



Characterization and Reactivity of Supported Pd/Au Dilute Limit Alloy Nanoparticles

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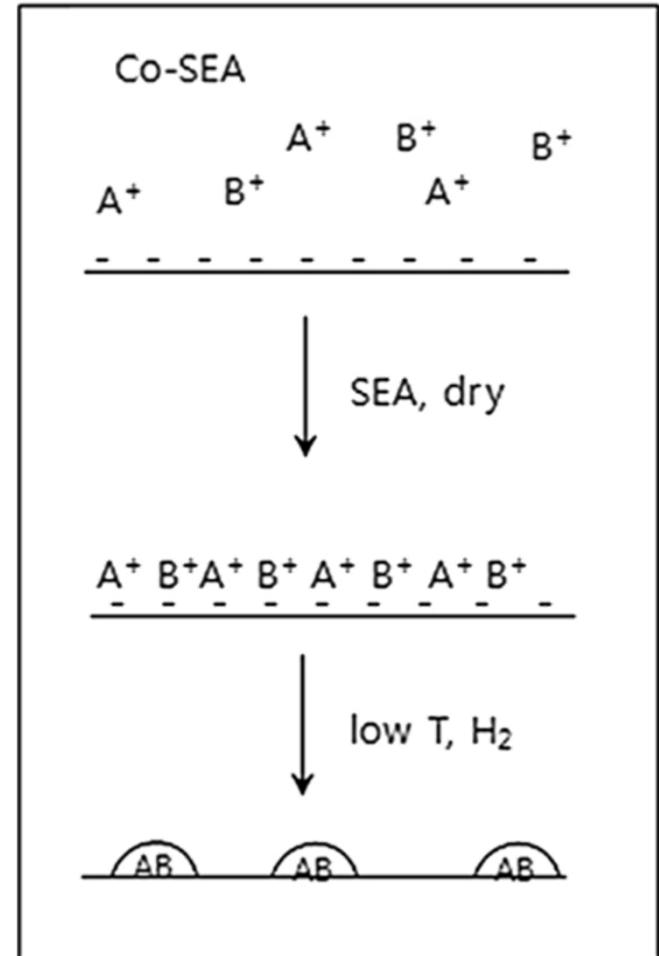
Isolated single atom catalysts

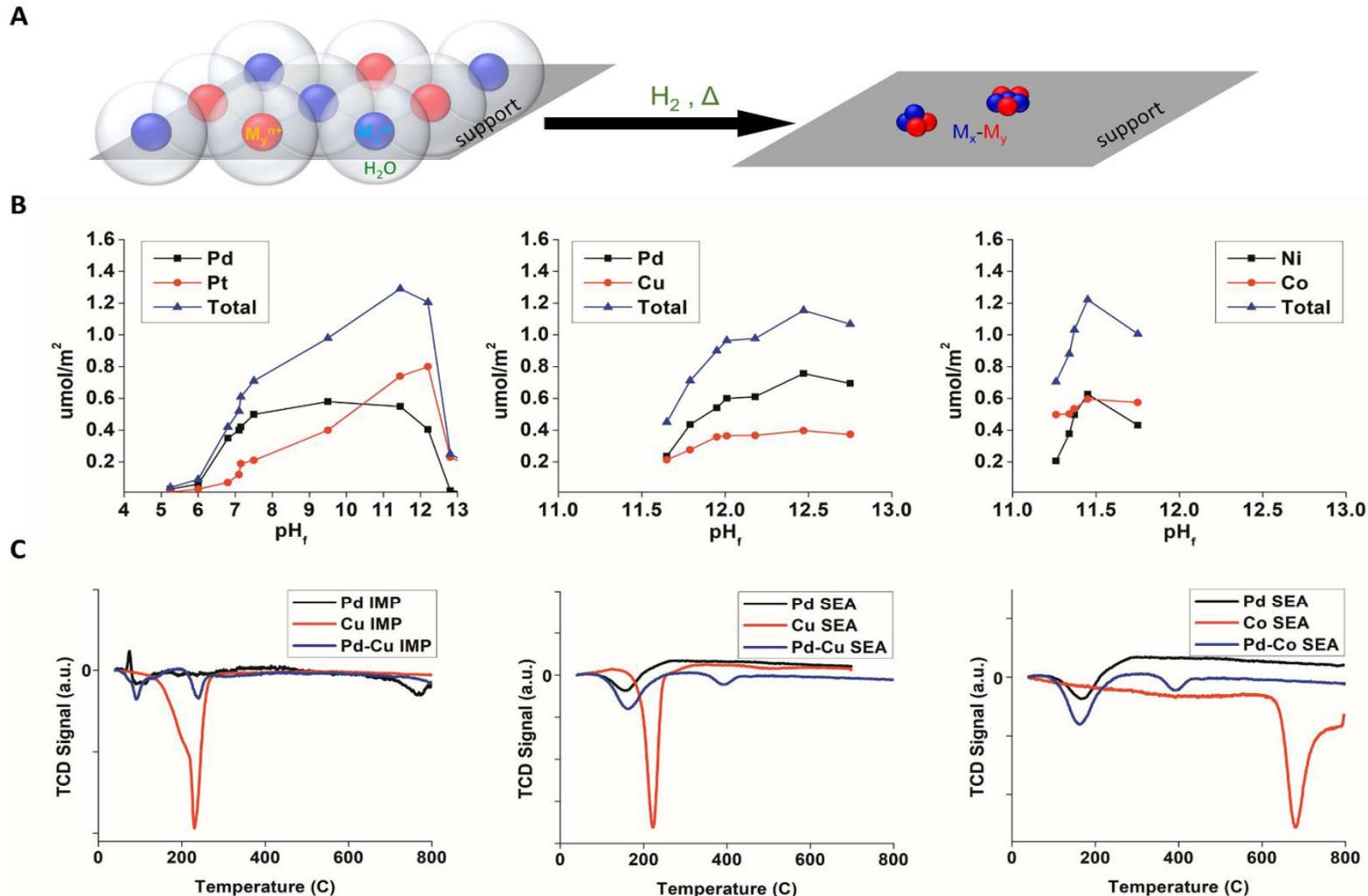
- Stable isolated site catalysts could be a bridge between homogeneous and heterogeneous catalysis promising well-defined and highly selective active centers.
 - Supported single atoms
 - Isolated single atoms on another supported nanoparticle



Schematic of working hypothesis for bimetallic catalyst preparation:

- Simultaneous-SEA will yield highly dispersed, alloyed metal particles with low T reductions.
- Sequential SEA will give rise to highly dispersed, core–shell structures at low reduction T, and larger, alloyed particles at high reduction T.

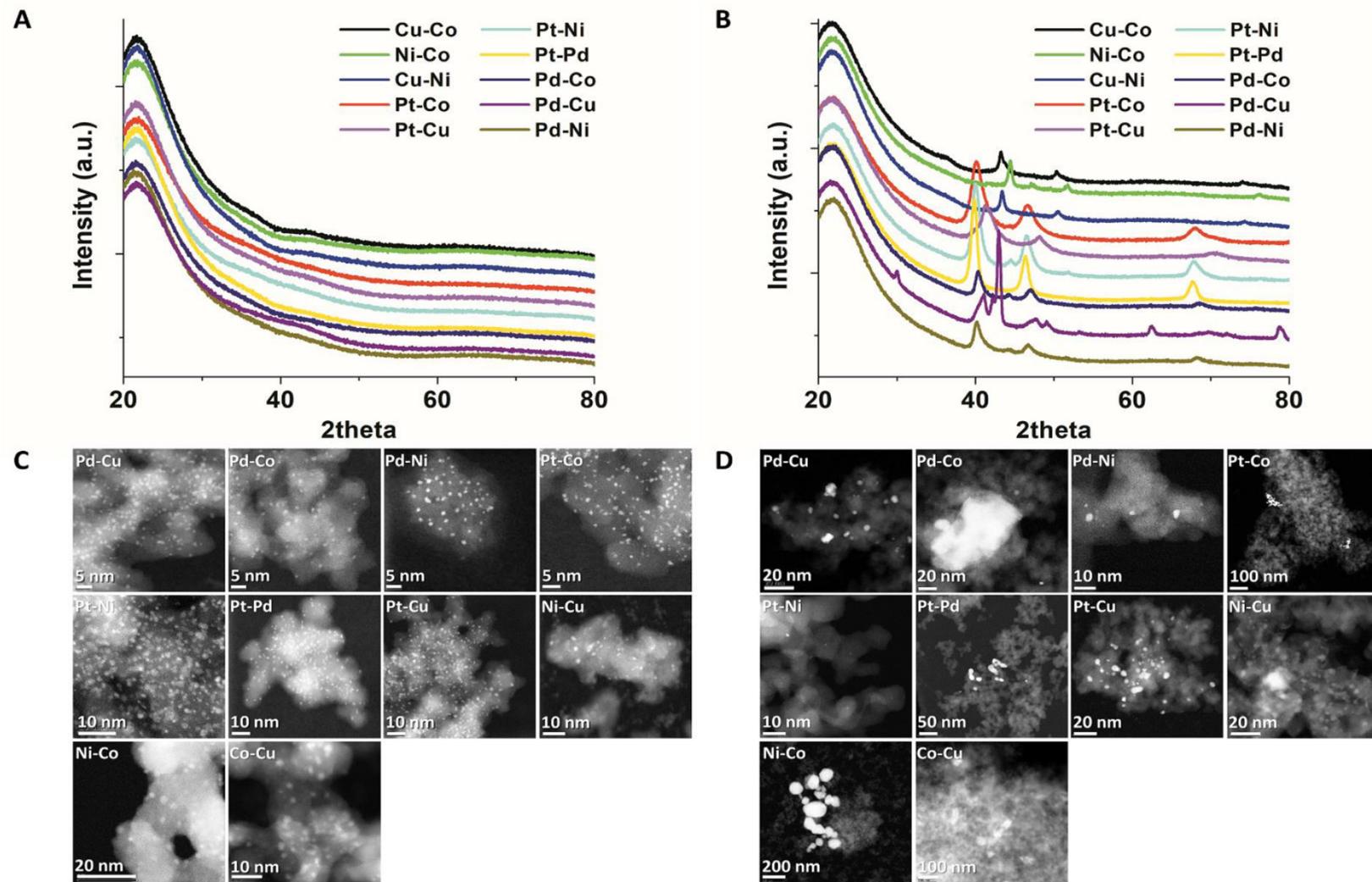




SEA bimetallic adsorption schematic, adsorption density, and temperature-programmed reduction profiles

