

# Effects of Reduction Temperature on Negatively Charged Au Species over Non-reducible Supports

Anhua Dong, Christopher Williams, John R. Regalbuto\*

Nov. 10<sup>th</sup>, 2021

*Department of Chemical Engineering  
University of South Carolina, Columbia, SC, 29208*



# Introduction

- ❑ In 1987, highly dispersed Au NPs was firstly reported for excellent activity in low-temperature CO oxidation;
- ❑ Particle size and supports affect activity through metal-support interaction and contact boundary;
- ❑ Controversy exists what creates  $\text{Au}^{\delta-}$  species;
  - We have employed Strong Electrostatic Adsorption (SEA) to produce ultra-small NPs to explore the effect of particle size as well as thermochemical atmosphere on the formation of  $\text{Au}^{\delta-}$  on a nonreducible support (silica).
  - Different pretreatments affect gold states and activity in CO oxidation.

# Overview: Au<sup>δ-</sup> on Reducible and Non-reducible supports

Samples (SA)	NP size (nm)	method	pretreatment	Au <sup>δ-</sup> (cm)	Au <sup>0</sup> (cm)	Au <sup>δ+</sup> (cm)	Reason for Au <sup>δ-</sup>
Au/TiO <sub>2</sub>	3-13	Colloidal-deposition	Cal. 450°C	<b>2077-2068</b>	2105-2103	ND	<b>Electron from the reduced support</b>
	3.6; 2.5	Deposition-precipitation	Cal. at 400°C	<b>2055-1990</b>	2110	2186-2154	
Au/CeO <sub>2</sub>	1-3	Deposition-precipitation	Cal. at 400°C	<b>2065, 2060</b>	2100	2148-2140	
(0.5-2%) Au/CeZrO <sub>4</sub>	---	Deposition-precipitation	150°C in WGS feed	<b>2070-1850</b>	2098	2125	
3%Au/Fe <sub>2</sub> O <sub>3</sub>	3-4	Deposition-precipitation	Cal. at 400°C	<b>2020-1990, 1940</b>		2120	
Au/MgO	large	Deposition onto MgO film	550K in O <sub>2</sub>	<b>2074-1855</b>	2097	2150	Charge transfer from electron-rich oxide defects
1.84%Au/SiO <sub>2</sub> (204m <sup>2</sup> /g)	5	Direct anionic exchange (DAE)	Cal. at 400°C	<b>2080-1952</b>	2122-2103	2129-2114	CO reduction
Au/SBA15	~3	Wet chemical process	Cal. at 500°C	<b>2077-2054</b>	2114-2111	2175	<b>Organic ligands from precursor</b>
1%Au/SiO <sub>2</sub>	5.7	Deposition-precipitation	Cal. at 400°C	<b>2065-2044</b>	2115		
1.0%Au/NaY	<5	Adsorption of Au(CH <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>7</sub> O)		<b>2083-2036</b>	2122	2207-2183	
1%Au/SiO <sub>2</sub> (175 m <sup>2</sup> /g)	2.0	Slurry then filter	Cal. at 500°C	<b>2070</b>	2112		<b>Au restructuring</b>
Au/SiO <sub>2</sub>		Suspension then filter	Cal. at 300°C	<b>2080-2056</b>		>2120	
2.1%Au/Al <sub>2</sub> O <sub>3</sub> (208 m <sup>2</sup> /g)	3.0	Slurry then filter	Cal. at 500°C	<b>2079-2040,1886</b>	2107		
1%Au/Al <sub>2</sub> O <sub>3</sub> (140 m <sup>2</sup> /g)	1.8	Anionic exchange	Cal. at 300°C	<b>2070-1950</b>	2105-2095		

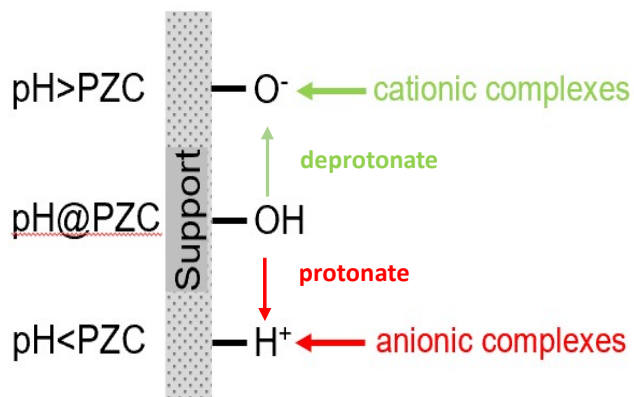
\*All information in the table is from literature

❑ Over reducible supports: Electrons transferred from supports to Au during reduction process;

❑ Over non-reducible supports: Controversial origin of electrons on Au<sup>δ-</sup>.

# Catalysts Synthesis: SiO<sub>2</sub> supported Au NPs via SEA or DI

SEA (strong electrostatic adsorption):



❖ Support surface charged by adjusting solution pH

❖ Adsorb positively charged metal precursor

❖ Strong precursor-support interaction

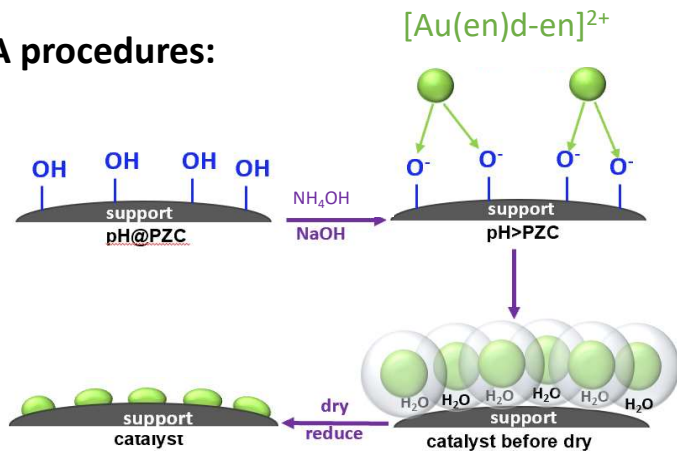
❖ Ultra-small particle size (<2nm)

mass loading: 2.2 wt%; Au precursor: gold ethylene diamine [Au(en)<sub>2</sub>]<sup>3+</sup>

SEA particle size: 1.6 nm; Dry impregnation: 11 nm

All Au samples were reduced in 20% H<sub>2</sub> at 400°C for 1hr before pressing IR discs.

SEA procedures:

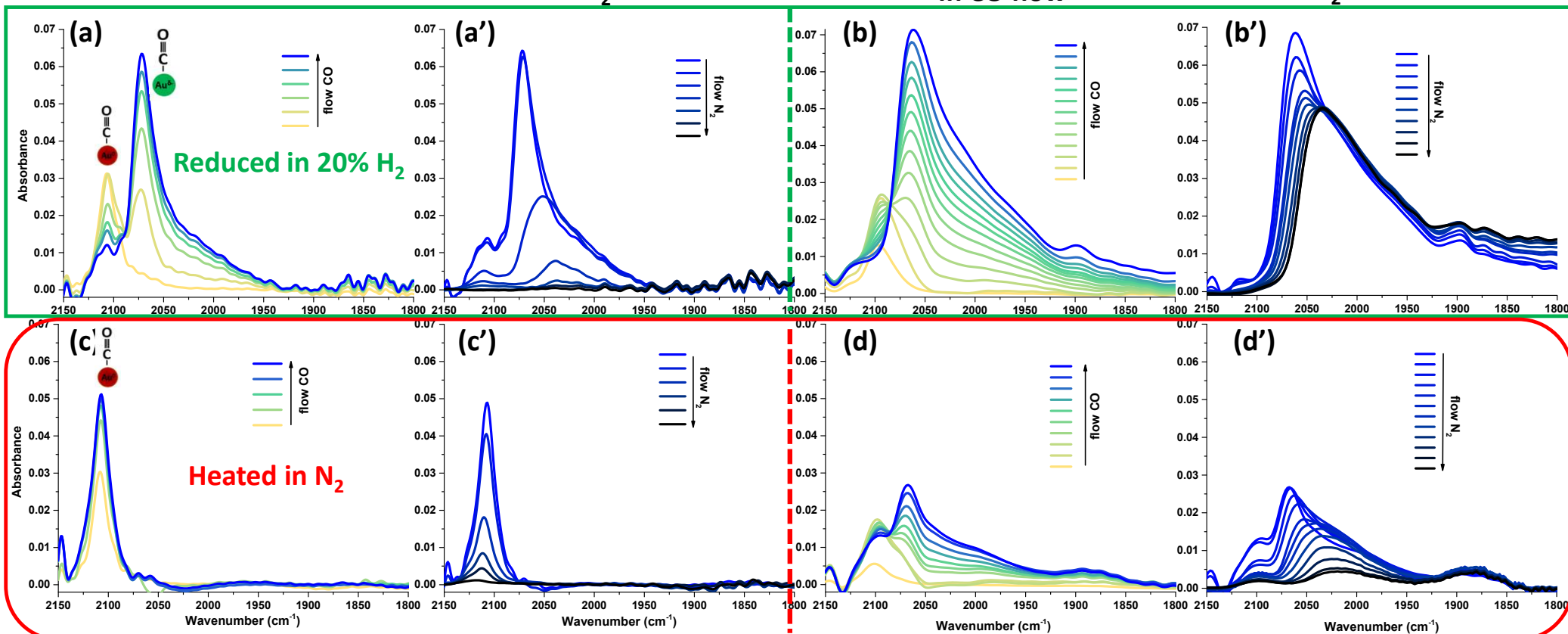


# Effects of Thermochemical atmosphere

Au/SiO<sub>2</sub> 1.6nm

180°C pretreatment  
In CO flow → In N<sub>2</sub> flow

400°C pretreatment  
In CO flow → In N<sub>2</sub> flow



- ❑ IR spectra were recorded at room temperature and shown with gas CO phase subtracted.
- ❑ In flowing CO, Au<sup>0</sup> rapidly accumulates and falls as various species of Au<sup>δ-</sup> accumulate.
- ❑ H<sub>2</sub> and high T in-situ reduction needed for the formation of strongly bound, negatively charged gold species.
- ❑ Small amount of Au<sup>δ-</sup> forms without H<sub>2</sub> at high annealing T.

# Effects of Temp. & Particle size

IS-R\* @180°C

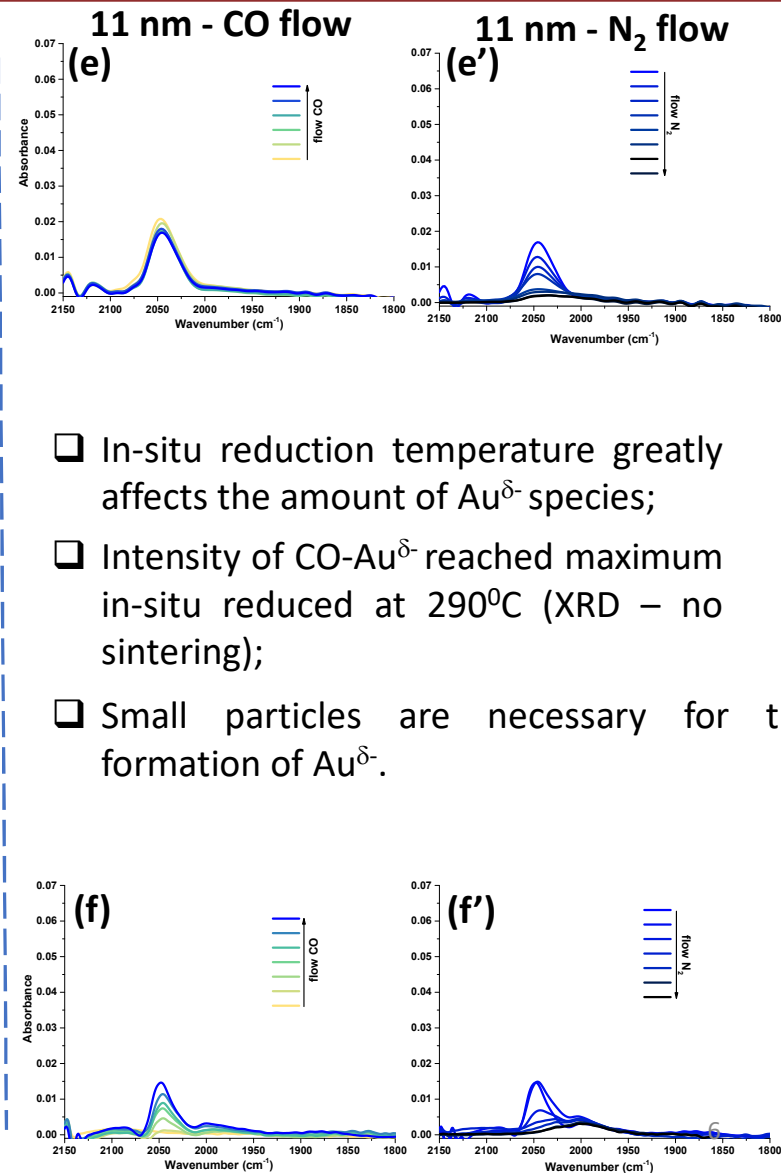
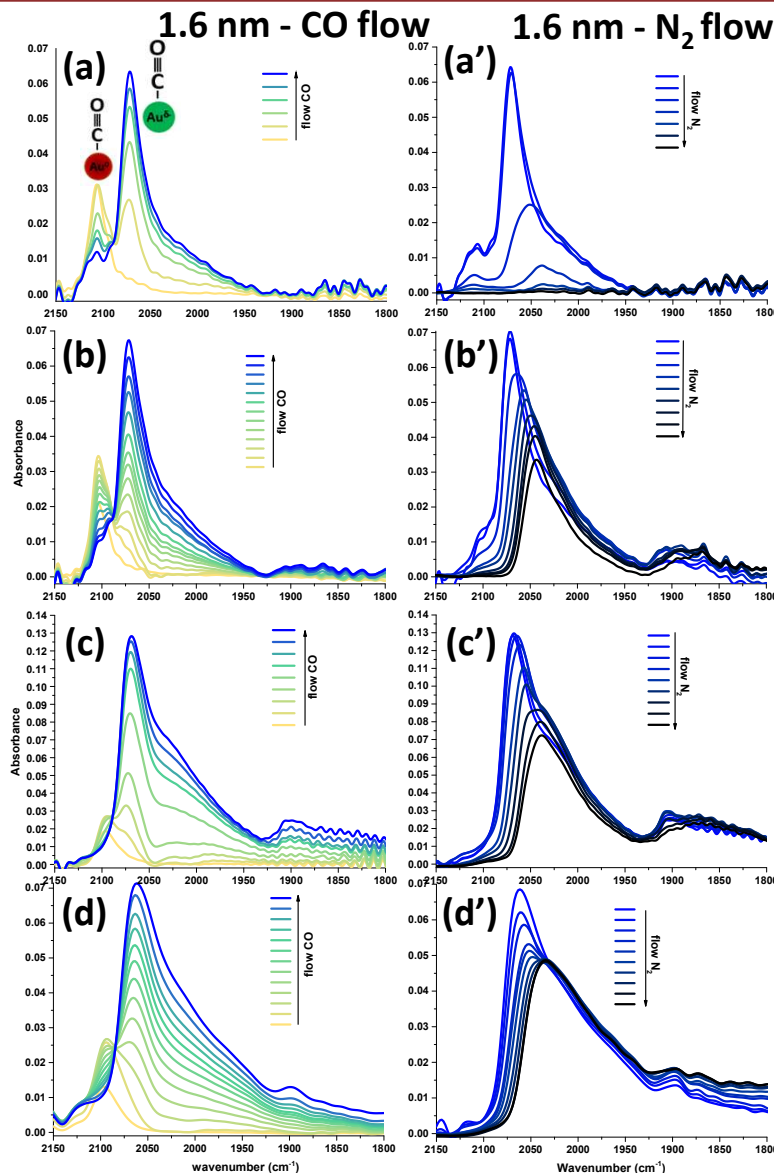
SEA: 1.6 nm  
DI: 11 nm

