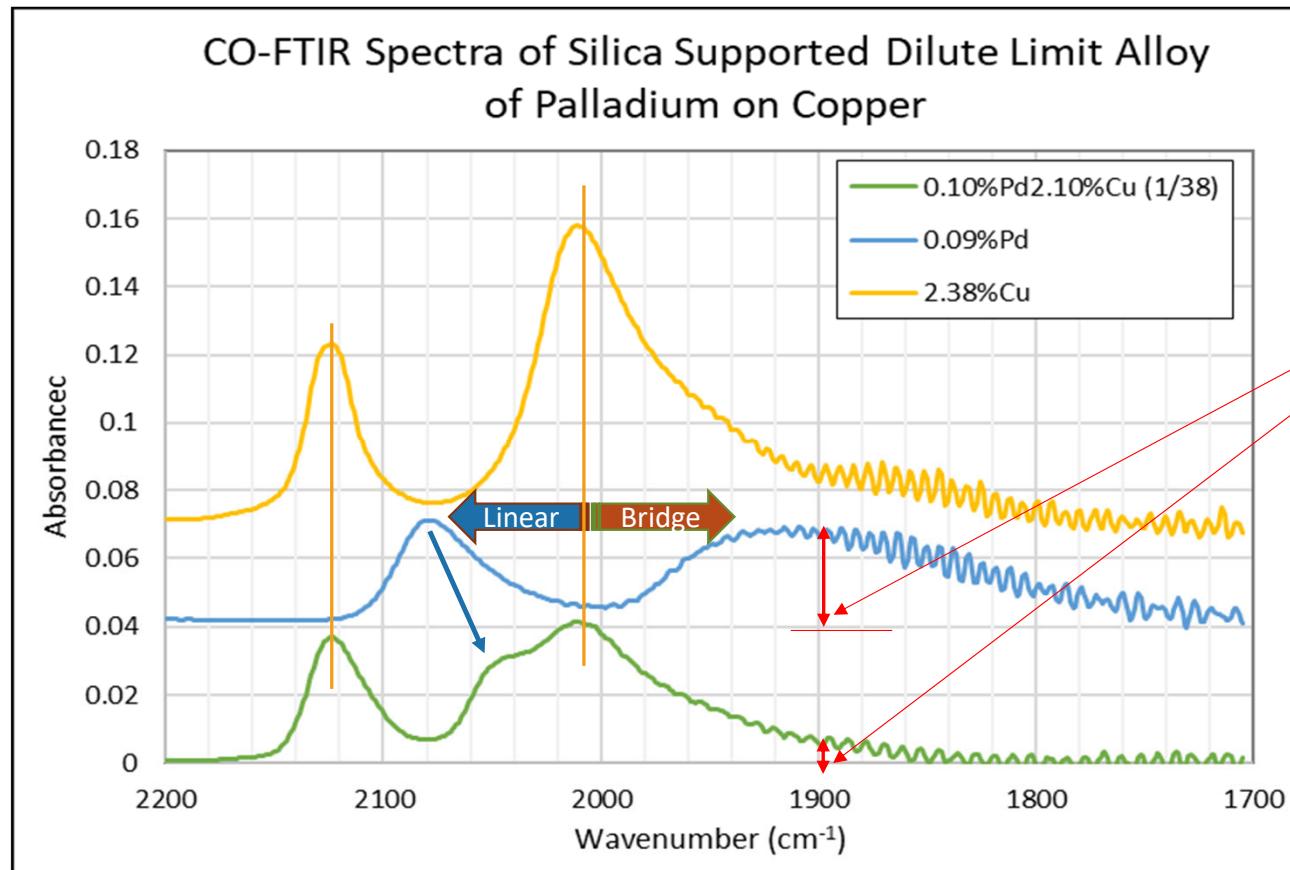
- decrease of Cu reduction T even with very dilute amount of Pd (1/74)

Results: TPR Profile of Monometallic and Bimetallic at Dilute Limit



- Generally, the addition of dilute amount of palladium, platinum or ruthenium lowers the reduction Temperature of the abundant metal

Results:



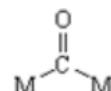
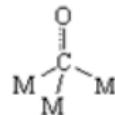
A significant decrease in intensity of the bridged CO region was observed with the dilute limit alloy of Pd on Cu

Red shift in linear Pd-CO peak

No Shift of Copper CO adsorption peak



L: Linear Pd-CO: 2078 cm^{-1}



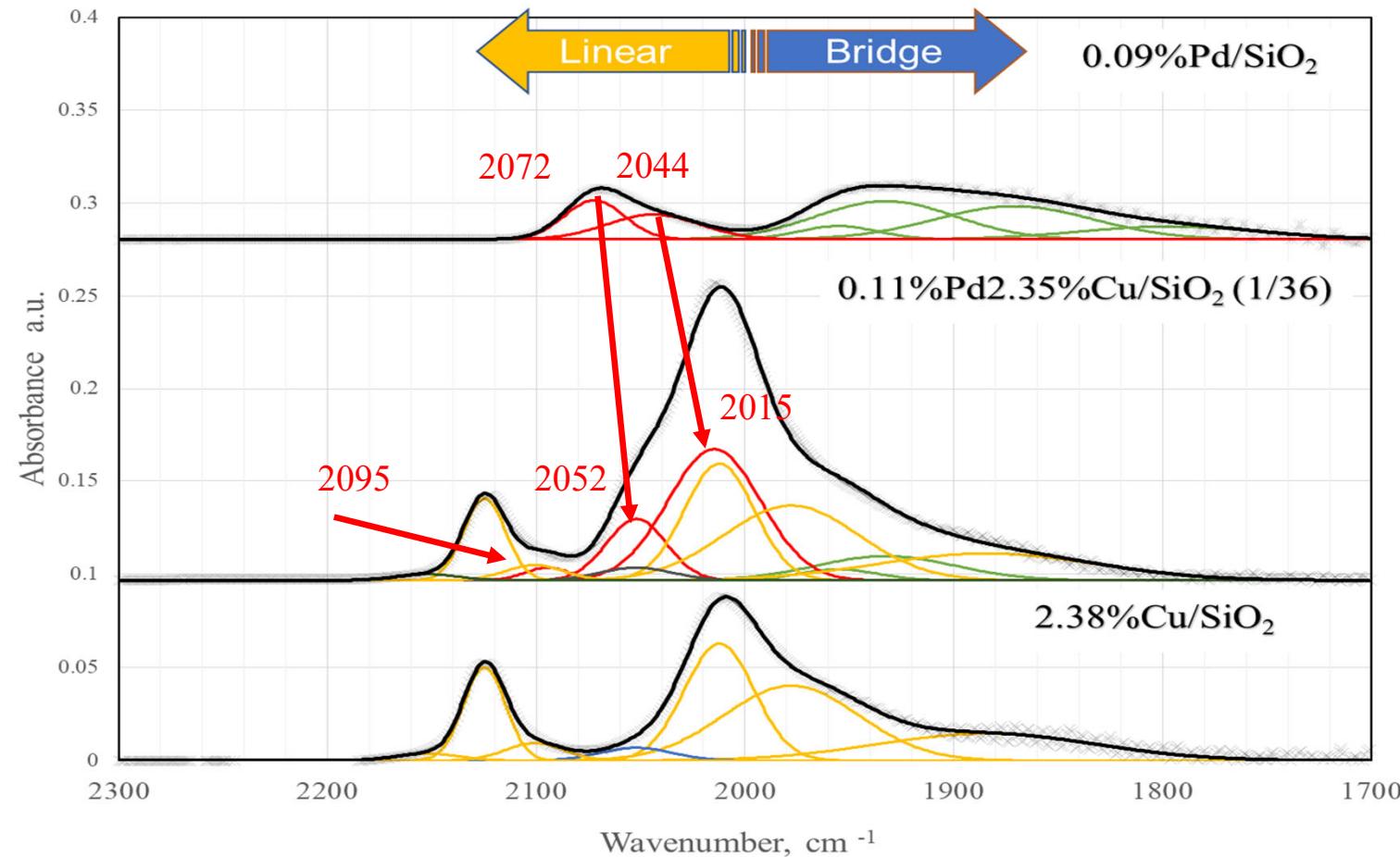
B: di-coordinated, bridging CO, $\text{Pd}_2\text{-CO}: 1948, 1970 \text{ cm}^{-1}$