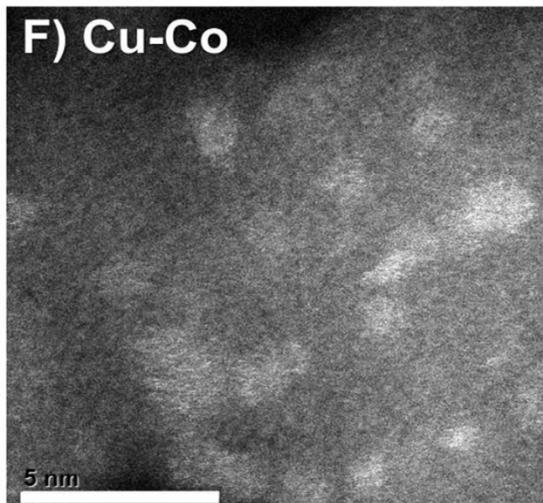
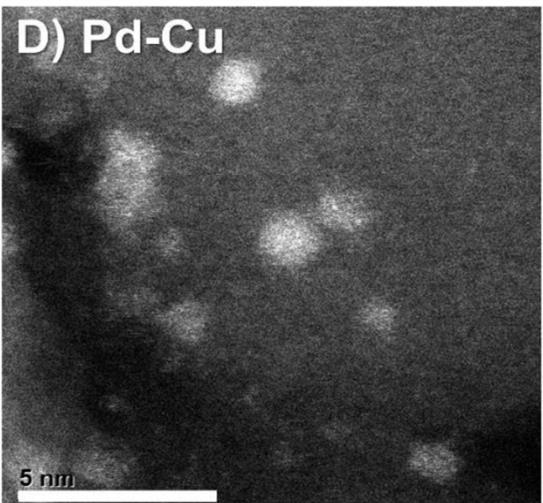
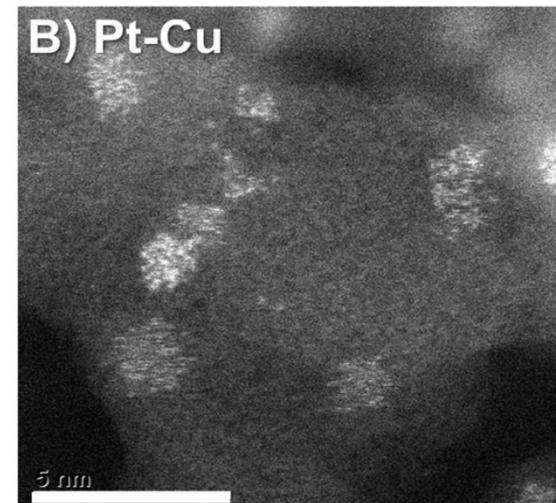
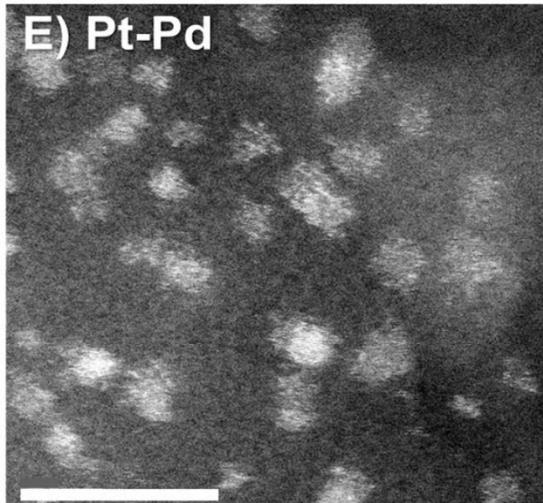
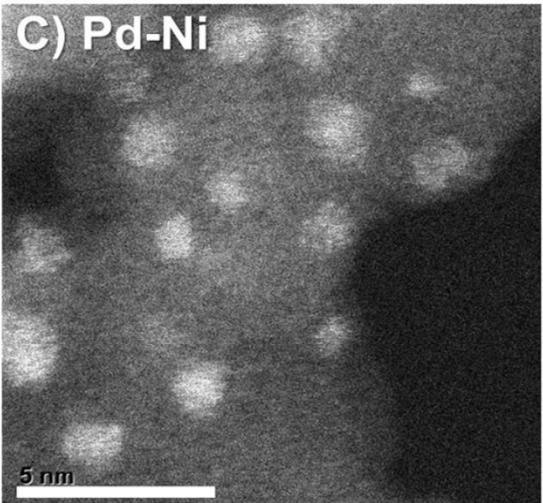
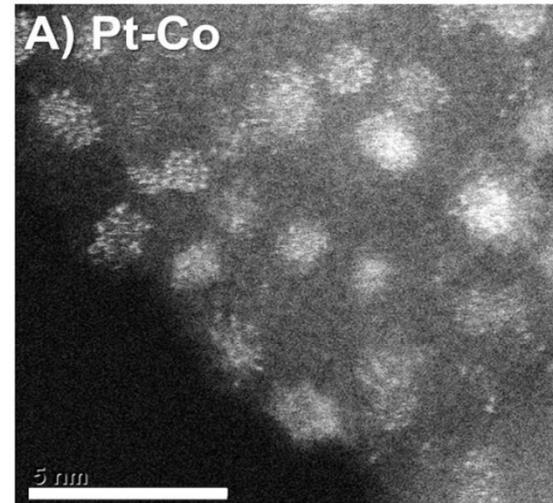


Wong, A.; Liu, Q.; Griffin, S.; Nicholls, A.; Regalbuto, J. R. Science (80-). 2017, 358 (6369), 1427–1430.



Bimetallic NP size characterization after reduction in 10% H₂ balanced in He for 1 hour at 400°C.

Wong, A.; Liu, Q.; Griffin, S.; Nicholls, A.; Regalbuto, J. R. Science (80-). 2017, 358 (6369), 1427–1430.



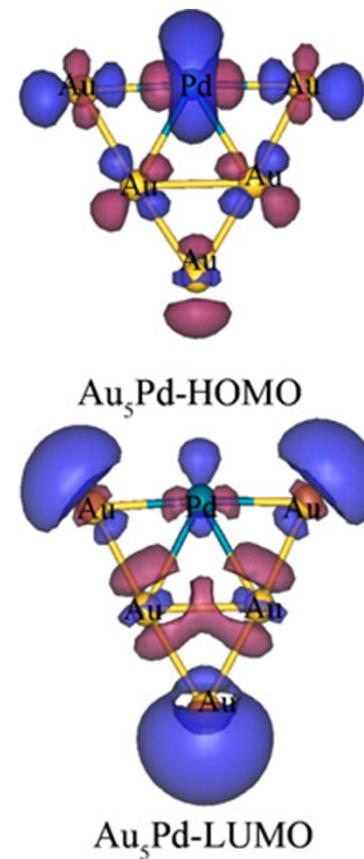
Atomically resolved Z-contrast images showing NP speckling of alloys.

Wong, A.; Liu, Q.; Griffin, S.; Nicholls, A.; Regalbuto, J. R. Science (80-). 2017, 358 (6369), 1427–1430.



Pd-Au/SiO₂ Dilute Limit Alloy Catalysts

- Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the bimetallic clusters are located on the Pd atoms, indicating the active centers.



Catalyst
Pd
Au
3:1 Pd:Au
1:1 Pd:Au
1:3 Pd:Au
1:5 Pd:Au
1:14 Pd:Au
1:28 Pd:Au
1:53 Pd:Au

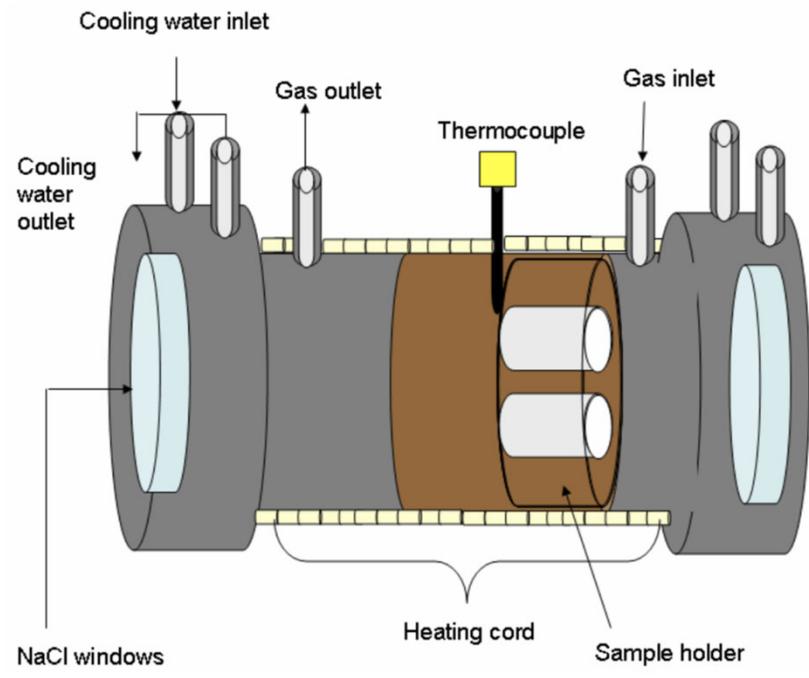
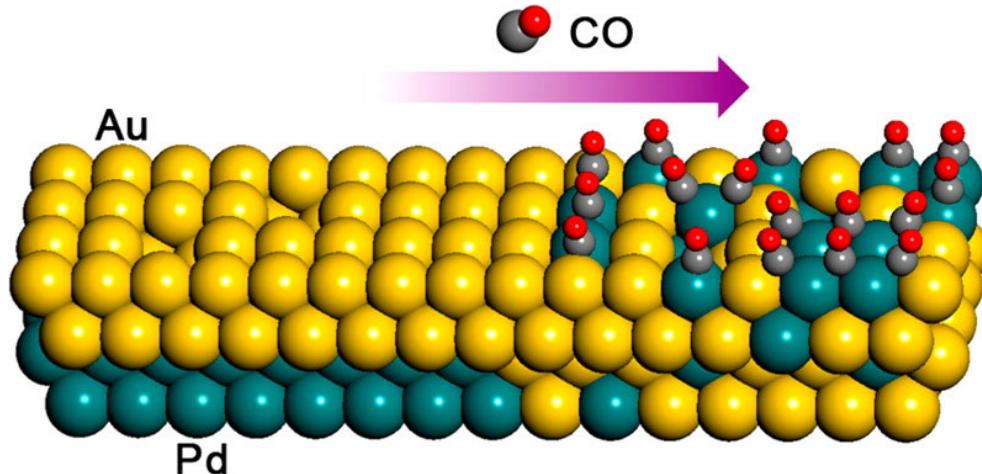