IS-R @240°C

IS-R @290°C

IS-R @400°C

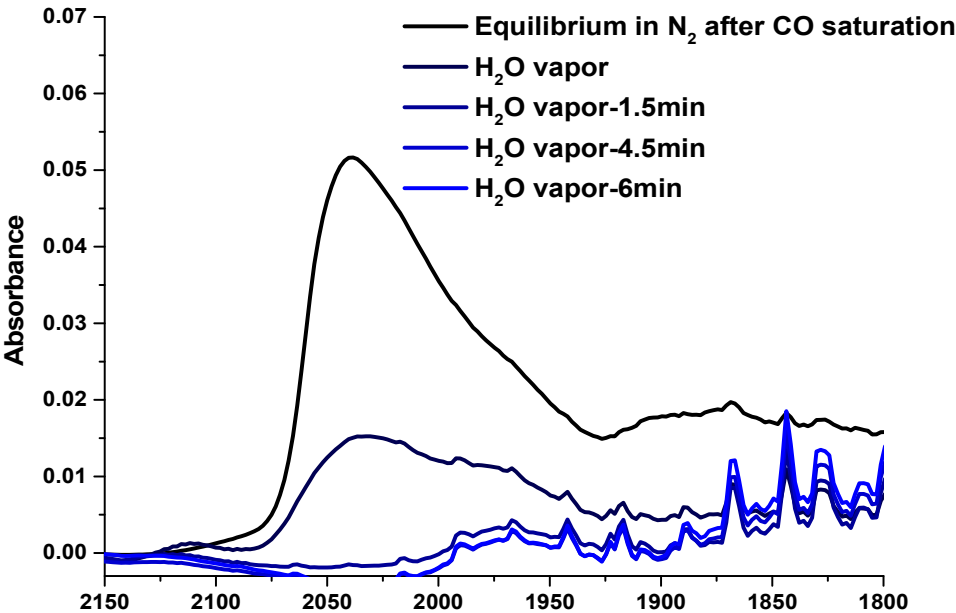
\*IS-R: in-situ reduced



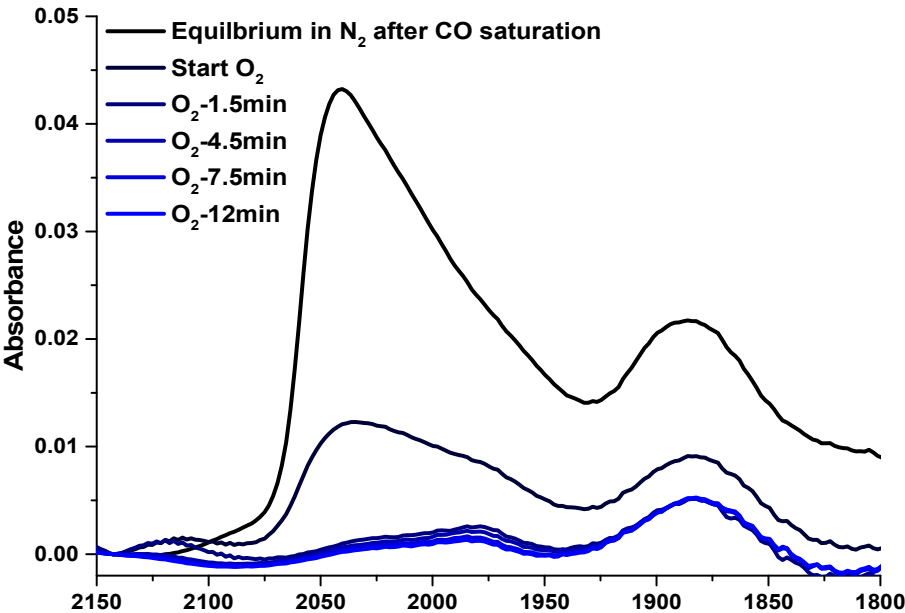
- ☐ In-situ reduction temperature greatly affects the amount of  $\text{Au}^\delta$  species;
- ☐ Intensity of CO-Au $^\delta$  reached maximum in-situ reduced at 290°C (XRD – no sintering);
- ☐ Small particles are necessary for the formation of  $\text{Au}^\delta$ .

# Effects of O<sub>2</sub> and water vapor

Effect of H<sub>2</sub>O vapor



Effect of O<sub>2</sub>



☐ H<sub>2</sub>O vapor removes Au<sup>δ-</sup> quickly and thoroughly

☐ Small amount of adsorbed CO at 1880 cm<sup>-1</sup> persists in presence of O<sub>2</sub>

## Three hypotheses for CO-bands (by IR) lower than 2080 cm<sup>-1</sup>

- I. CO-Au<sup>δ-</sup>, anionic Au species from **organic residuals**;
- II. CO-Au<sup>δ-</sup>, anionic Au species from **CO reduction** of metallic Au;
- III. CO-Au<sup>0</sup>, Au restructuring.



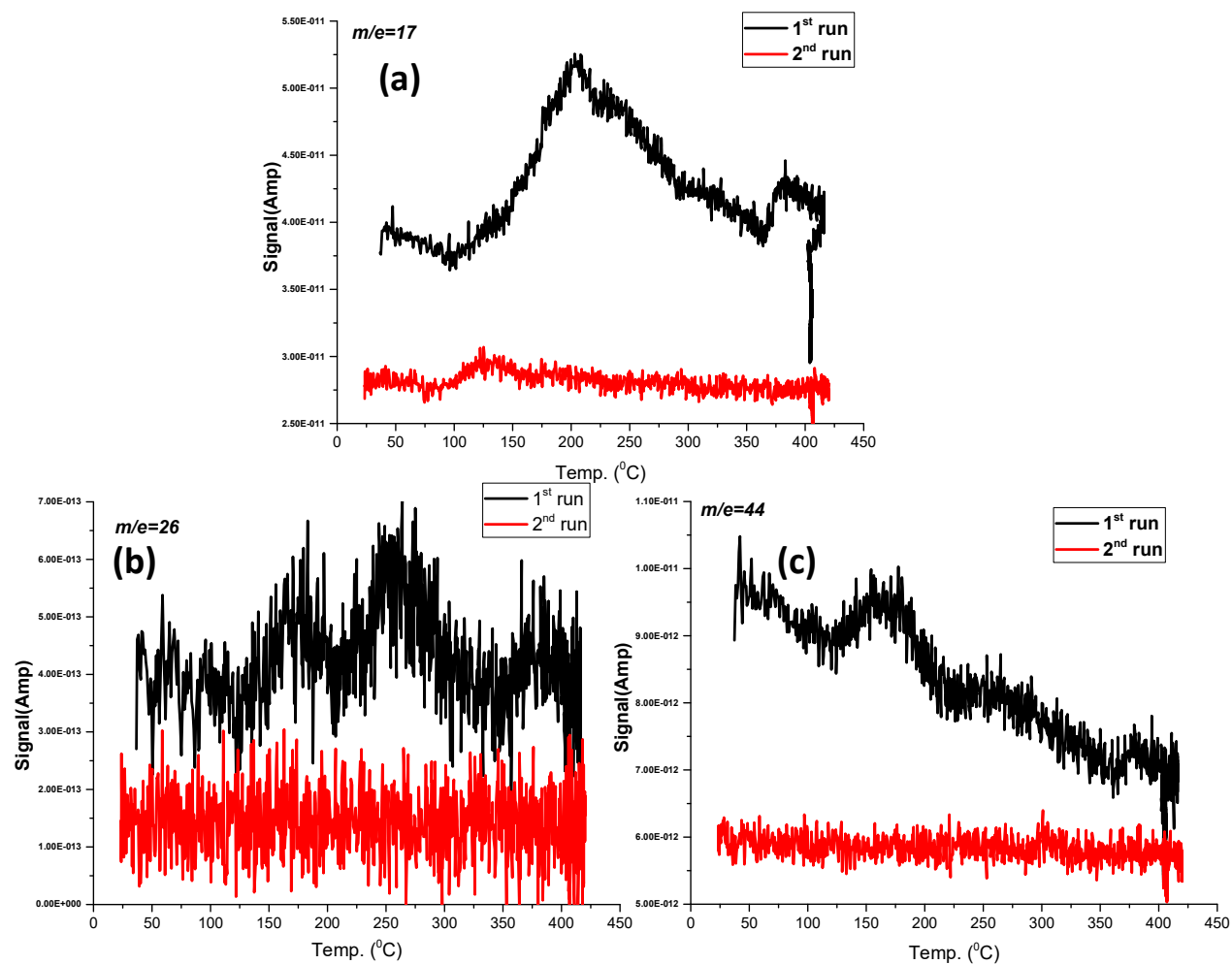
# I. TPR-mass spectra disproves the hypothesis of from organic residuals