H: triply bridging CO, $\text{Pd}_3\text{-CO}: 1815, 1830, 1889 \text{ cm}^{-1}$

Results:

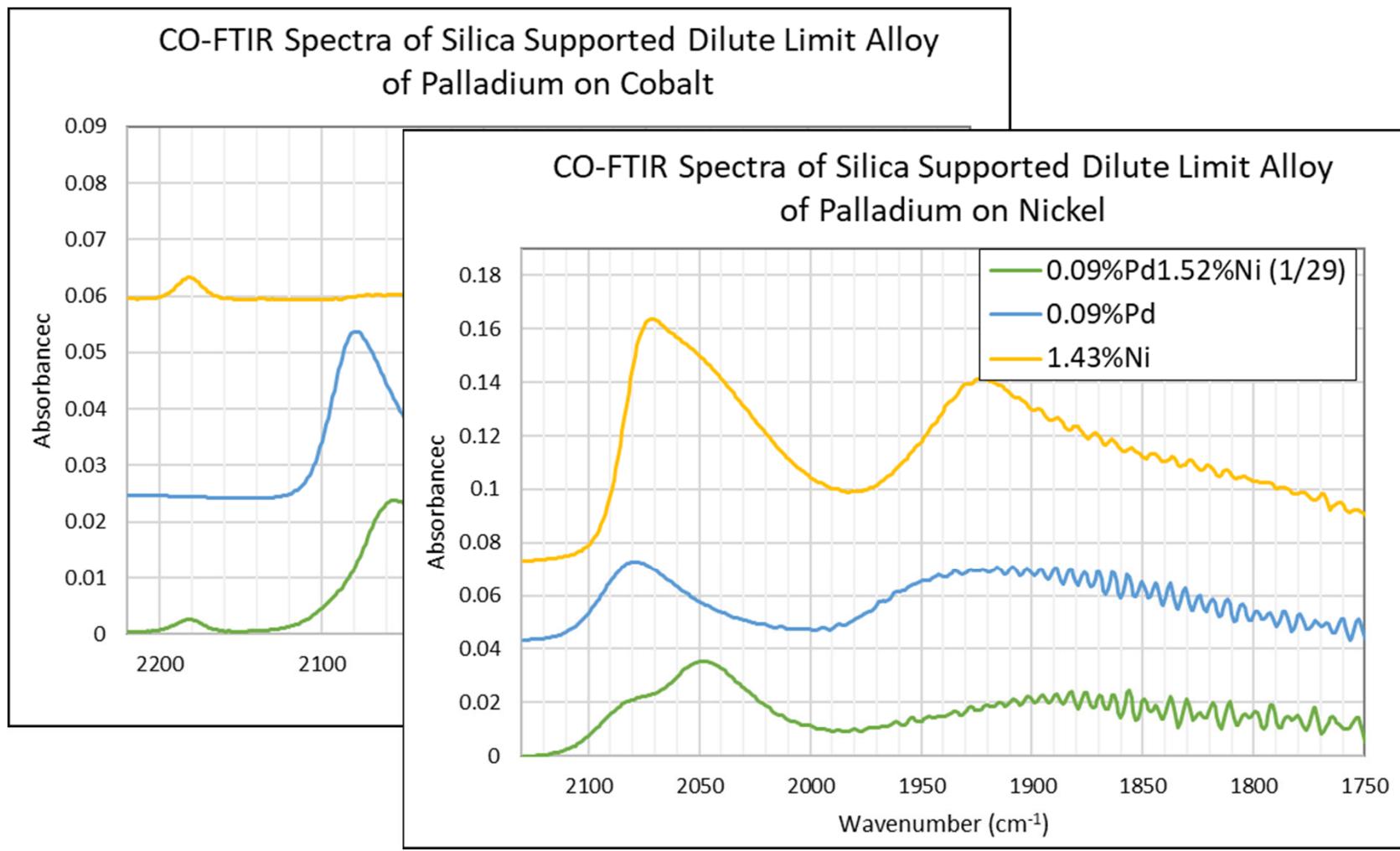
The palladium wavenumber corresponding to linearly adsorbed CO on palladium shifted from 2044 and 2072 to 2015 and 2052 cm^{-1} , respectively.

The Pd-CO species with wavenumber of 2094 cm^{-1} which disappeared in the monometallic Pd catalyst after N₂ Purging is present at dilute limit alloy 2095 cm^{-1}