Questions to be answered

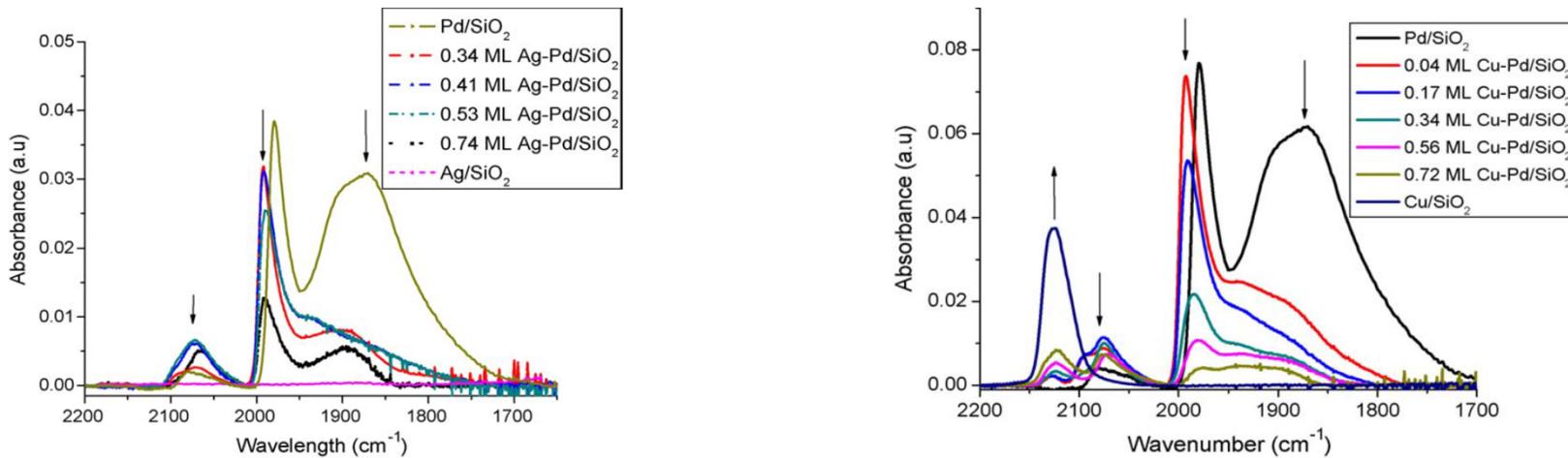
1. Are the Pd atoms are on the surface of our bimetallic nano-structures?
2. Can we find evidence of single atoms of Pd on the surface of our Pd-Au/SiO₂ using in situ FTIR?
3. Are the Pd single atoms on the Au-Pd/SiO₂ or on the support?

Approach:

Use FTIR spectroscopy of CO Adsorption



Expected frequencies of linear and nonlinear adsorbed CO on Pd



1.85 %wt Pd/SiO₂

FTIR peak positions and intensity ratios for Pd/SiO₂, Cu/SiO₂, Cu-Pd/SiO₂ and Ag-Pd/SiO₂ catalysts.

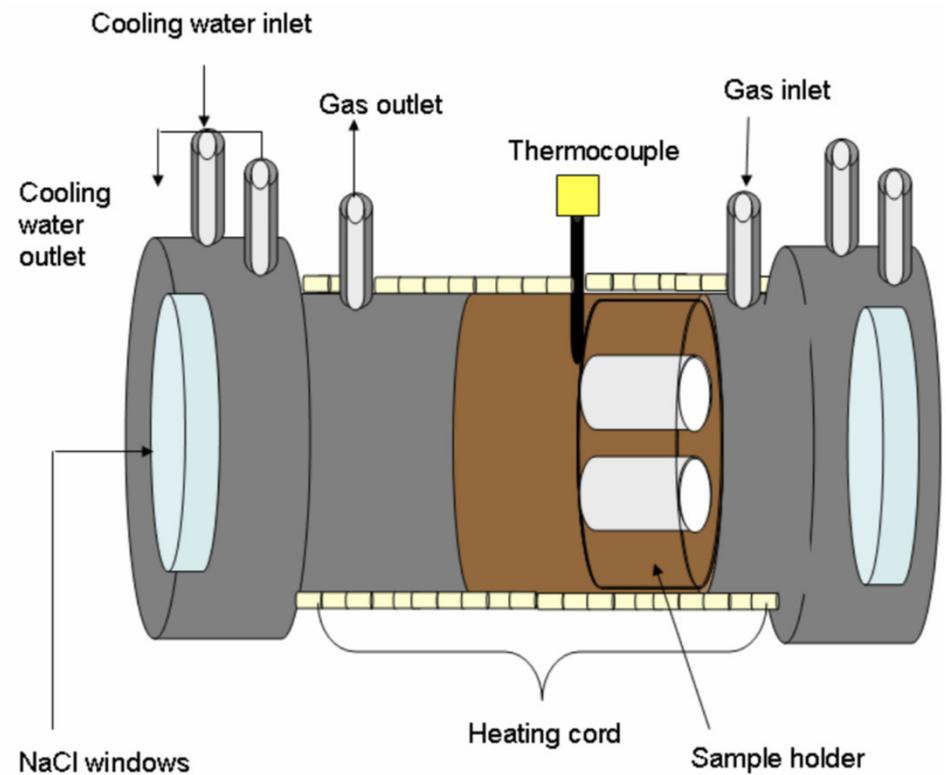
wt.%	ML (on Pd)	Cu/Cu ⁺	Linear region (L)		Non-linear region (NL)				Linear/ non-linear (L/NL)	L1/L2
			L1	L2	NL1	NL2	NL3	NL4		
Pd/SiO ₂	-	-	2077	2050	1979	1935	1880	1840	0.018	1.817
0.09% Cu-Pd/SiO ₂	0.17	2125	2095	2074	1991	1974	1929	1865	0.160	0.298
0.62% Cu-Pd/SiO ₂	0.72	2122	2100	2069	1982	1968	1951	1900	0.500	0.113
Cu/SiO ₂	-	2125	-	-	-	-	-	-	-	-
0.20% Ag-Pd/SiO ₂	0.41	-	2090	2068	1992	1979	1940	1866	0.143	0.163
2.08% Ag-Pd/SiO ₂	0.73	-	2090	2068	1991	1978	1940	1866	0.257	0.050

Note: Only selected compositions are shown.