**1<sup>st</sup> run:** flow 20% H<sub>2</sub>, increase from RT to 400°C and hold for 1hr



Cool down to RT

**2<sup>nd</sup> run:** flow 20% H<sub>2</sub>, increase from RT to 400°C and hold for 1h

□ In the 2<sup>nd</sup> run of TPR by mass-spectra, the flat spectra suggest all the organic ligands were removed in the 1<sup>st</sup> reduction at 400°C.



## Three hypothesis over CO-bands (by IR) lower than 2080 cm<sup>-1</sup>

- I. CO-Au<sup>δ-</sup>, anionic Au species from **organic residuals**; 
- II. CO-Au<sup>δ-</sup>, anionic Au species from **CO reduction** of metallic Au; 
- III. CO-Au<sup>0</sup>, Au restructuring.

## II. Pretreatment of in-situ reduction in 1%CO disproves the hypothesis of CO reduction

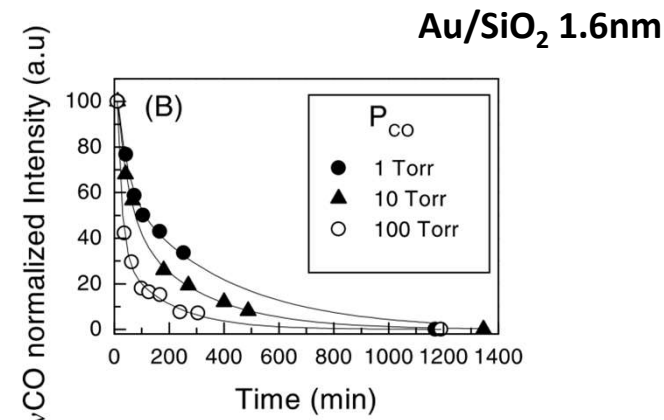
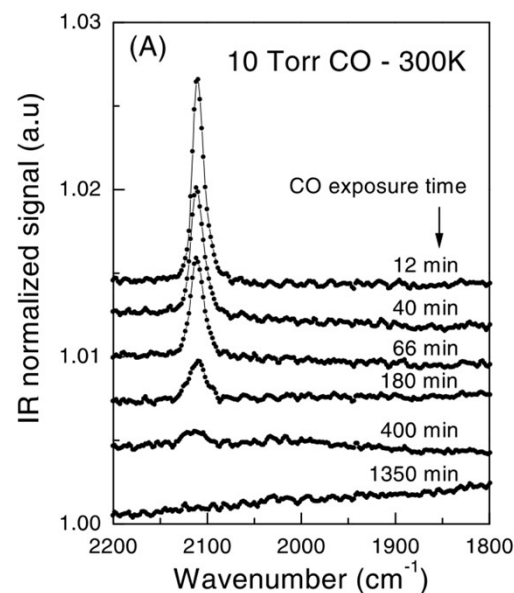
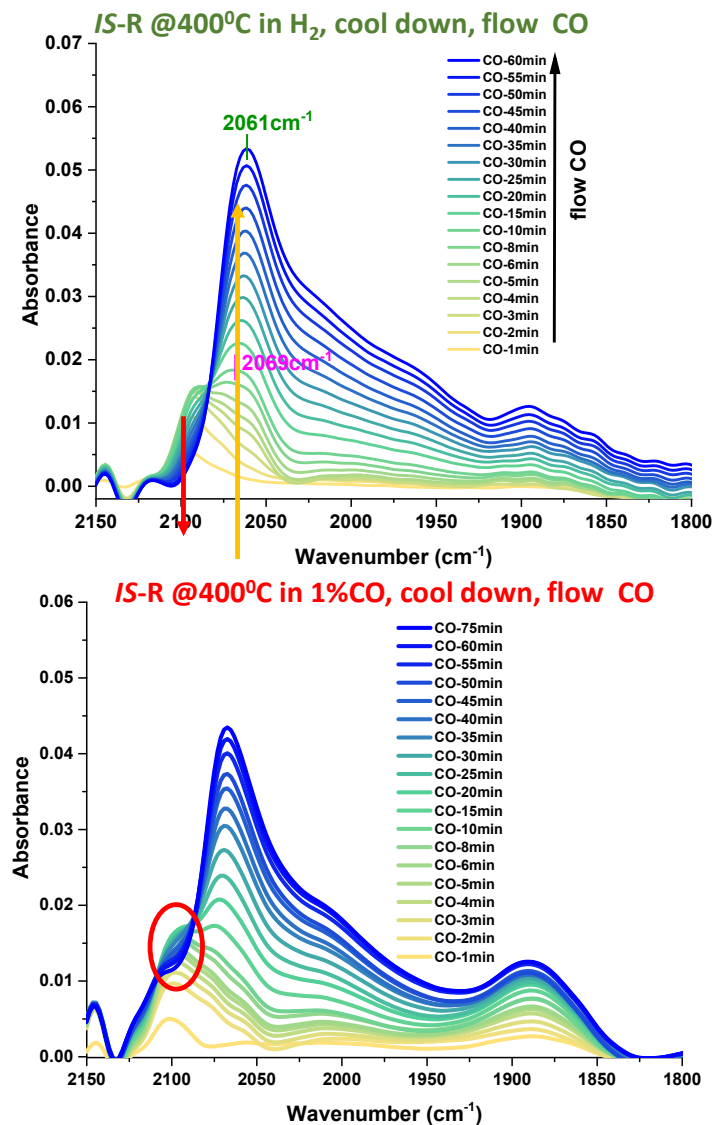


Fig. 2. (A) Time dependence of polarized RARS spectra for 10 Torr CO on Au(110) at 300 K. (B) Evolution of the CO stretching vibration intensity as a function of time under various CO pressures; each curve is normalized at  $t = 10$  min in order to compare the decay rate. Continuous lines are guides to eye.