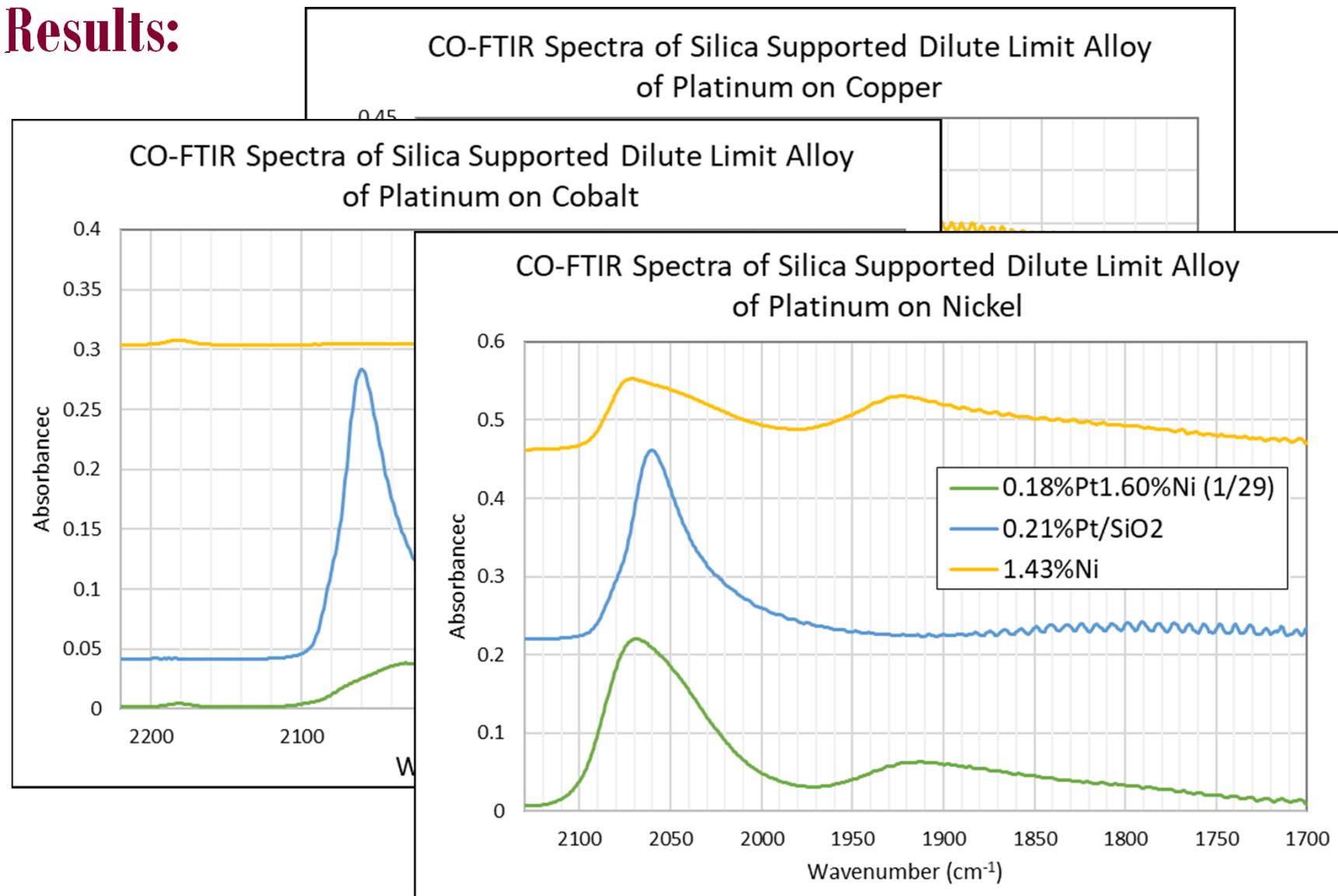


		Palladium							Copper						
		Peak wavenumber	1797	1871	1933	1955	2044	2072	2094	1884	1978	2012	2052	2101	2125
Monometallic	Peak wavenumber	1797	1871	1933	1955	2044	2072	2094	1884	1978	2012	2052	2101	2125	2152
	Width	102	89	79	44	52	34	26	124	76	39	41	33	23	35
Dilute Limit Alloy	Peak wavenumber	1797	1871	1933	1955	2015	2052	2095	1884	1978	2012	2052	2101	2125	2152
	Width	102	89	79	44	52	34	26	124	76	39	41	33	23	35

Results:



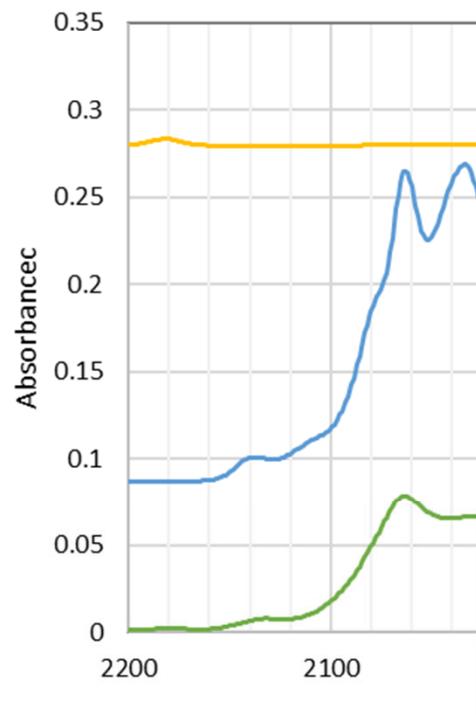
Results:



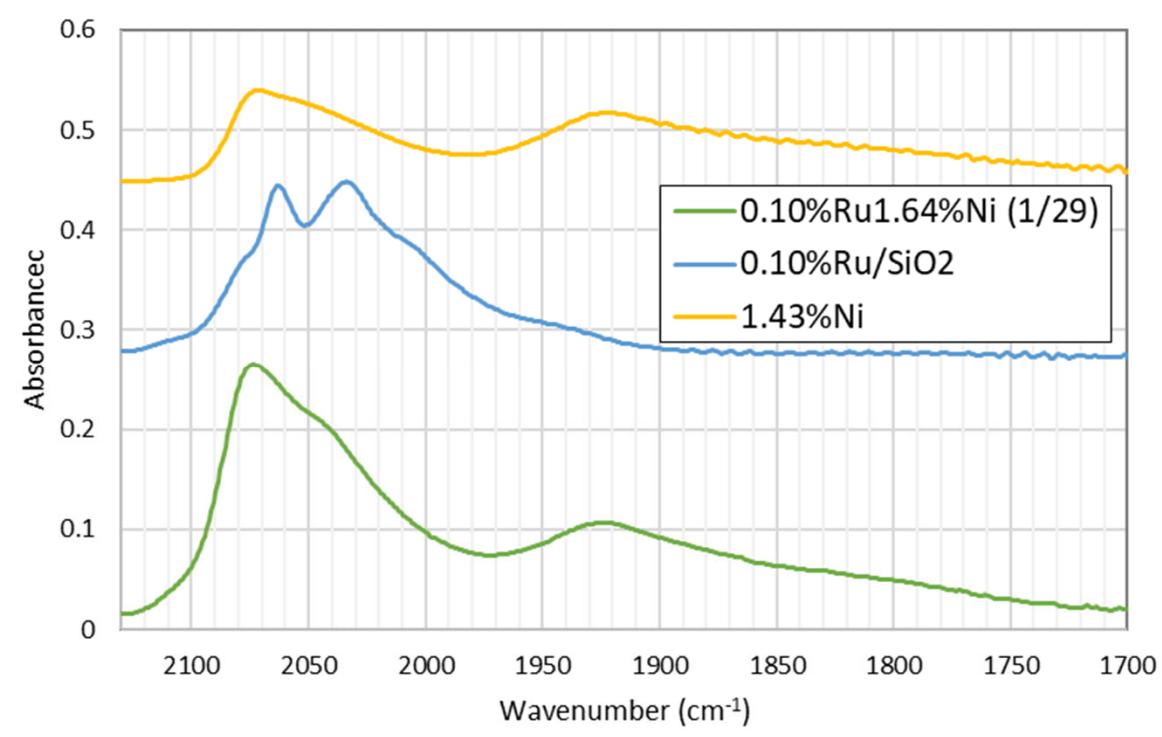
Results:

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Ruthenium on Copper

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Ruthenium on Cobalt



CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Ruthenium on Nickel

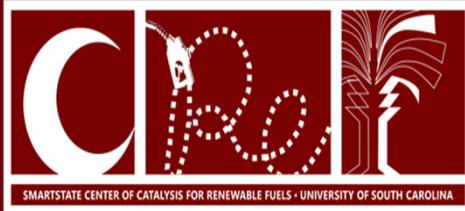


Conclusions and Future Work:

- co-SEA is a facile method in preparing dilute limit alloy bimetallic catalyst
- Particle size for DLA is comparable with the 1:1 bimetallic catalyst
- Proximity of the two metals in DLA is shown by the decrease in reduction temperature (interaction).
- co-FTIR analysis is a viable diagnostic tool for single atom sites.
- The chemical shift in linear CO adsorption peak for the dilute bimetallic as compared with a monometallic suggest a unique environment which strongly support the presence of single atom sites on another metal.
- The charging on silica support during stem analysis makes the imaging of single atom sites difficult especially for low Z-contrast sample.
- Catalyst activity and selectivity using a model catalytic reaction will be made to determine how a dilute limit alloy compares with a monometallic and 1:1 bimetallic catalyst.

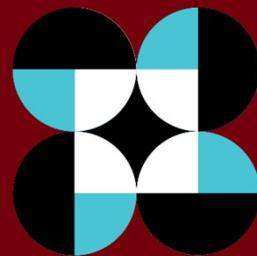
Reference:

- [1] J. Shan, J. Liu, M. Li, S. Lustig, S. Lee, and M. Flytzani-Stephanopoulos, “NiCu single atom alloys catalyze the CH bond activation in the selective non- oxidative ethanol dehydrogenation reaction,” *Appl. Catal. B Environ.*, vol. 226, pp. 534–543, Jun. 2018.
- [2] L. Zhang *et al.*, “Efficient and durable Au alloyed Pd single-atom catalyst for the Ullmann reaction of aryl chlorides in water,” *ACS Catal.*, vol. 4, no. 5, pp. 1546–1553, 2014.
- [3] M. B. Boucher *et al.*, “Single atom alloy surface analogs in Pd_{0.18}Cu₁₅ nanoparticles for selective hydrogenation reactions,” pp. 12187–12196, 2013.
- [4] A. Wong, Q. Liu, S. Griffin, A. Nicholls, and J. R. Regalbuto, “Synthesis of ultrasmall, homogeneously alloyed, bimetallic nanoparticles on silica supports,” vol. 1430, no. December, pp. 1427–1430, 2017.
- Thang, H. V., Pacchioni, G., DeRita, L., & Christopher, P. (2018). Nature of stable single atom Pt catalysts dispersed on anatase TiO₂. *Journal of Catalysis*, 367, 104–114.