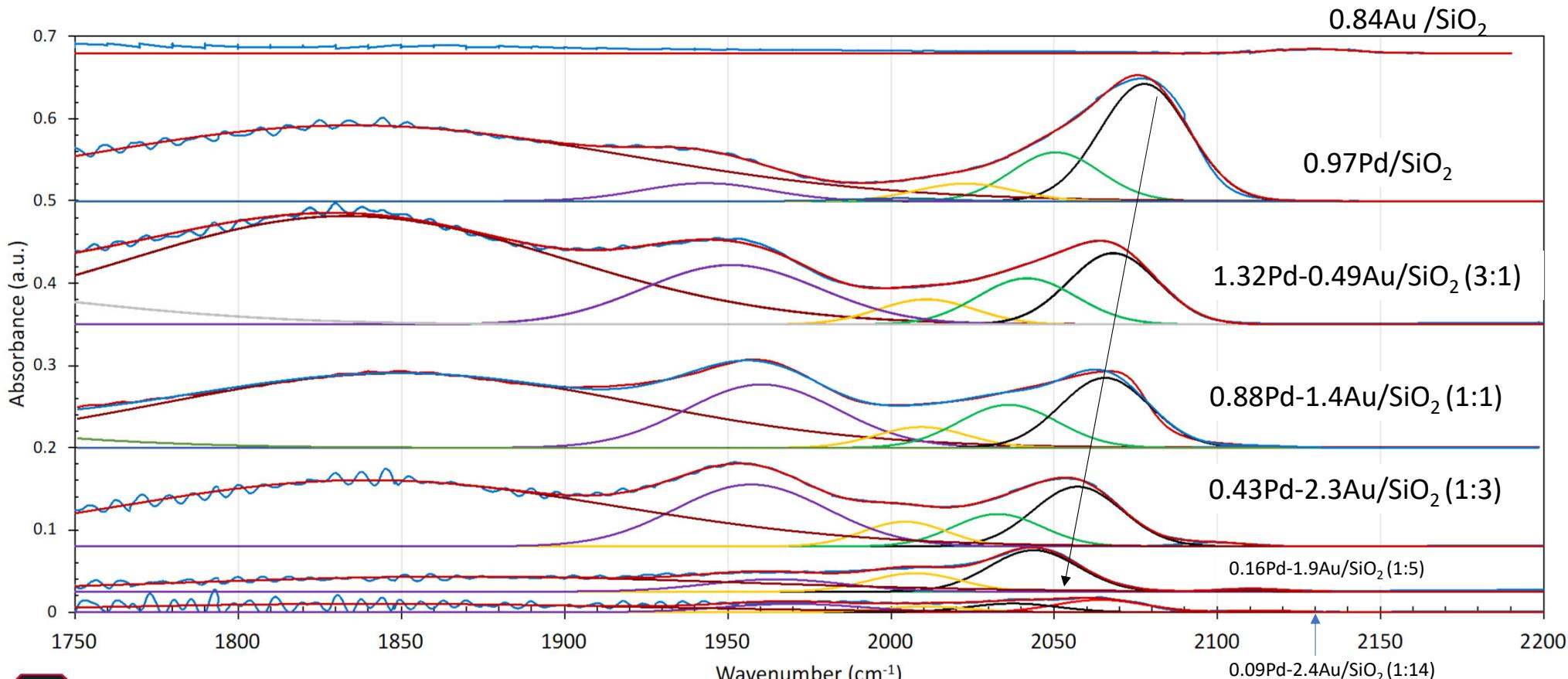


Procedure FTIR spectroscopy of CO Adsorption

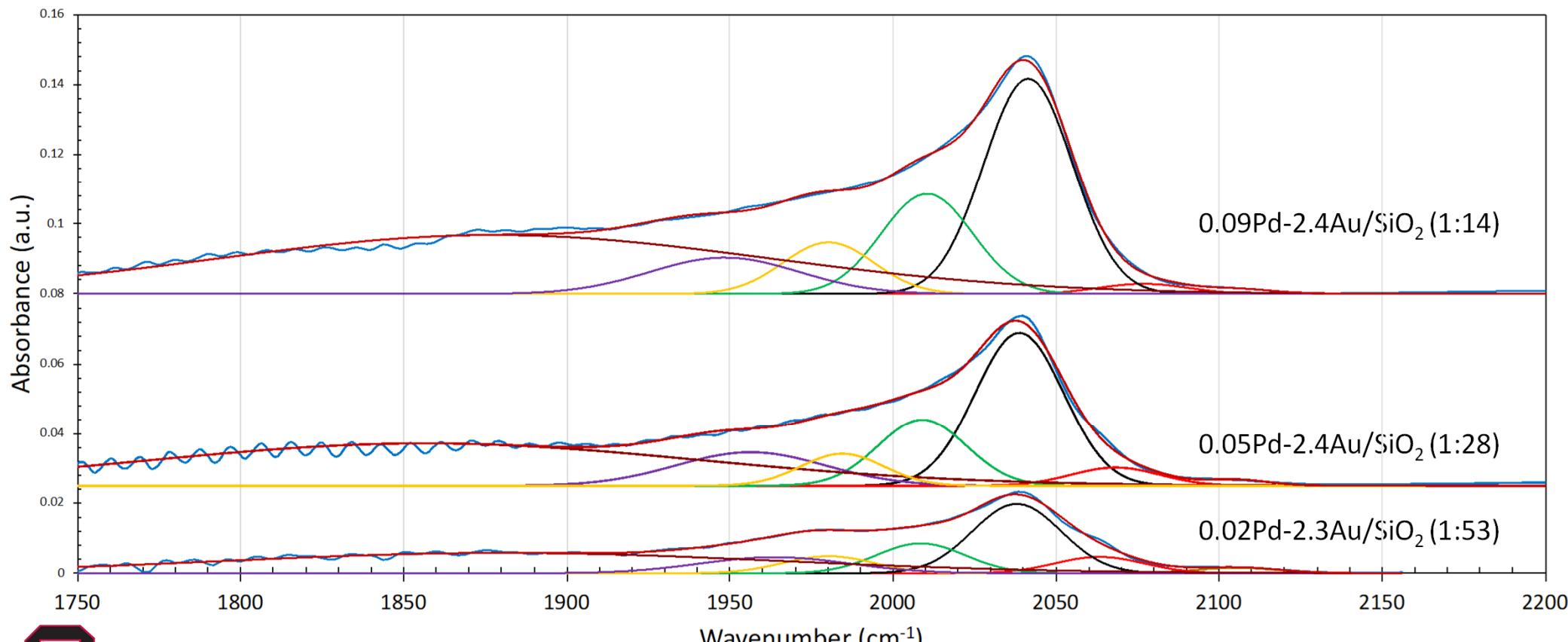
1. In situ sample reduction
2. Flow of CO and collection of spectra until the surface is saturated
3. Removal of gas phase CO



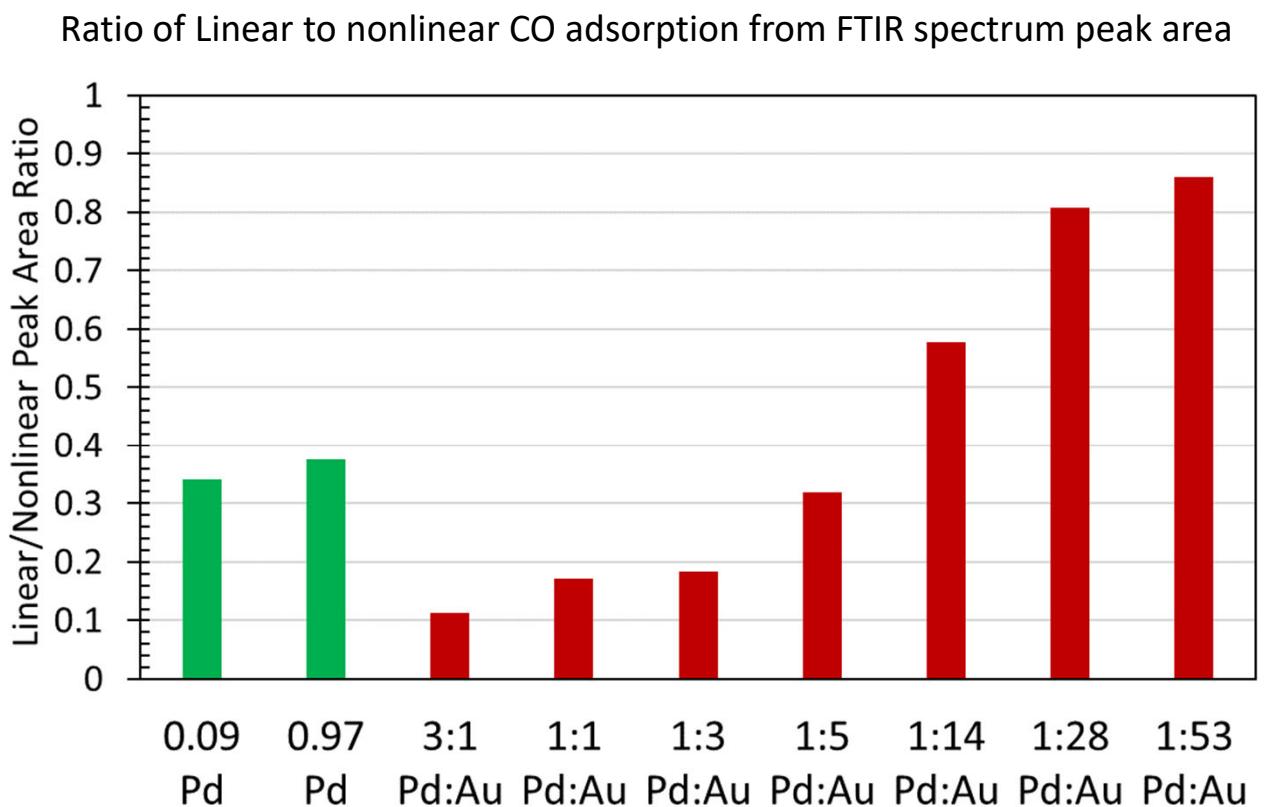
FTIR spectrum of CO adsorption on different catalysts and deconvolution of linear and non-linear adsorption peaks



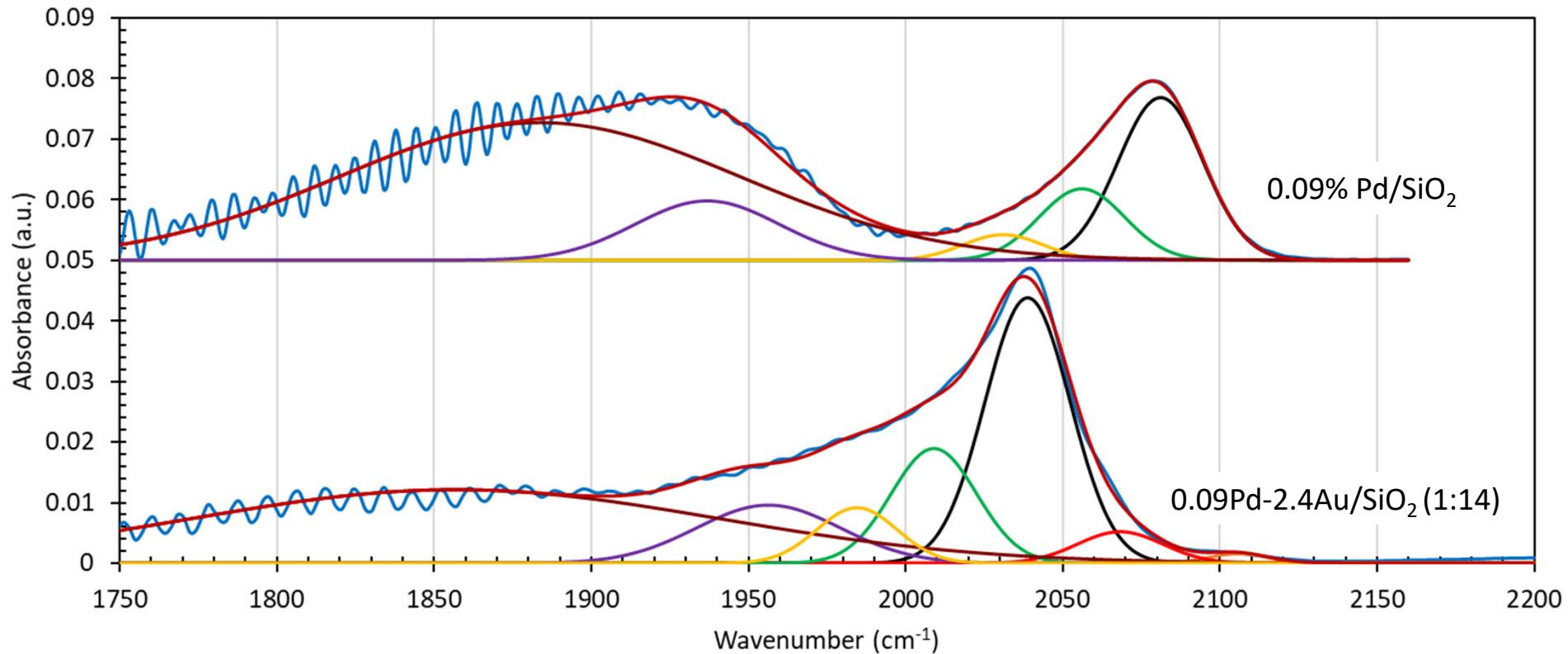
FTIR spectrum of CO adsorption on different catalysts and deconvolution of linear and non-linear adsorption peaks



- Evidence for having Single atoms on the surface of the bimetallic catalysts:
 - Increasing the linear/nonlinear peak area ratio by decreasing the Pd:Au
 - Adding Au causes more non-linear bonds relative to linear bonds. It may be due to having more Pd atoms on the surface of bimetallic particles.