Y. Jugnet et al. / Surface Science 521 (2002) L639–L644

❑ Au<sup>0</sup> persists after high T exposure to CO

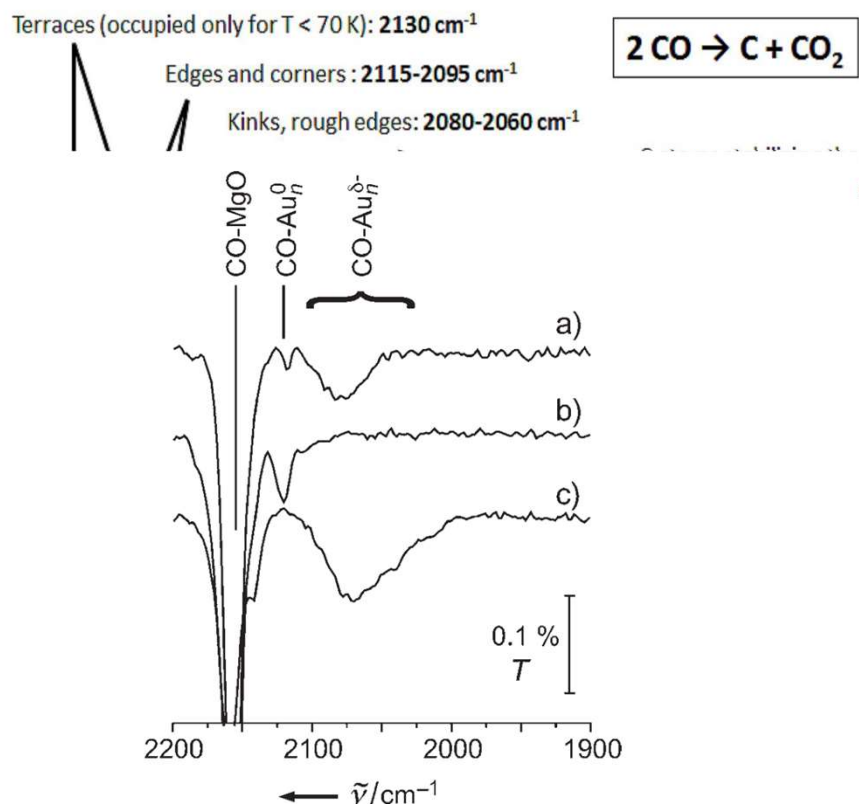
❑ Literature: Reconstruction of Au induced by CO

- Intensity of CO decreases with time and decay rate increases with pressure;
- Reconstruction-missing row of Au atoms, roughening of the surface;
- XPS showed presence of Carbon after exposure to CO and growing with time.

## Three hypothesis over CO-bands (by IR) lower than 2080 cm<sup>-1</sup>

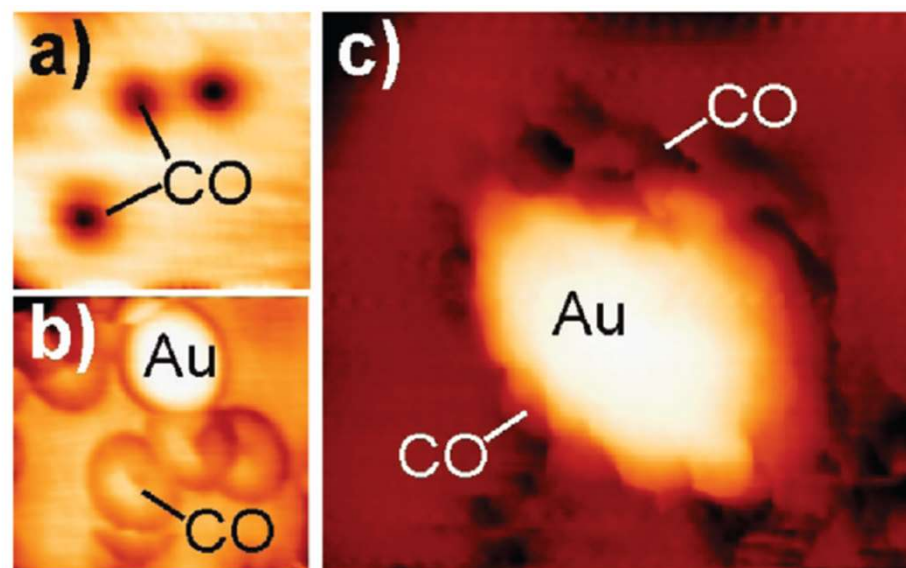
- I. CO-Au<sup>δ-</sup>, anionic Au species from **organic residuals**; 
- II. CO-Au<sup>δ-</sup>, anionic Au species from **CO reduction** of metallic Au; 
- III. CO-Au<sup>0</sup>, Au restructuring. 

### III. Hypothesis of Au reconstruction



**Figure 2.** IR spectra after saturation coverage by CO on Au clusters formed on differently pretreated MgO films. a) film after medium-dose electron bombardment and deposition of 0.05 ML Au at 30 K; b) pristine MgO film after deposition of 0.025 ML Au at 80 K; c) film after high-dose electron bombardment and deposition of 0.025 ML Au at 30 K; film annealed to 90 K prior to CO adsorption;  $T$  = transmission.

Angew. Chem. Int. Ed. 2006, 45, 2630–2632



**Figure 1.** STM topographic images of CO molecules on 2 ML MgO/Ag(001) imaged with (a) a metallic and (b) a CO-covered tip ( $3 \times 3\text{ nm}^2$ , 150 mV, 3 pA). The CO(tip)–CO(sample) interaction leads to a ring-like appearance of the adsorbates in (b). (c) STM image of a CO-saturated Au island taken with a CO-covered tip ( $4 \times 4\text{ nm}^2$ , 100 mV, 3 pA). CO-induced contrast is only revealed at the perimeter of the Au island.

J. Am. Chem. Soc. 2010, 132, 22, 7745–7749

- ❑ CO adsorbed on gold island perimeter (with electrons), instead of on the center (adsorbate-free);
- ❑ Au with more electrons shows broader and lower wavenumbers.
- ❑  $\text{Au}^{\delta-}$  species indeed exist and density of electrons affects the IR signal and frequency.

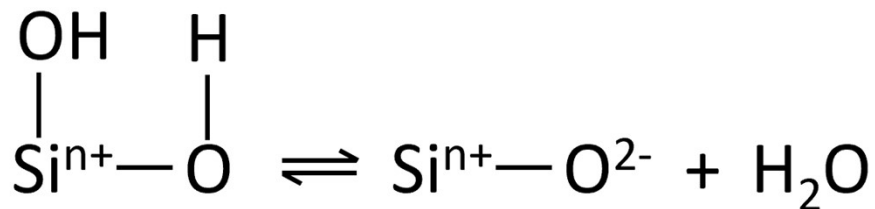
## Proposed Hypothesis for the formation of $\text{Au}^{\delta-}$

I.  $\text{CO-Au}^{\delta-}$ , anionic Au species from **organic residuals**;

II.  $\text{CO-Au}^{\delta-}$ , anionic Au species from **CO reduction** for metallic Au;

III.  $\text{CO-Au}^0$ , Au restructuring.

☐ Charge defects on  $\text{SiO}_2$  surface induced by dehydroxylation at high temperatures.



Proposed mechanism:

- defective  $\text{Si}^\cdot$  and  $\text{SiO}^\cdot$ ,  
electron transfer to Au  
atoms at the perimeter