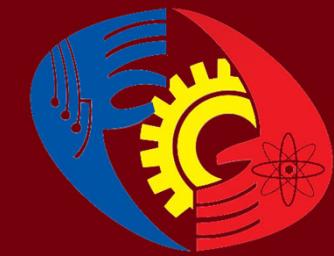


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THANK YOU!



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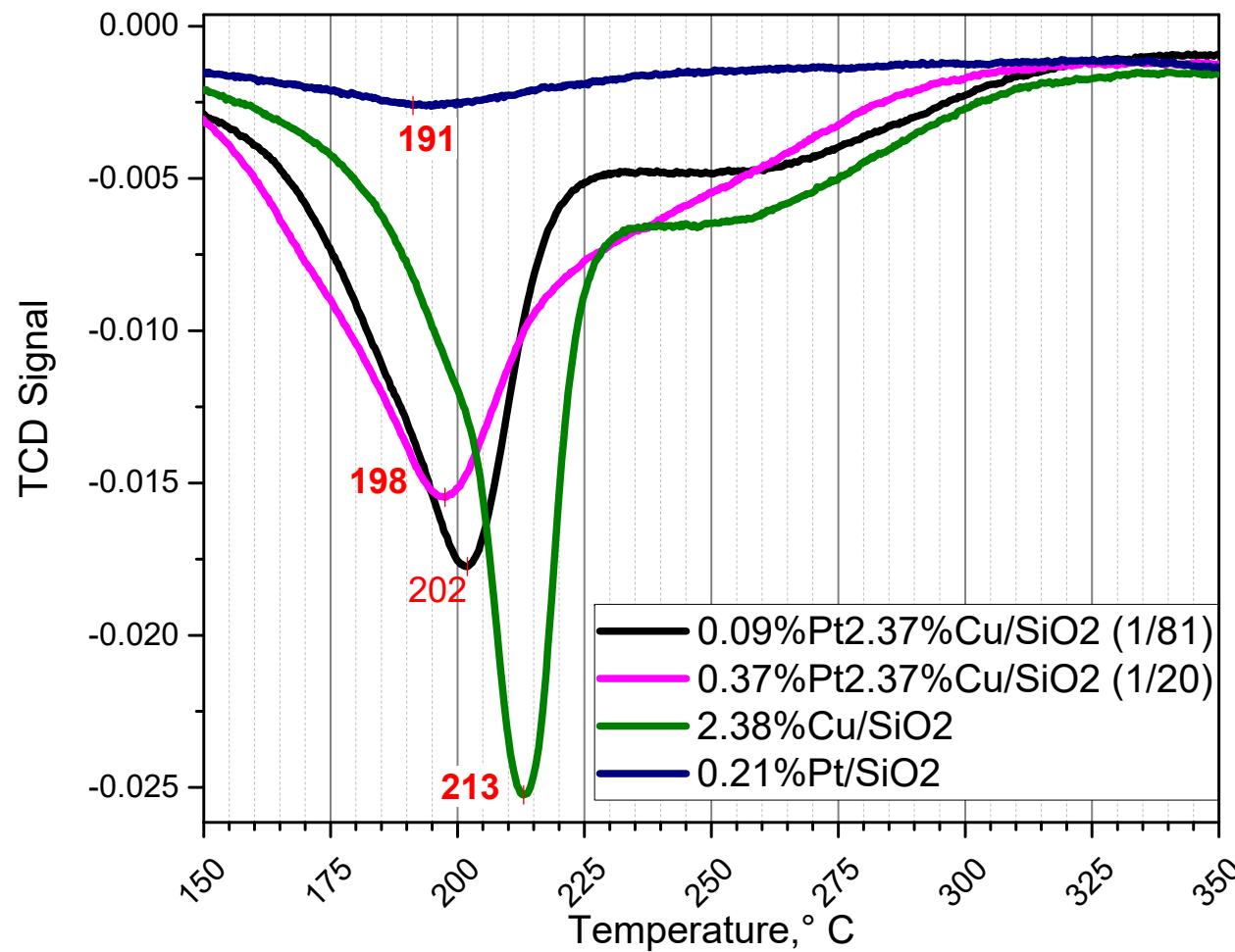
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QUESTIONS?

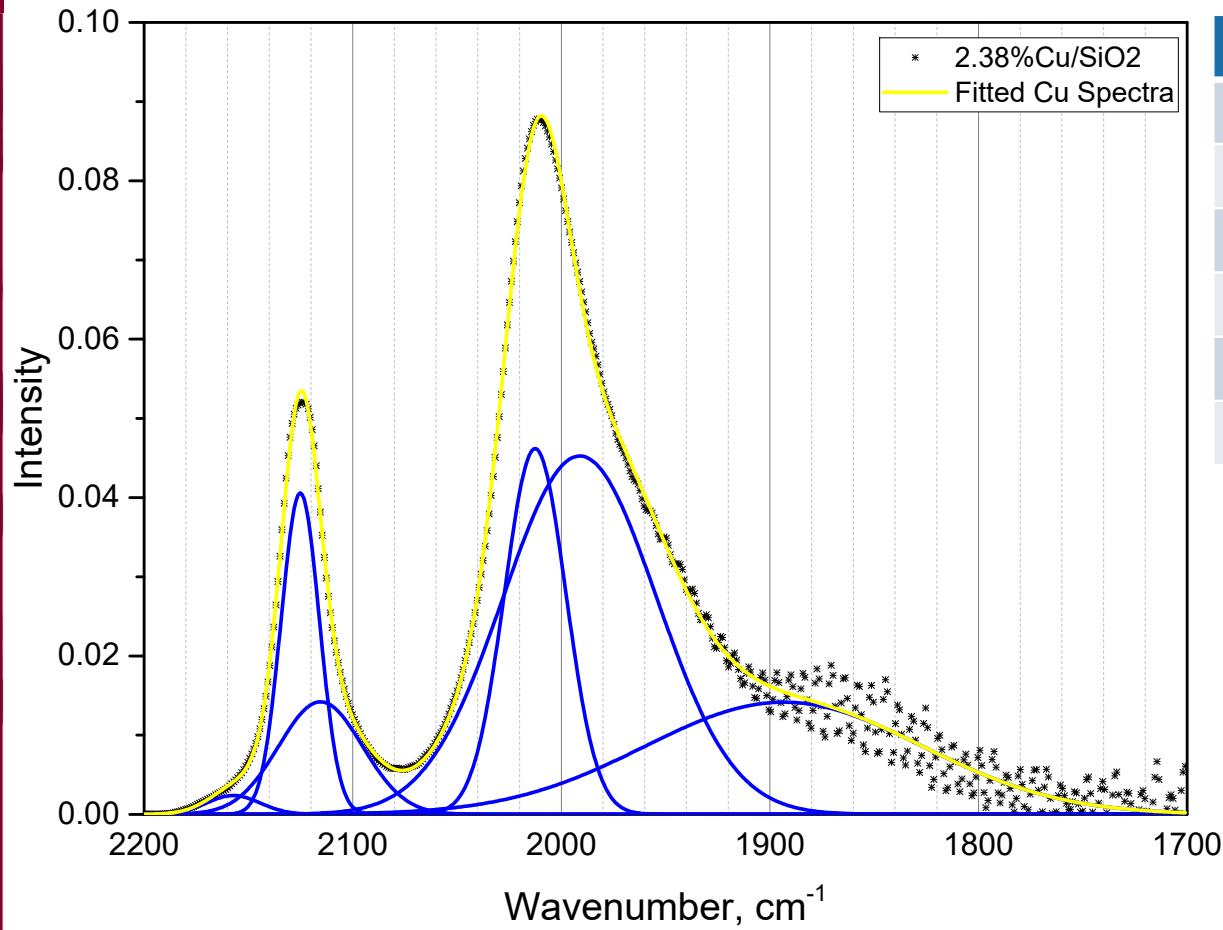
Results: TPR Profile of Dried SEA samples of Pt, Cu, and PtCu on Amorphous Silica Support