Evidence for having the Pd particles on the top of the Au-Pd/SiO₂ not on the support



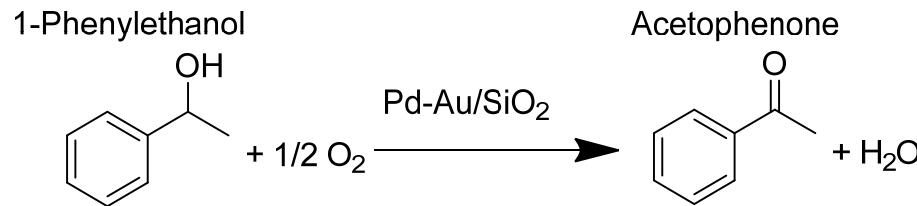
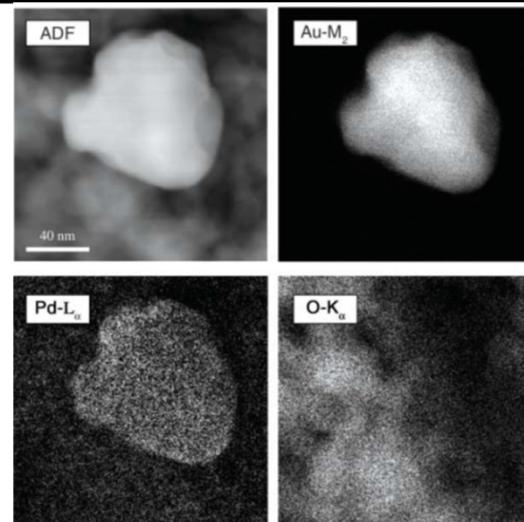


Table 1. Effect of Pyridine Ligands on Palladium-Catalyzed Air Oxidation of Alcohols^a

run	alcohol	ligand ^b	time (h)	% yield ^c	Pd black formation ^d	Entry	Alcohol	Reaction conditions <i>T</i> (K) <i>P</i> (10 ⁵ Pa)	[Metal] (10 ⁻⁵ mol/liter) Au Pd	TOF (/hour)
						11	1-Phenylethanol	433 1	1.8 3.2	269,000
1	1-phenylethanol ^e	none	7	trace	+	29	1-Phenylethanol††	433 1	0 3.1	11,600
			24	trace	+					
2		Py	2	23	+					
			24	23	+					
3		3-PhPy	6	34	+					
4		3,5-diPhPy	6	32	+					
5	Bipy		24	3	—					
			72	6	—					
6	1		24	57	—					
			72	87	—					
7	2		24	78	—					
			72	>99 (95)	—					
8 ^f	2		96	74	—					
			24	44	—					
9	4		72	63	—					



- Pressure has no effect on the activity.
- The support has considerable effect on the activity and selectivity.
 - TiO₂
 - Al₂O₃
 - SiO₂
 - Fe₂O₃
 - C

Iwasawa, T.; Tokunaga, M.; Obora, Y.; Tsuji, Y. J. Am. Chem. Soc. 2004, 126 (21), 6554–6555.
 Enache, D. I. et al. Science (80-.). 2006, 311 (5759), 362–365.

Reactivity of the Dilute Limit Alloy Catalyst

Reaction conditions:

Temperature: **160 °C**

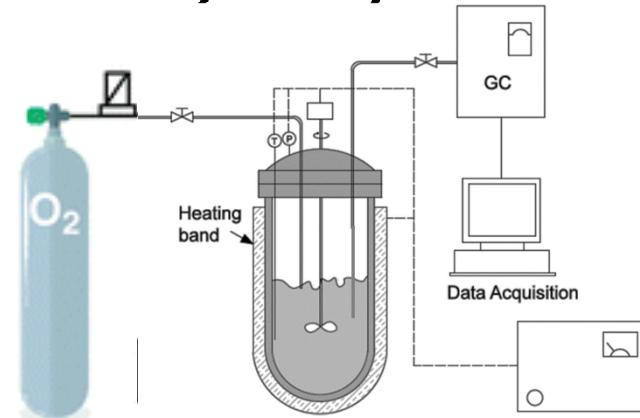
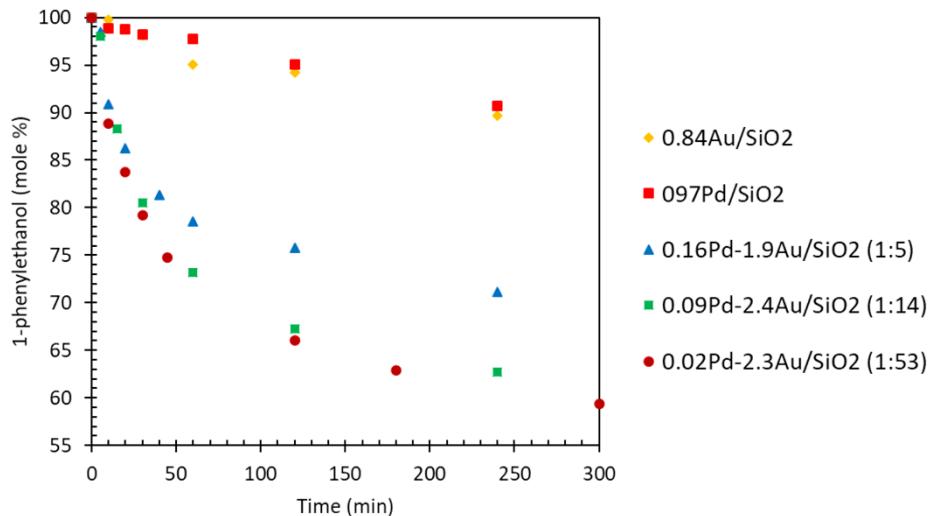
Pressure: **50 psi**

Agitation speed: **400 rpm**

Catalyst amount: **106 mg**

Reactant amount: **50 ml**

Solvent: **none**



Catalyst	Pd (10^{-3} mol/L)	Au (10^{-3} mol/L)	TOF _{total-metal} (h^{-1})	TOF _{Pd} (h^{-1})
Pd	19.4	0	0.5	0.5
Au	0	24.75	0.4	0.4*
1:5 Pd:Au	3.2	20.4	5.2	31
1:14 Pd:Au	1.8	25.8	4.4	68
1:28 Pd:Au	1	25.8	31	833
1:53 Pd:Au	0.4	24.75	74	4654



Conclusions

- Stabilized single pd sites on the surface Au has been synthesized.
- We successfully characterized
- More active and selective catalyst with much less amount of materials.
- Simultaneous SEA is a simple and scalable rational synthesis method.





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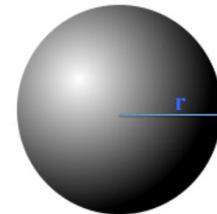


Thank
you





- X-ray crystallography: unit cell edge length for gold is 0.408 nanometers
- The volume of a cube = $0.408^3 = 0.0679$
- 4 atoms per unit cell



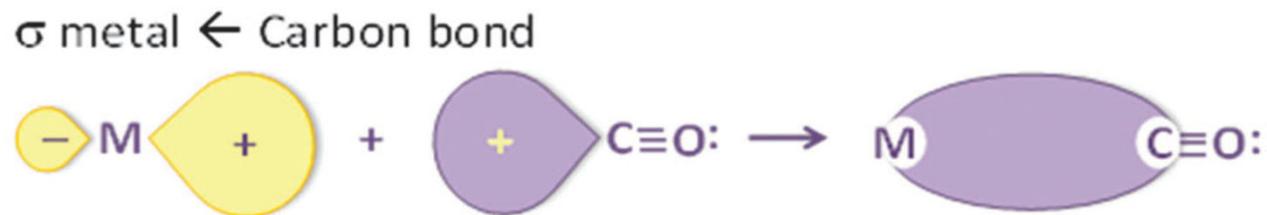
- 1.2 nm diameter of gold nanoparticle;
 - The sphere's volume = $\frac{4}{3} \pi r^3 = 0.90432 \text{ nm}^3$
-
- $\frac{0.90432}{0.0679} \times 4 = 53$ atoms in each particle



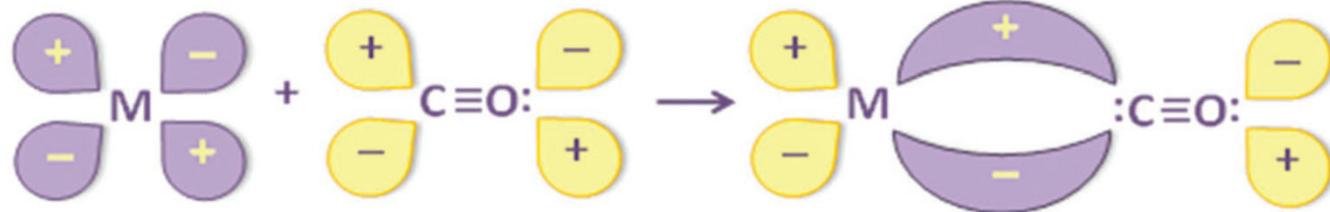
Mechanism of CO adsorption on metals

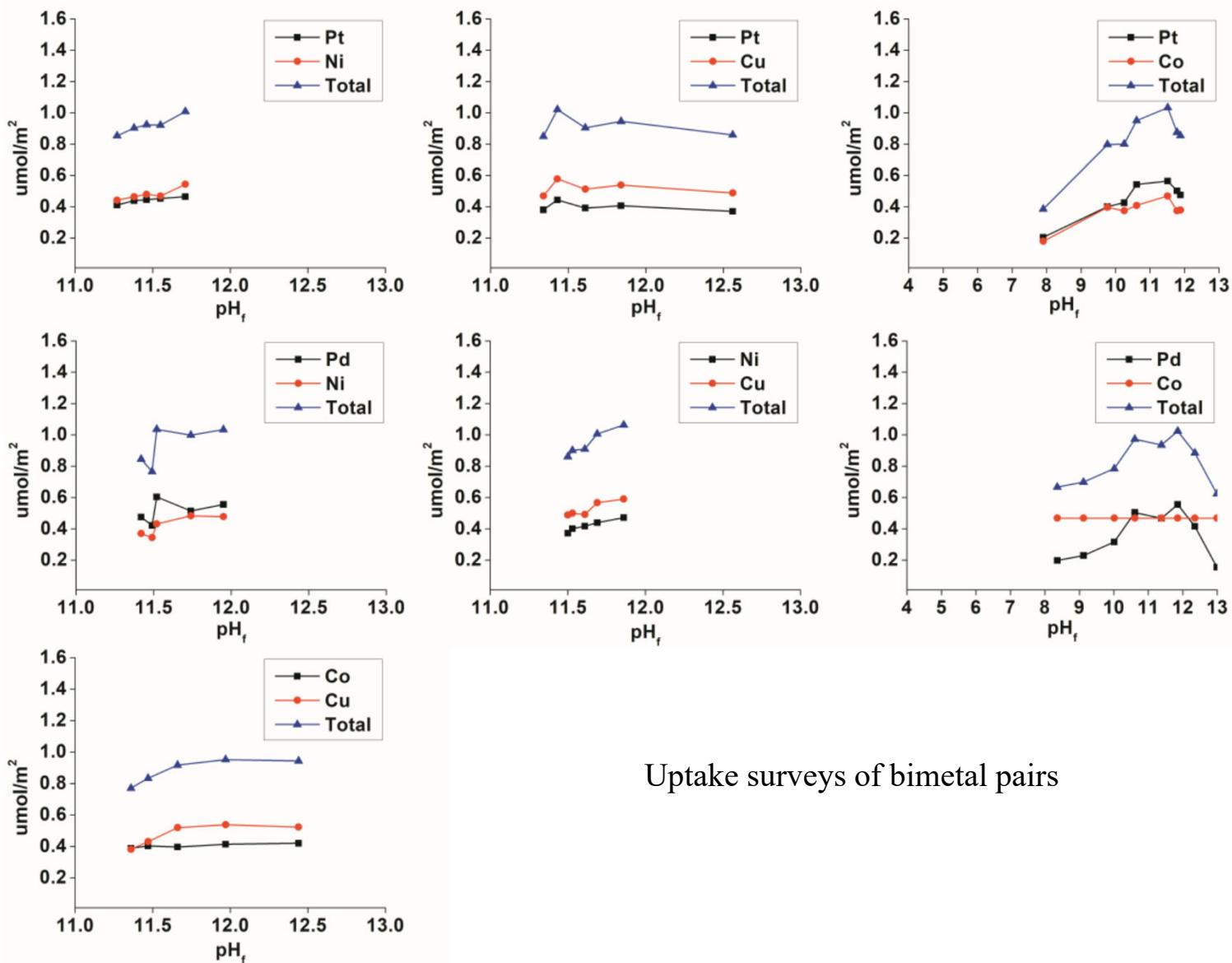
Metal–carbonyl bond:

- formation of a sigma metal–carbon bond and of a pi metal–carbon bond.
- The other CO molecular orbitals are omitted for the sake of clarity; the violet orbitals are full, the yellow one is empty.



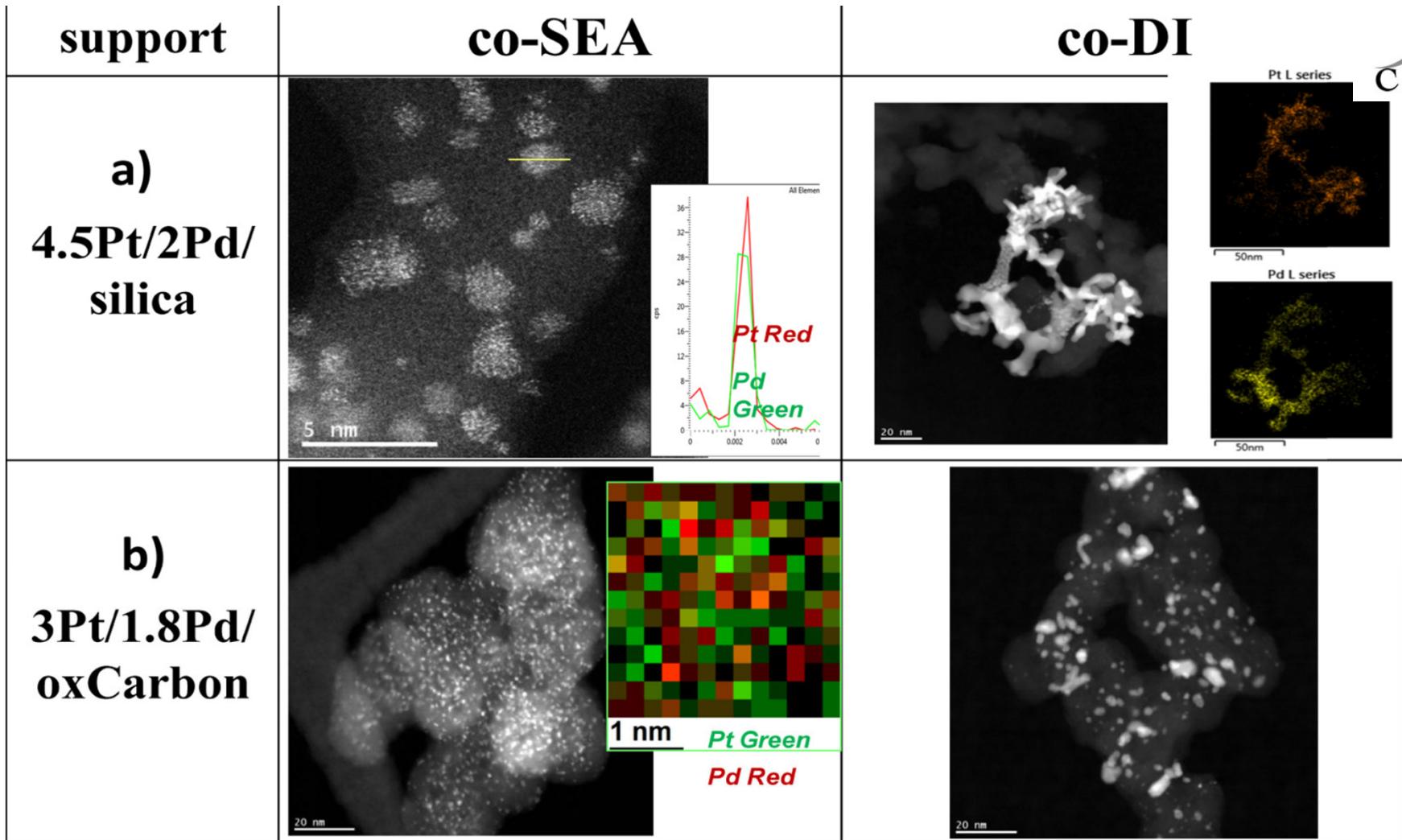
π metal \rightarrow Carbon bond





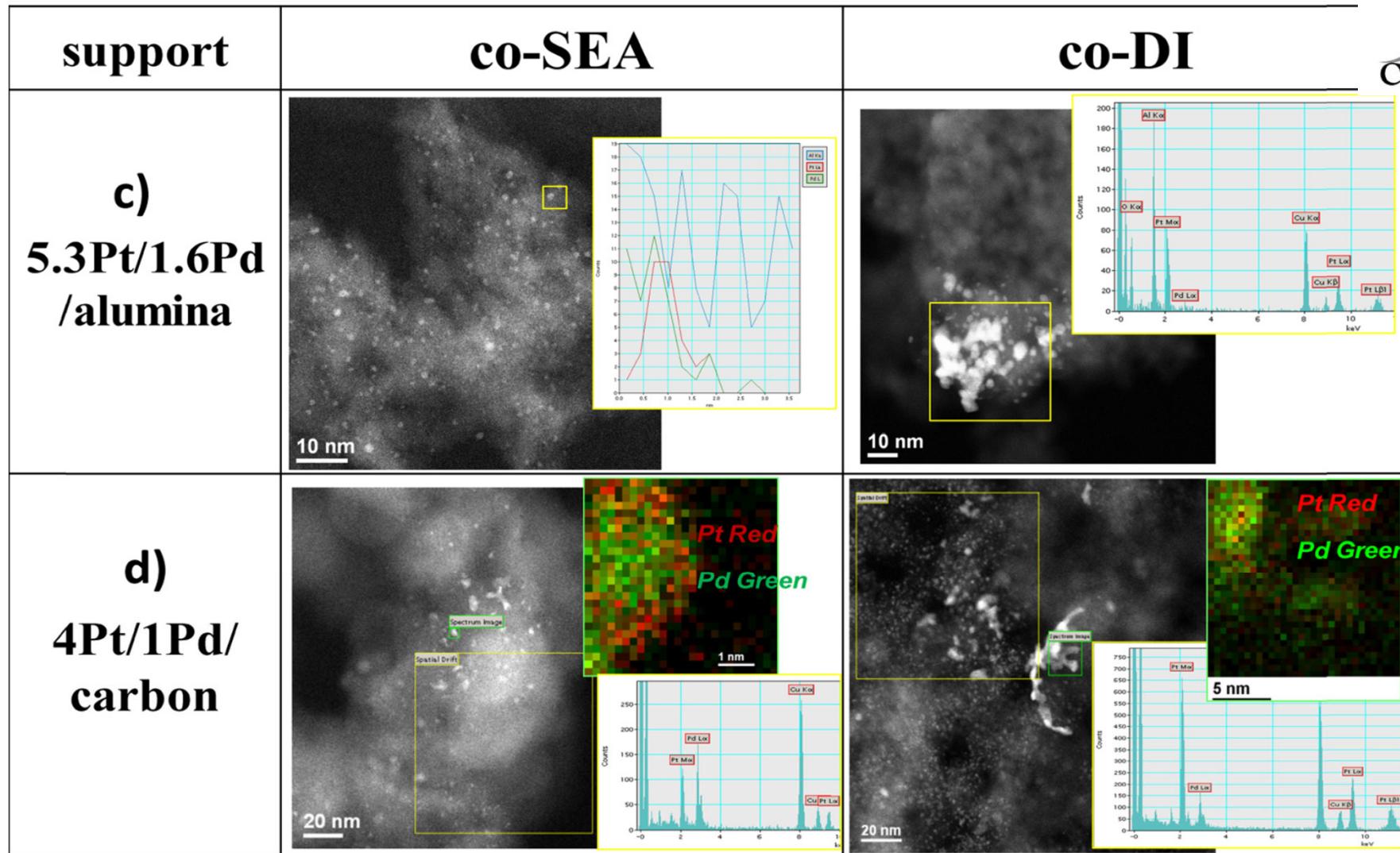
Uptake surveys of bimetal pairs





STEM and EDXS of seq-SEA-derived catalysts, a) silica b) oxC





STEM and EDXS of seq-SEA-derived catalysts, c) alumina d) C.



Metal wt% of PT/Pd core–shell catalysts.