## Dehydroxylation at elevated Ts

**Au/SiO<sub>2</sub>- N<sub>2</sub> annealed:**

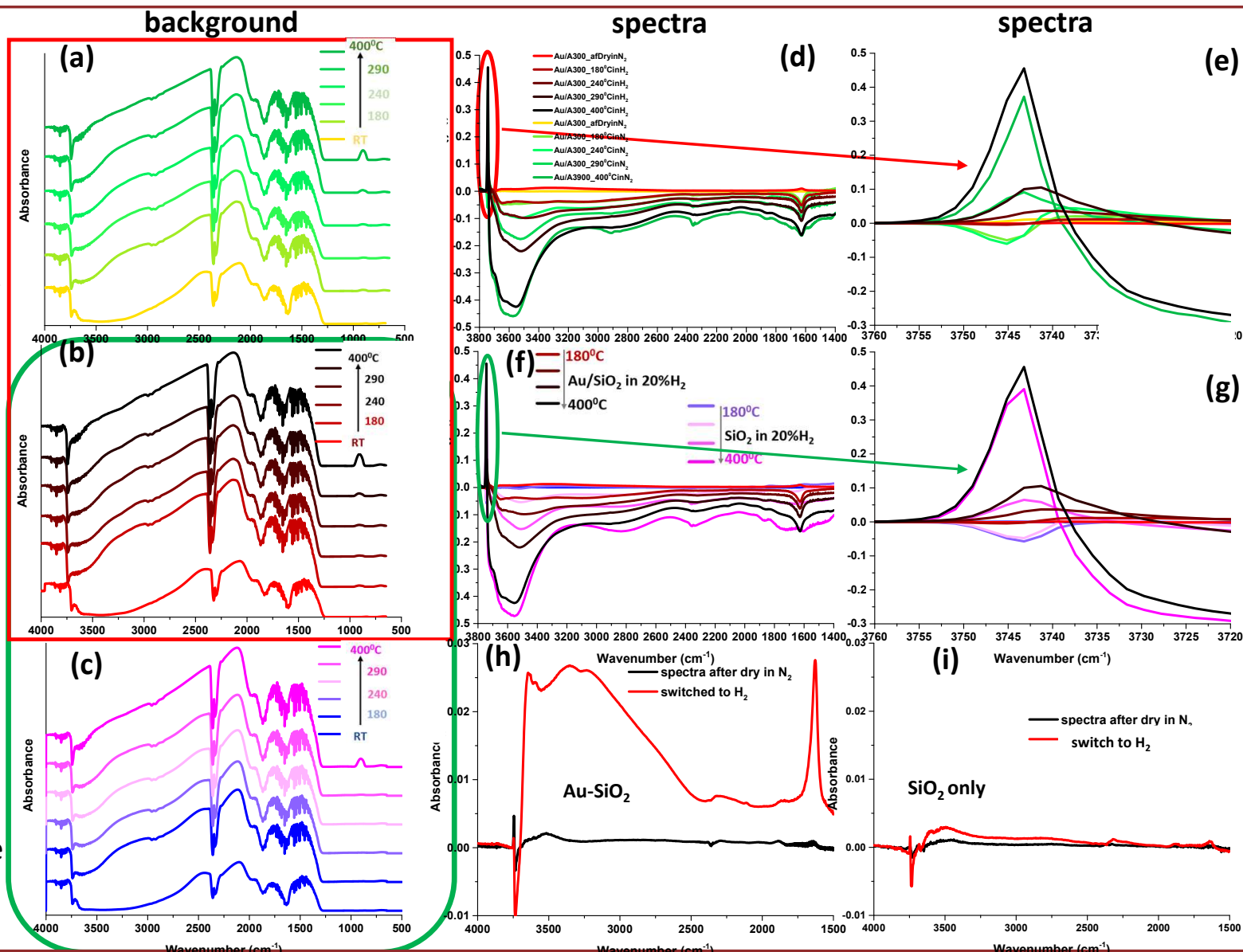
☐ H<sub>2</sub> enhanced the dehydroxylation of SiO<sub>2</sub>.

**Au/SiO<sub>2</sub>- H<sub>2</sub> reduced:**

☐ Au enhanced the dehydroxylation of SiO<sub>2</sub>.

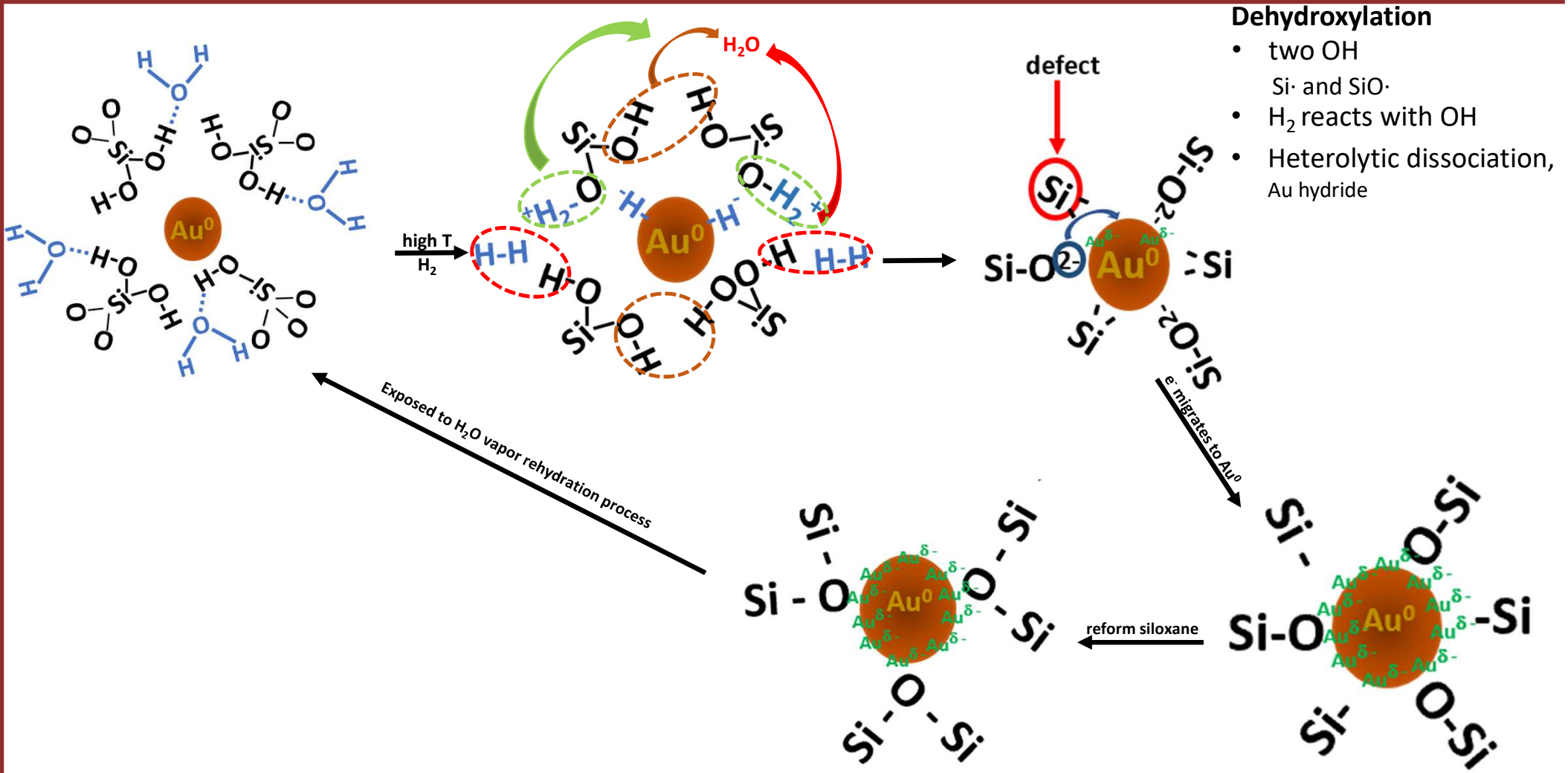
**SiO<sub>2</sub>- H<sub>2</sub> reduced:**

☐ Au can catalyze the oxidation of H<sub>2</sub> to H<sub>2</sub>O.