- decrease of Cu reduction T even with very dilute amount of Pt (1/81)

Results:

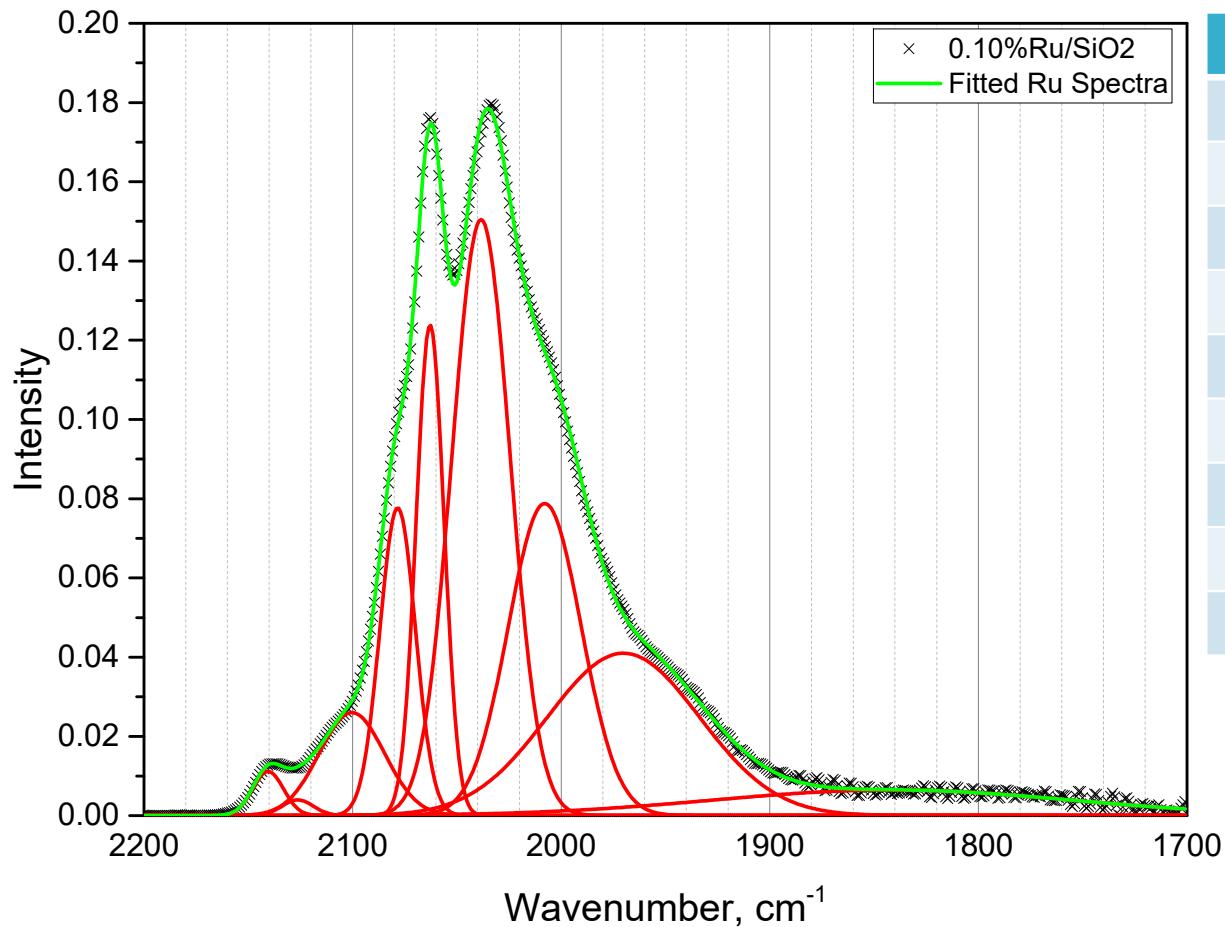
Fitted Cu/SiO₂ Spectra



Center	Height	Area	FWHM
1893	0.014	2.363	156
1991	0.045	4.165	86
2012	0.046	1.705	34
2115	0.014	0.716	47
2125	0.040	0.933	21
2157	0.002	0.076	30

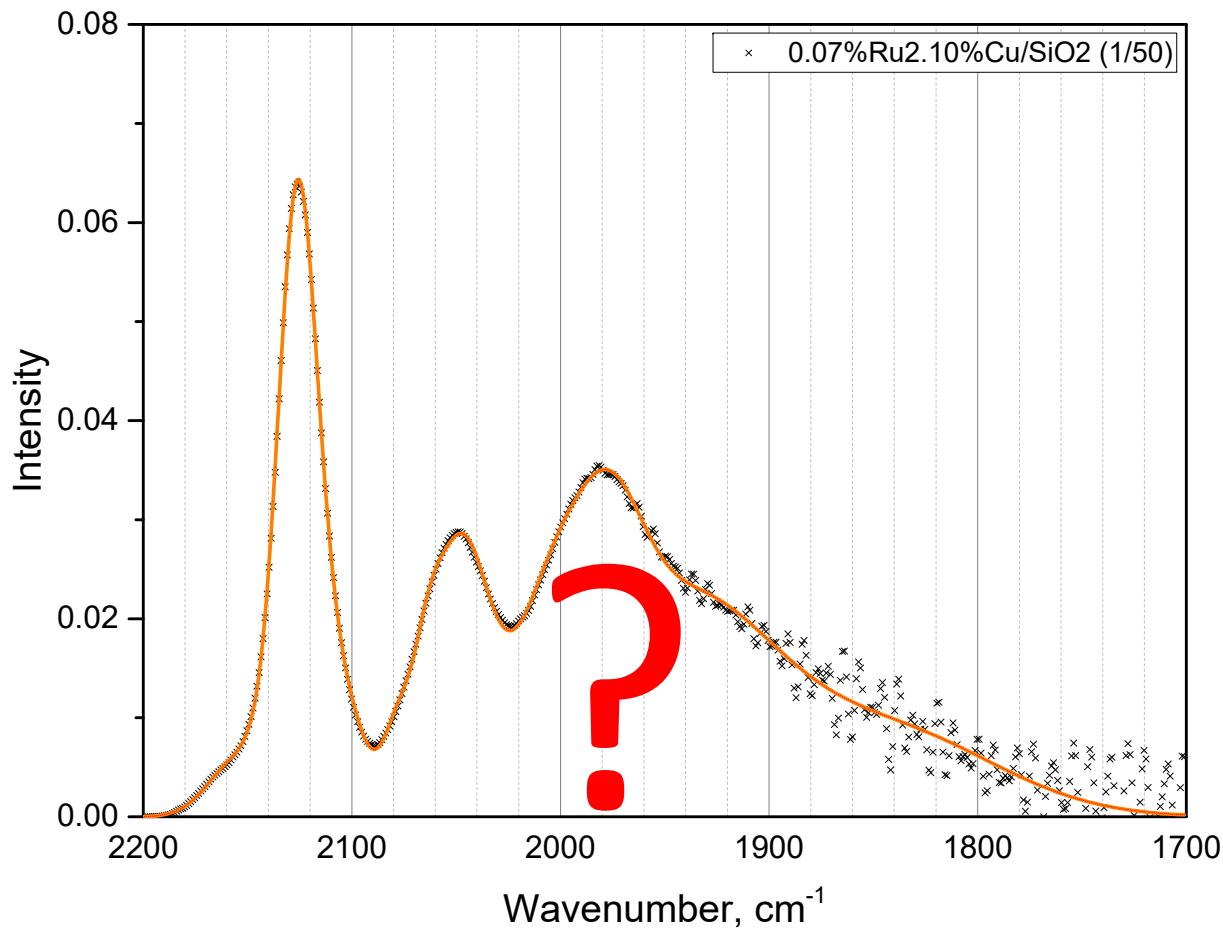
Results:

Fitted Ru/SiO₂ Spectra



Center	Height	Area	FWHM
1841	0.006	1.398	202
1970	0.041	3.749	86
2007	0.078	3.450	41
2038	0.150	5.243	33
2062	0.124	2.071	16
2078	0.077	1.660	20
2100	0.026	1.020	37
2126	0.004	0.074	18
2140	0.011	0.206	17

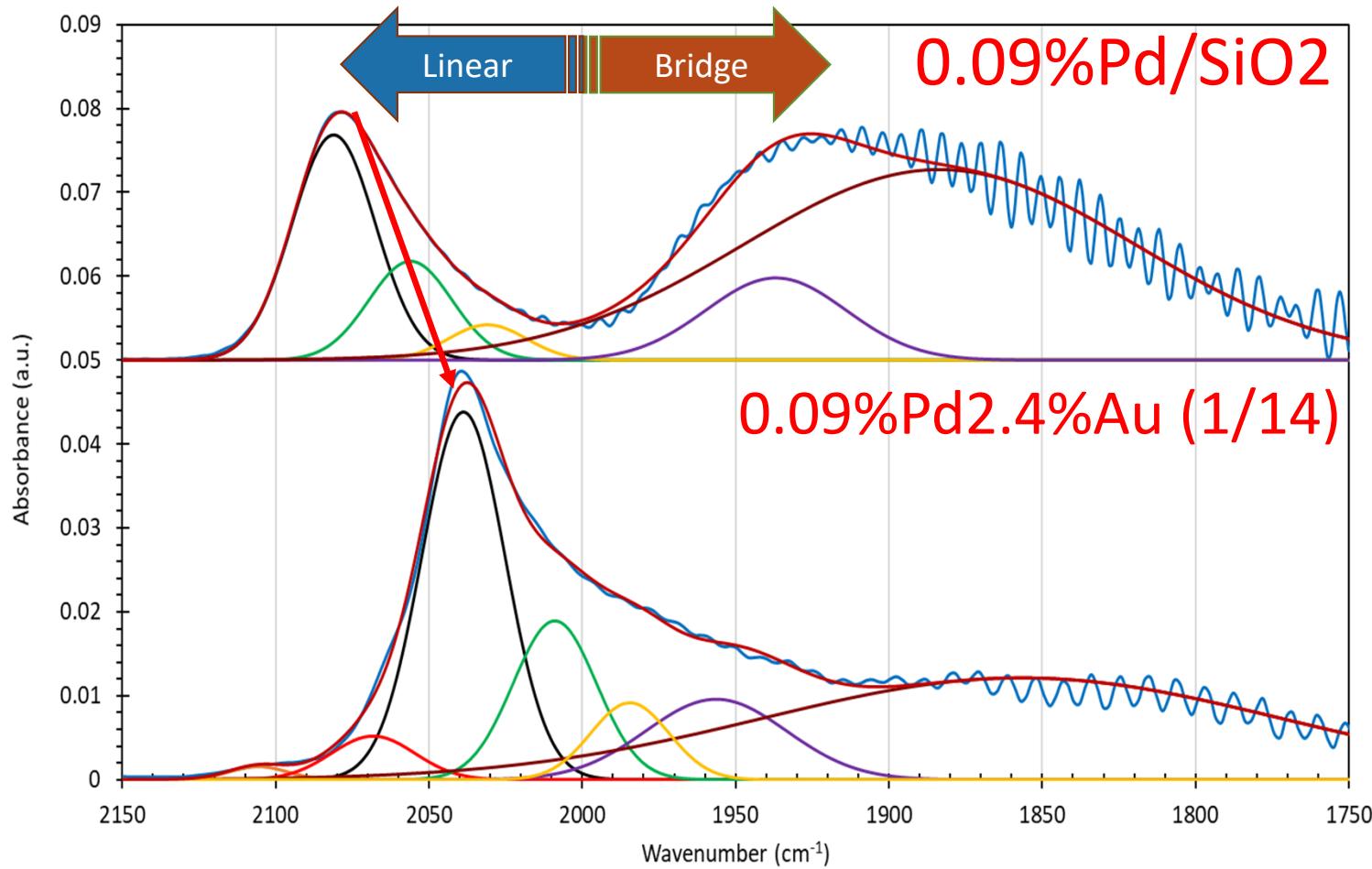
Results: What CO adsorption peaks would fit the Dilute Limit Alloy of RuCu/SiO₂?



Our Approach:

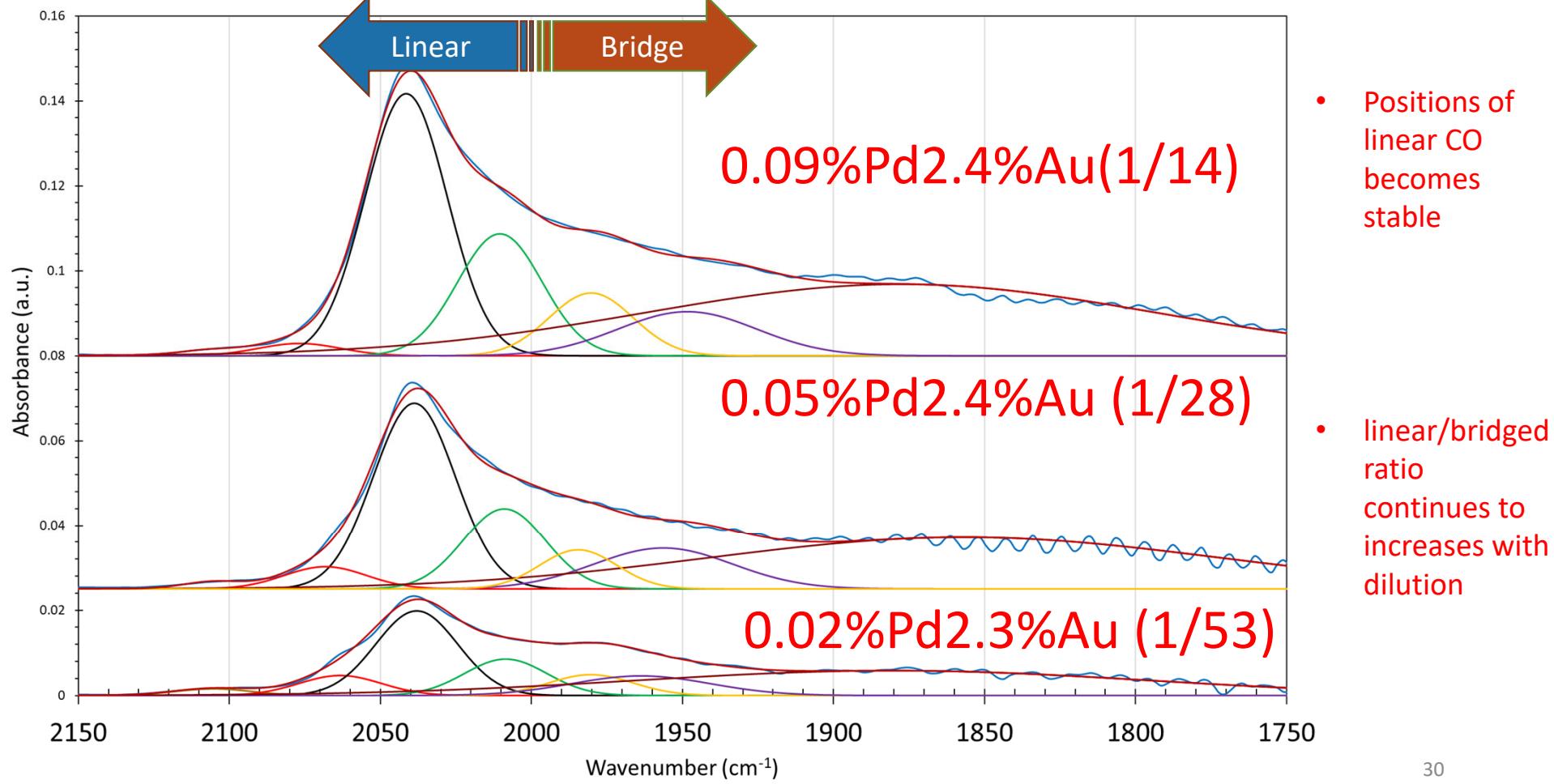
1. Properly Identify monometallic CO adsorption peaks at three stages:
 - At the onset of CO Flow
 - At the saturated CO
 - After Inert gas purging of CO
2. Use the identified peaks from monometallic and fit the dilute limit alloy spectra using the same center and FWHM of the monometallic
3. Peaks for linear-CO may imply single atom sites.