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

STEM and EDXS of seq-SEA-synthesized core–shell nanoparticles on

- a) Pd@Pt/silica
- b) Pt@Pd/alumina
- c) Pd@Pt/alumina

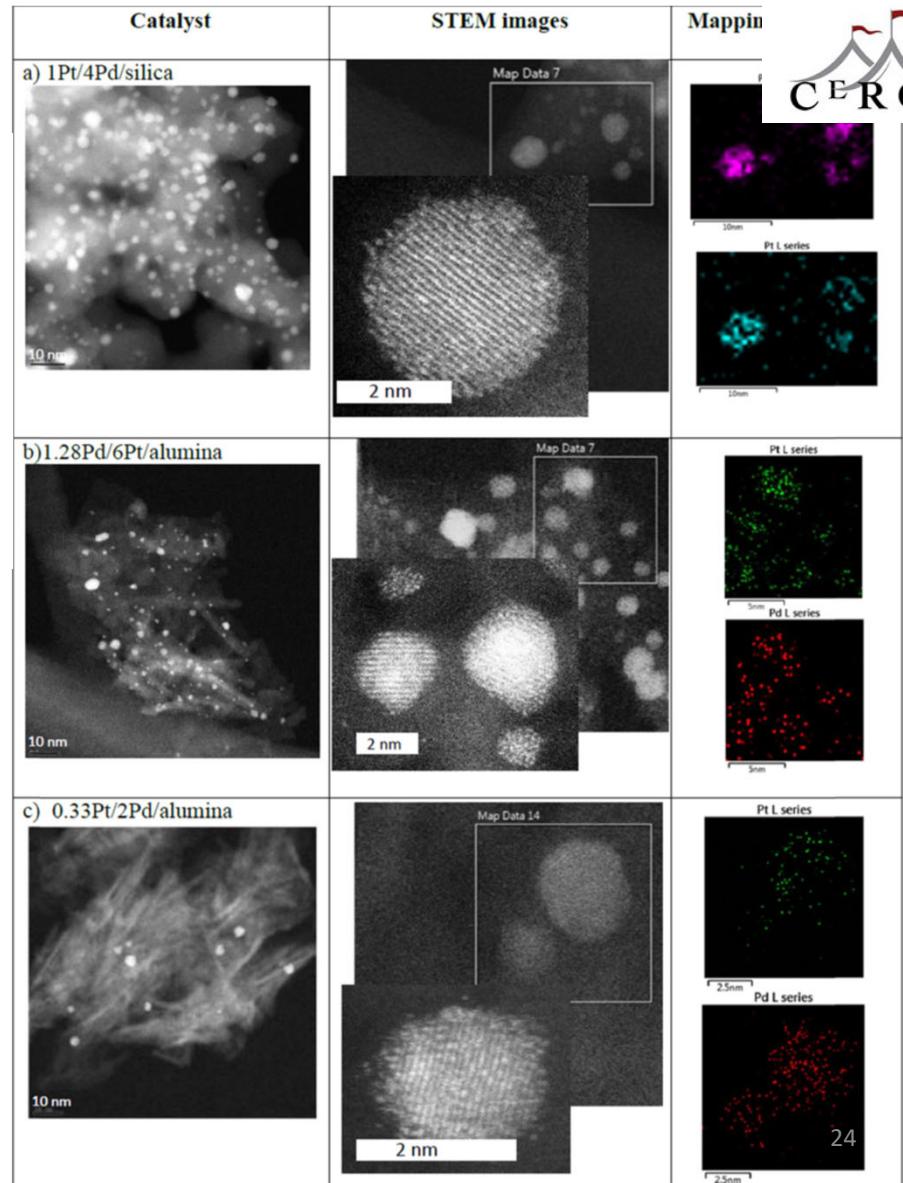


Table 1

The final binding sites obtained after ionic relaxation of the possible initial $c(4 \times 2)$ -2CO configurations shown in Fig. 1, using the PBE and optB88-vdW functionals.

Initial configuration	Final configuration (PBE)	Final configuration (optB88-vdW)
a: Bridge-Bridge	FCC-HCP	FCC-HCP
b: Bridge-FCC	FCC-HCP	FCC-HCP
c: Bridge-HCP	FCC-HCP	FCC-HCP
d: HCP-HCP	FCC-HCP	FCC-Bridge Hybrid
e: FCC-HCP	FCC-HCP	FCC-HCP
f: FCC-FCC	FCC-Bridge Hybrid	FCC-Bridge Hybrid
g: TOP-TOP	FCC-Bridge Hybrid	FCC-Bridge Hybrid
h: FCC-TOP	FCC-HCP	FCC-HCP
i: HCP-TOP	FCC-HCP	FCC-HCP
j: Bridge-TOP	FCC-HCP	FCC-Bridge Hybrid

Table 2

Calculated binding energies (in eV) and C-O stretch frequencies (in cm^{-1}) on Pd (111) at $\frac{1}{2}\text{ML}$ obtained using different DFT functionals.

		FCC-HCP	FCC-Bridge Hybrid
BE (eV)	PBE	–1.83 –1.82 ^a –1.85 ^b	–1.77
	PBE with zero-point energy correction	–1.78	–1.71
	PW91	–1.82 –1.85 ^c –1.84 ^d	–1.76
	optB88-vdW	–1.92	–1.86
C-O stretch frequency (cm^{-1})	PBE	1910, 1842 1917, 1852 ^a 1928, 1858 ^b	1923, 1855
	PW91	1913, 1846 1906, 1850 ^c	1923, 1855
	optB88-vdW	1908, 1838	1922, 1853

Where to expect the active sites in the bimetallic Pd-Au/SiO₂ catalyst

- Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the bimetallic clusters are located on the Pd atoms, indicating the active centers.

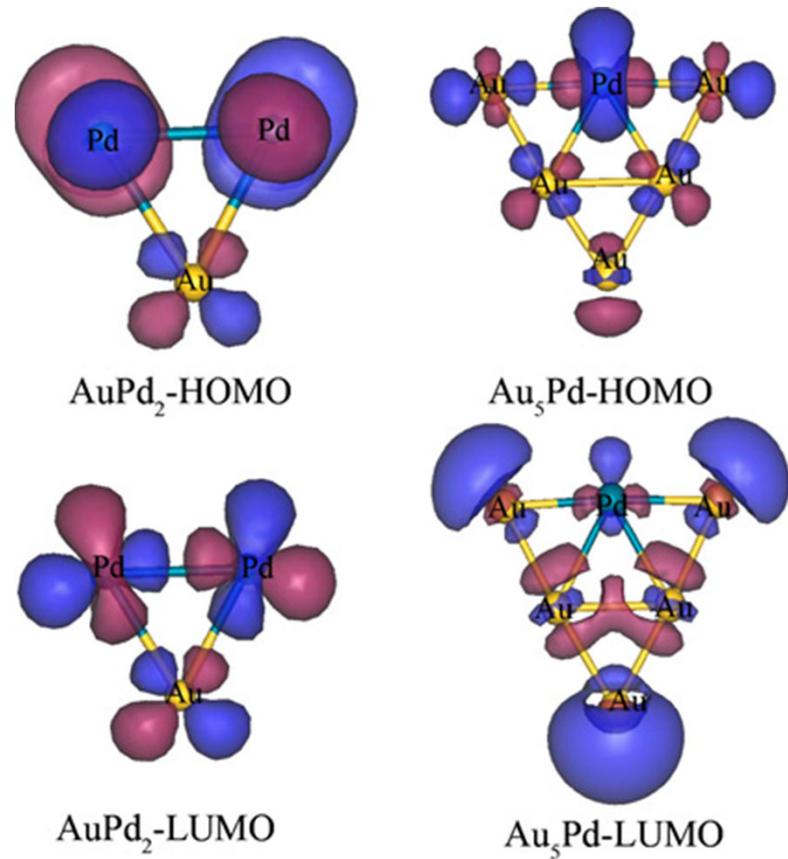
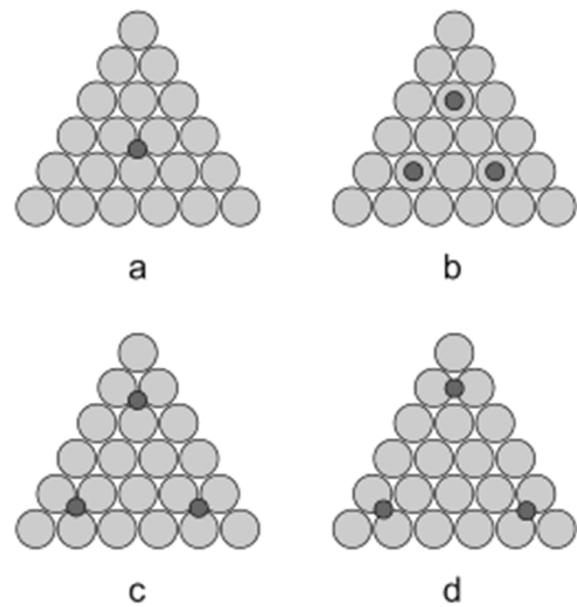


TABLE 1: Calculated Properties of CO Adsorbed on Different Sites of Regular (111) Facets of the Clusters Pd₁₄₆ (hcp, bridge, and on-top) and Pd₁₄₇ (on-top)

	hcp		bridge	on-top	
	Pd ₁₄₆ (CO) ₈	Pd ₁₄₆ (CO) ₂₄	Pd ₁₄₆ (CO) ₂₄	Pd ₁₄₆ (CO) ₂₄	Pd ₁₄₇ (CO) ₈
$r(\text{C}-\text{O}), \text{\AA}$	1.188	1.183	1.171	1.152	1.152
$r(\text{Pd}-\text{C}), \text{\AA}$	2.067	2.100	2.046	1.854	1.884
$D_e(\text{BP86}),^a \text{eV}$	1.77	1.69	1.47	1.15	1.16
$D_e(\text{PBEN}/\text{BP86}),^b \text{eV}$	1.49	1.38	1.18	0.92	0.93
$\nu_e(\text{C}-\text{O}),^c \text{cm}^{-1}$	1755	1803	1876	2012	1987
$\nu_e(\text{C}-\text{O}) \times 1.04,^d \text{cm}^{-1}$	1825	1875	1951	2092	2066

^a Adsorption energy from a relativistic BP86 calculation. ^b Relativistic PBEN adsorption energy calculated with BP86 geometry. ^c Calculated harmonic frequency of C–O vibration. ^d Scaled vibrational CO frequency, see text.

Different modes of CO adsorbate deposition at (111) facets of the cluster Pd₁₄₆: (a) central hcp position; (b) three on-top positions; (c) three hcp hollow sites; (d) three bridge positions.