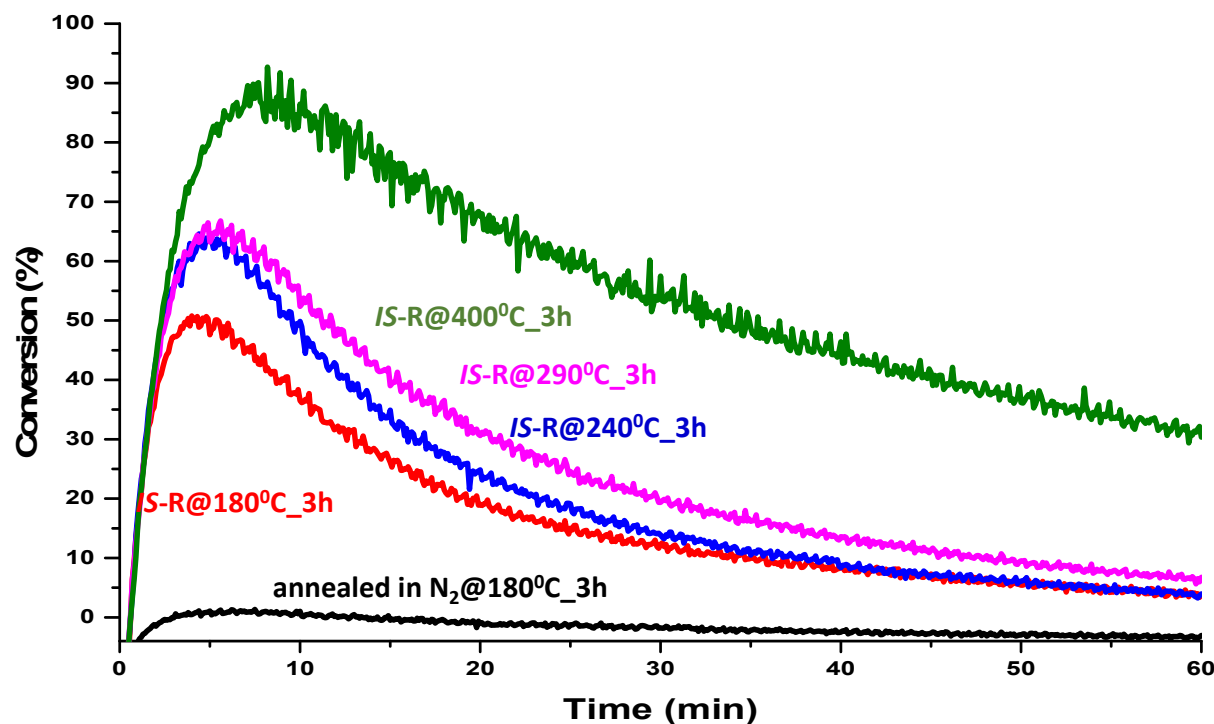
# Proposed Scheme for the formation of Au<sup>δ-</sup>





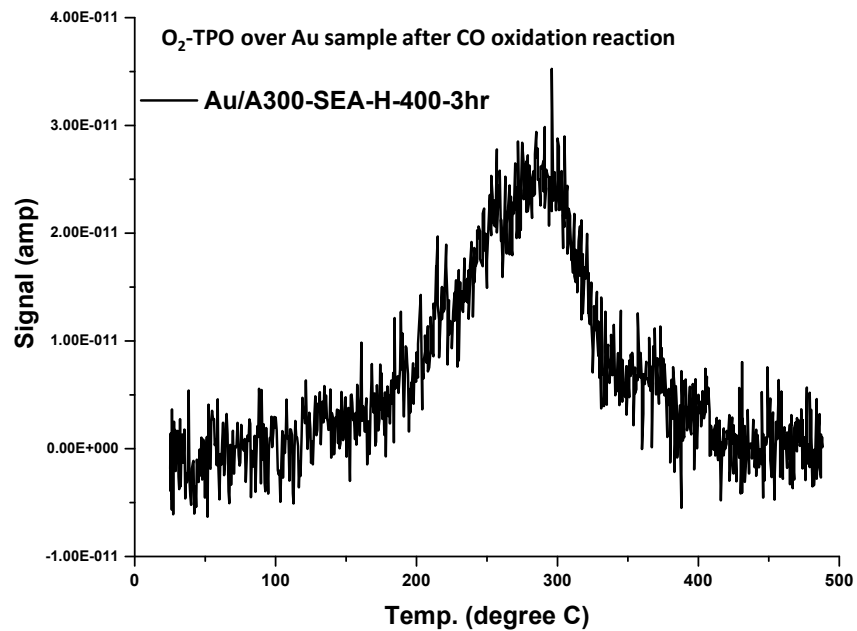
## Room temperature CO oxidation monitored by mass spectra

Sample: Au/SiO<sub>2</sub> 1.6nm; Loaded catalyst: ~100mg; RT CO oxidation: 1%CO, 1%O<sub>2</sub>, balance Ar.



- ❑ Higher in-situ reduction temperature led to a higher initial activity;
- ❑ Rapid deactivation may be caused by oxidation of the Au surface or carbon accumulation;
- ❑ Residual activity may be related to persistent 1880 cm<sup>-1</sup> species which persists in O<sub>2</sub>.

# TPO to check C accumulation

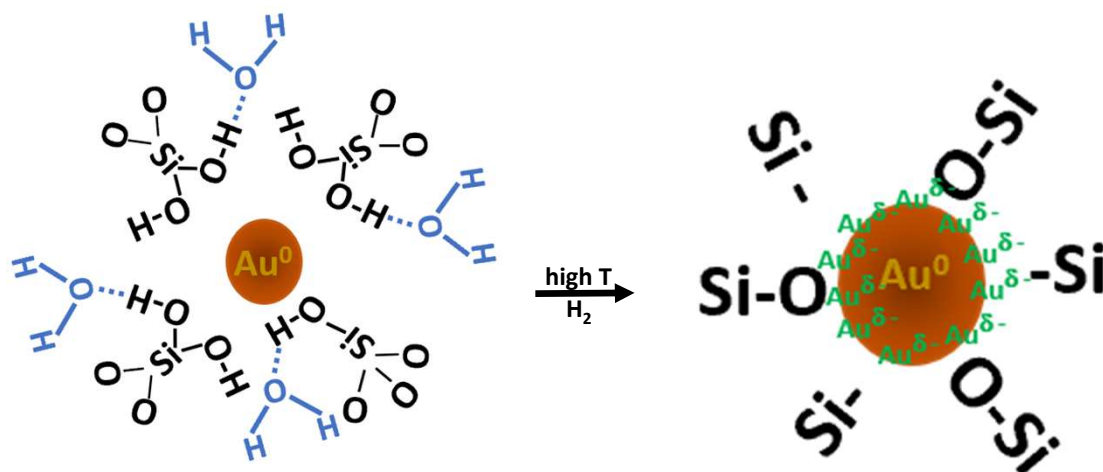


	O <sub>2</sub> -TPO	CO oxidation
Peak area	4.3E-10	5.4E-08
Amount of CO <sub>2</sub> (μmol/0.1g)	6.4	7900
Conversion of CO (%)	0.55	68

- ☐ Carbon deposition appears to occur only to a small extent.
- ☐ Main deactivation due to loss of Au<sup>δ-</sup>

## Conclusion

- ❑ SEA can be used to synthesize ultra-small Au nanoparticles;
- ❑ Small NPs, high T and  $H_2$  is necessary for the formation of  $Au^{\delta-}$  on  $SiO_2$ ;
- ❑ Water vapor can easily rehydrate silica surface and reoxidize  $Au^{\delta-}$  species



- ❑ Increased activity in RT CO oxidation is achieved over Au sample in-situ reduced at a higher T; rapid deactivation is caused by the consumption of  $Au^{\delta-}$ .

## Acknowledgements

- Center for Renewable Fuels for the funding.
- Dr. John Regalbuto for instruction.
- Dr. Christopher Williams for consultations.
- Dr. Regalbuto group at University of South Carolina.

*Thanks!!!*

Questions?