Results: CO-FTIR Spectra Analysis for Silica-Supported Dilute Limit Alloy of Palladium on Gold

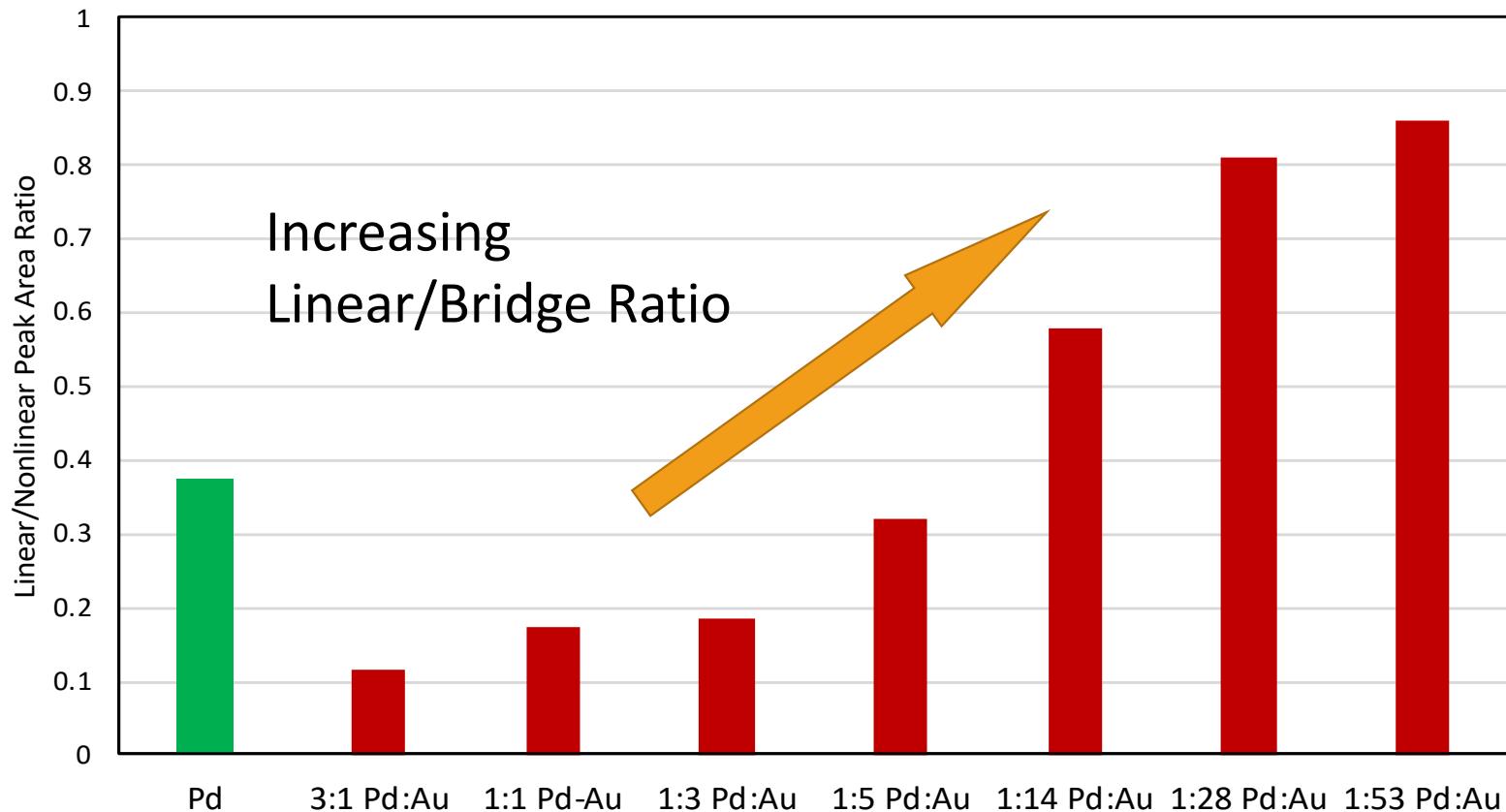


- linear CO appears to exist on a variety of sites
- linear /bridged ratio increases with dilution
- Linear CO peak shifted to a lower wavenumber sites