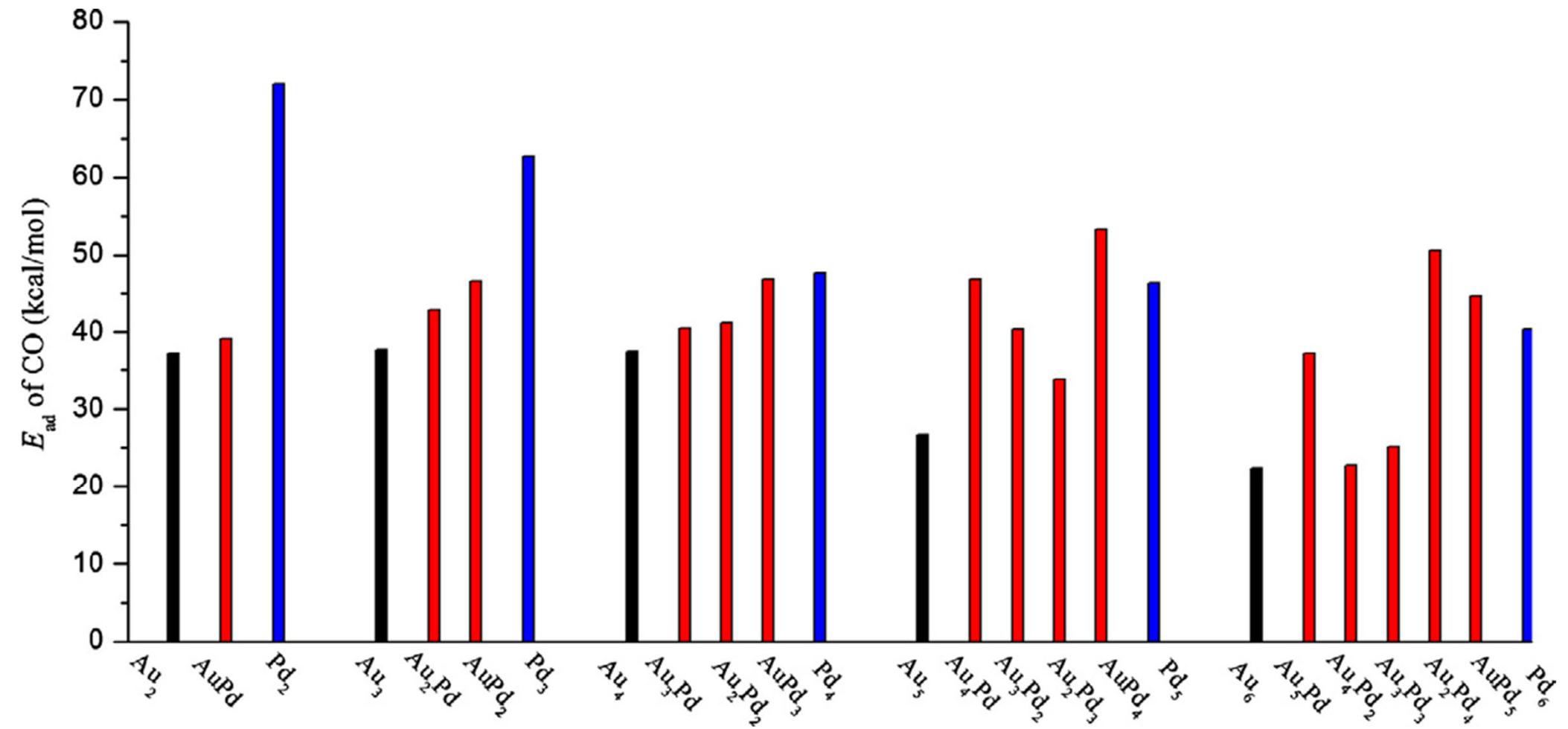
J. Phys. Chem. B, Vol. 107, No. 1, 2003 Yudanov et al.

TABLE 2: Calculated Properties^a of CO Adsorbed on Cluster Edges, Kinks, and (001) Facet

	bridge		on-top		4-fold	
	Pd ₁₄₆ (CO) ₁₂	Pd ₁₄₆ (CO) ₆	Pd ₁₄₈ (CO) ₈	Pd ₁₁₆ (CO) ₆	Pd ₁₄₀ (CO) ₆	Pd ₁₄₇ (CO) ₆
<i>r</i> (C–O), Å	1.175	1.154	1.154	1.153	1.198	1.193
<i>r</i> (Pd–C), Å	1.982	1.885	1.883	1.875	2.229	2.248
D _e (BP86), ^b eV	1.95	1.43	1.46	1.23 (1.00)	1.54	1.50
<i>v</i> _e (C–O), cm ⁻¹	1859	1997	1988	2004	1656	1687
<i>v</i> _e (C–O) × 1.04, cm ⁻¹	1933	2076	2068	2084	1722	1754

^a For the designation of the various properties, see Table 1. ^b Adsorption energy D_e(PBEN//BP86) calculated with PBEN exchange-correlation potential for the geometry optimized at the BP86 level given in parentheses.

J. Phys. Chem. B, Vol. 107, No. 1, 2003 Yudanov et al.



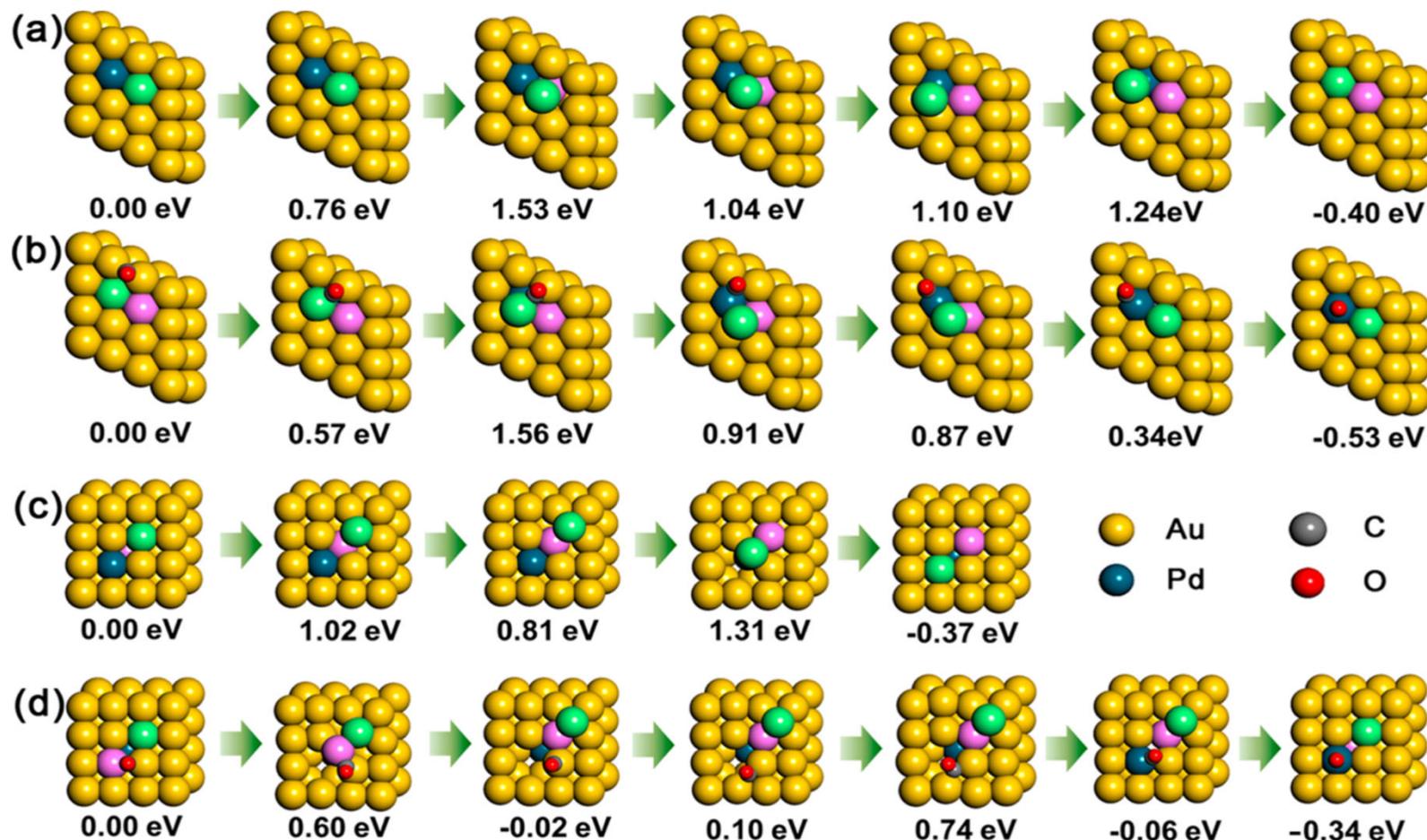
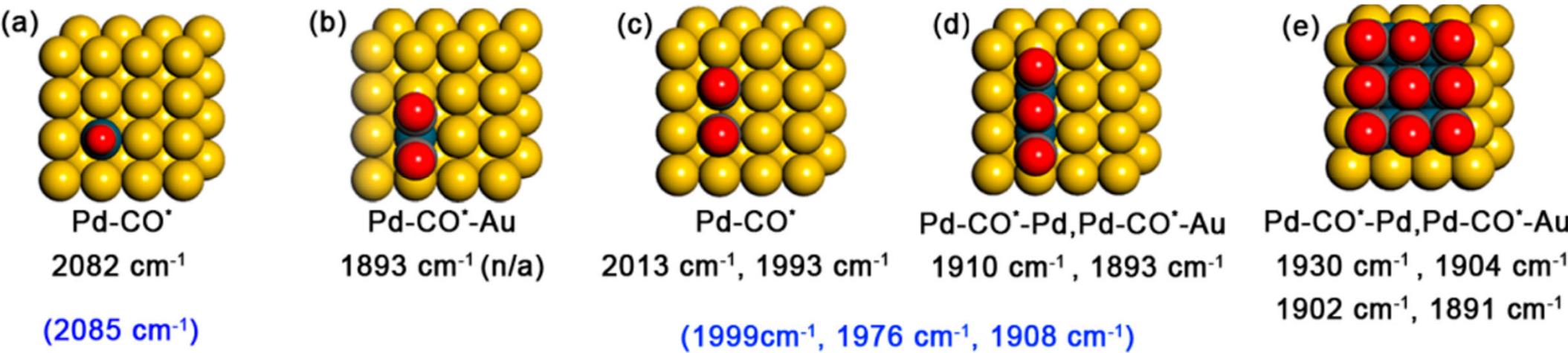


Figure 1. Pd–Au swapping process and relative energy of swapping intermediates in clean Pd–Au surfaces: (a) Pd–Au(111), (b) Pd–Au(111)–CO, (c) Pd–Au(100), and (d) Pd–Au(100)–CO. The relative energy of the intermediates was calculated relative to the unstable position of the Pd atom. The Pd–Au swapping proceeds from left to right, stabilizing the system. Au atoms involved in the swapping process are colored in light green and pink.



DFT calculated IR frequencies of surface CO species: (a, b) Pd monomer, (c, d) Pd dimer, and (e) Pd cluster consisting of six Pd atoms.

Values in parentheses show experimental IR data

Kim et al., dx.doi.org/10.1021/cs4006259 | ACS Catal. 2013, 3, 2541–2546