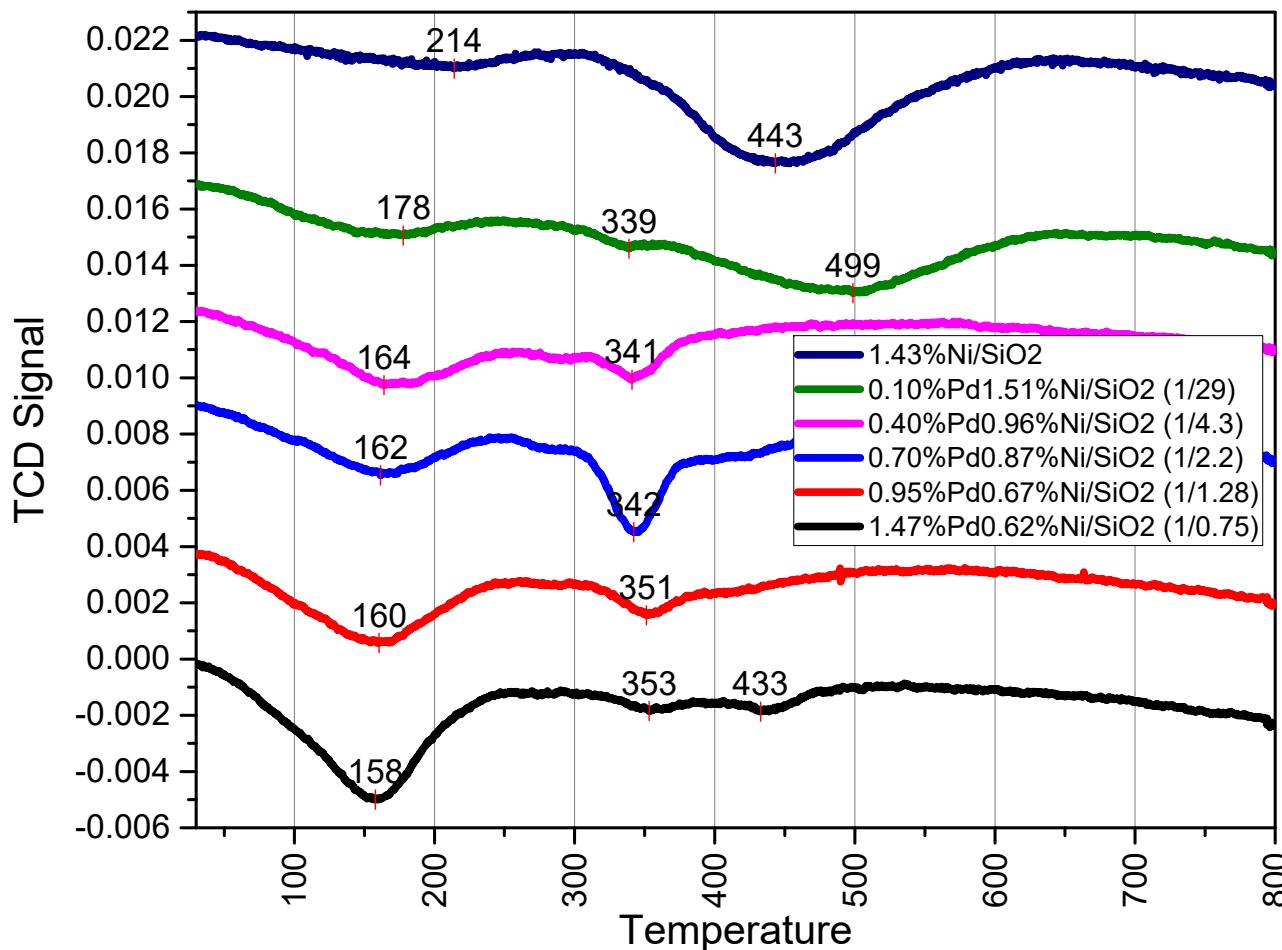
Results: CO-FTIR Spectra Analysis for Silica-Supported Dilute Limit Alloy of Palladium on Gold



Results: Area Ratio of Linear to Bridge CO adsorption vs Pd/Au Ratio



Results: TPR profile of Pd-X Bimetallic up to Dilute Limit



- Lowering of copper reduction peak with dilute amount Palladium
- Lowering of cobalt reduction peak with dilute amount Palladium
- Lowering of nickel reduction peak with dilute amount Palladium

Review of Literature – Characterization by CO-FTIR

CO Adsorption on 1%Pd/SiO₂

Monnier, J. R., Medlin, J. W., & Kuo, Y. J. (2000). Selective isomerization of 2,5-dihydrofuran to 2,3-dihydrofuran using CO-modified, supported Pd catalysts. *Applied Catalysis A: General*, 194, 463–474. [https://doi.org/10.1016/S0926-860X\(99\)00392-0](https://doi.org/10.1016/S0926-860X(99)00392-0)

Species	Linear, Pd-CO	Two-Fold Pd ₂ -CO	Three-Fold Pd ₃ -CO	Three-fold with Dipole-dipole coupling	Three-Fold Pd ₃ -CO
Wavenumber , cm ⁻¹	2078	1948	1889	1830	1815
Conditions	50-1000 ppm CO, 90C at Equilibrium	50 ppm CO, 90C at Equilibrium	25 ppm CO, 90C at Equilibrium	10 ppm CO (low) 90C at equilibrium	
Characteristic	On set of linear CO	1948 assigned to two-fold sites	1815 is also present	Shift in wavenumber to a higher value due to dipole-dipole coupling	Broad band
			coordinatively saturated Pd surface sites such as (111, 100)		
Current Study, monometallic	2094, 2078,2050	1955,1933		1871	1797

Review of Literature – Characterization by CO-FTIR

CO Adsorption on Cu/SiO₂

Hadjivanov, K., Venkov, T., & Knözinger, H. (2001). FTIR spectroscopic study of CO adsorption on Cu/SiO₂: Formation of new types of copper carbonyls. *Catalysis Letters*, 75(1–2), 55–59.
<https://doi.org/10.1023/A:1016759123842>

Species	Cu ⁰ -CO, Cu ⁺ -CO band	Cu-(CO) ₂ , dicarbonyl Species B	Cu-CO, monocarbonyls, Species A	Cu-(CO) ₂ Dicarbonyls
Wavenumber, cm ⁻¹	2129	2045	2018	2003
Conditions		appears after Prolong CO exposure	sample reduced at 573 K,	samples reduced at 673 K
Characteristic	Decrease in intensity with decreasing CO	with a lower frequency shoulder, decrease in intensity of the principal Cu ⁰ - CO , Blue Shifted	decrease in intensity of the principal Cu ⁰ - CO band, Appears at the expense of Species B	
Observed Peak	2125		2012	

Review of Literature – Characterization by CO-FTIR

CO adsorption on Ru/SiO₂

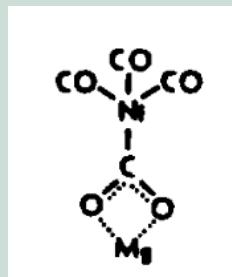
Chin, S. Y., Williams, C. T., & Amiridis, M. D. (2006). FTIR studies of CO adsorption on Al₂O₃- and SiO₂-supported Ru catalysts. *Journal of Physical Chemistry B*, 110(2), 871–882.

Adsorption Band	HF1 (High Frequency 1)	HF2 (High Frequency 2)	LF (Low Frequency)	Bridge-Bonded CO
Wavenumber range (cm ⁻¹)	2120-2156	2060-2110	2000-2060	1866,1988
Adsorbed CO Species		Type II Carbonyls Ru ⁿ⁺ -(CO) _x	Type III Carbonyls Ru ⁿ⁺ -(CO) ₂	Type I carbonyls Ru ⁰ -CO Ru ₂ -(CO)

Review of Literature – Characterization by CO-FTIR

CO adsorption on High Loading Ni/MgO

Martra, F. Arena, M. Baricco, S. Coluccia, L. Marchese, A. Parmaliana, Catal. Today 17 (1993) 449–458.

Adsorption Band	HF(>2000)		Overlap between linear and bridge (2000-1950)	Bridged carbonyls	asymmetric stretching vibrations of the carboxylate-like group	Bands of carbonate like species.
Wavenumber (cm ⁻¹)	2060-2050	2131,2080, 2020	1990,1975	1950-1800	1500-1450	1750-1600 1400-1300
CO Species	Ni-CO	Ni(CO) ₄	tricarbonylic	Ni _x CO (x = 2,3)		2CO→CO ₂ +C
Characteristics	Depend on CO exposure time, sharper peak after 1hr CO adsorption			Larger # of Ni atoms involved, the lower the stretching frequency of the bonded CO	asymmetric stretching vibrations of the carboxylate-like group anchoring the tetracarbonyl species to the MgO. a) increase with time, b) decrease upon decarbonylation and c) are restored by CO readmission	species are slowly produced when CO is allowed on oxidized nickel supported catalysts (Boudouard reaction on metal Ni ⁰ sites)

Pd, Cu and PdCu CO-FTIR SPECTRA (N₂ Purged)