# I. TPR-mass spectra disproves the hypothesis of from organic residuals

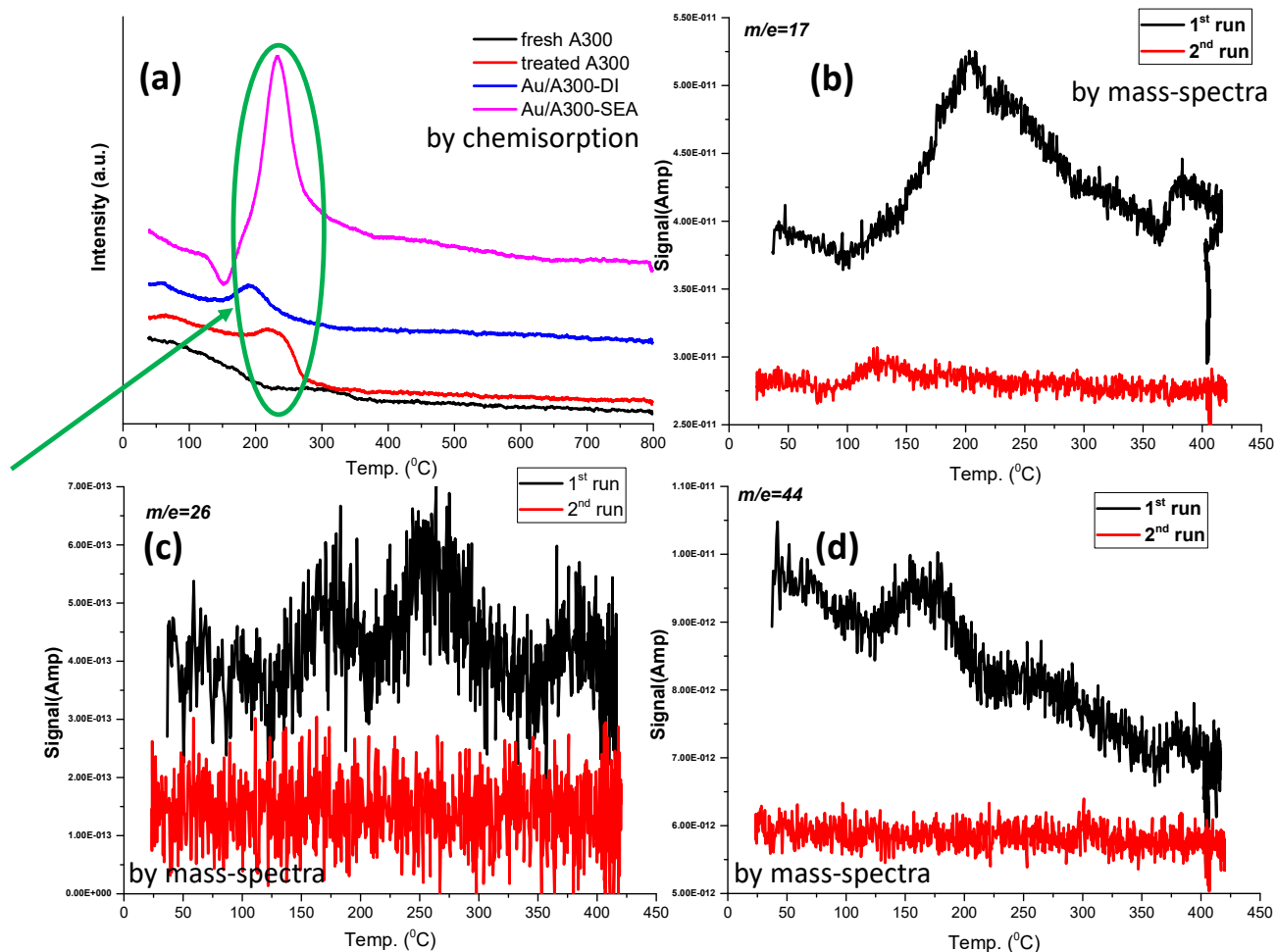
**1<sup>st</sup> run:** flow 20% H<sub>2</sub>, increase from RT to 400°C and hold for 1hr

Cool down to RT

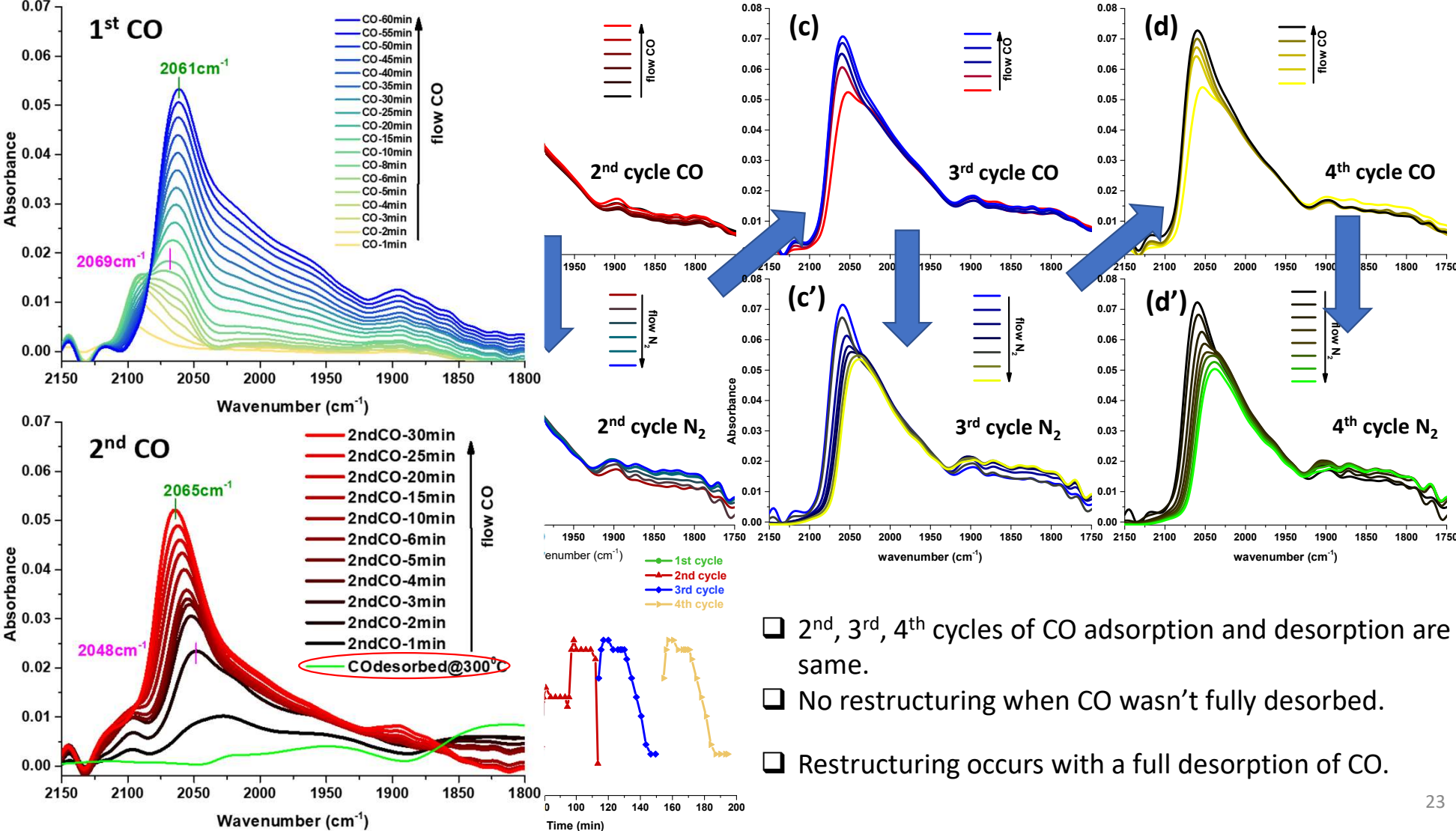
**2<sup>nd</sup> run:** flow 20% H<sub>2</sub>, increase from RT to 400°C and hold for 1h

□ Decomposition of ethylenediamine;

□ In the 2<sup>nd</sup> run of TPR by mass-spectra, the flat spectra suggest all the organic ligands were removed in the 1<sup>st</sup> reduction at 400°C.



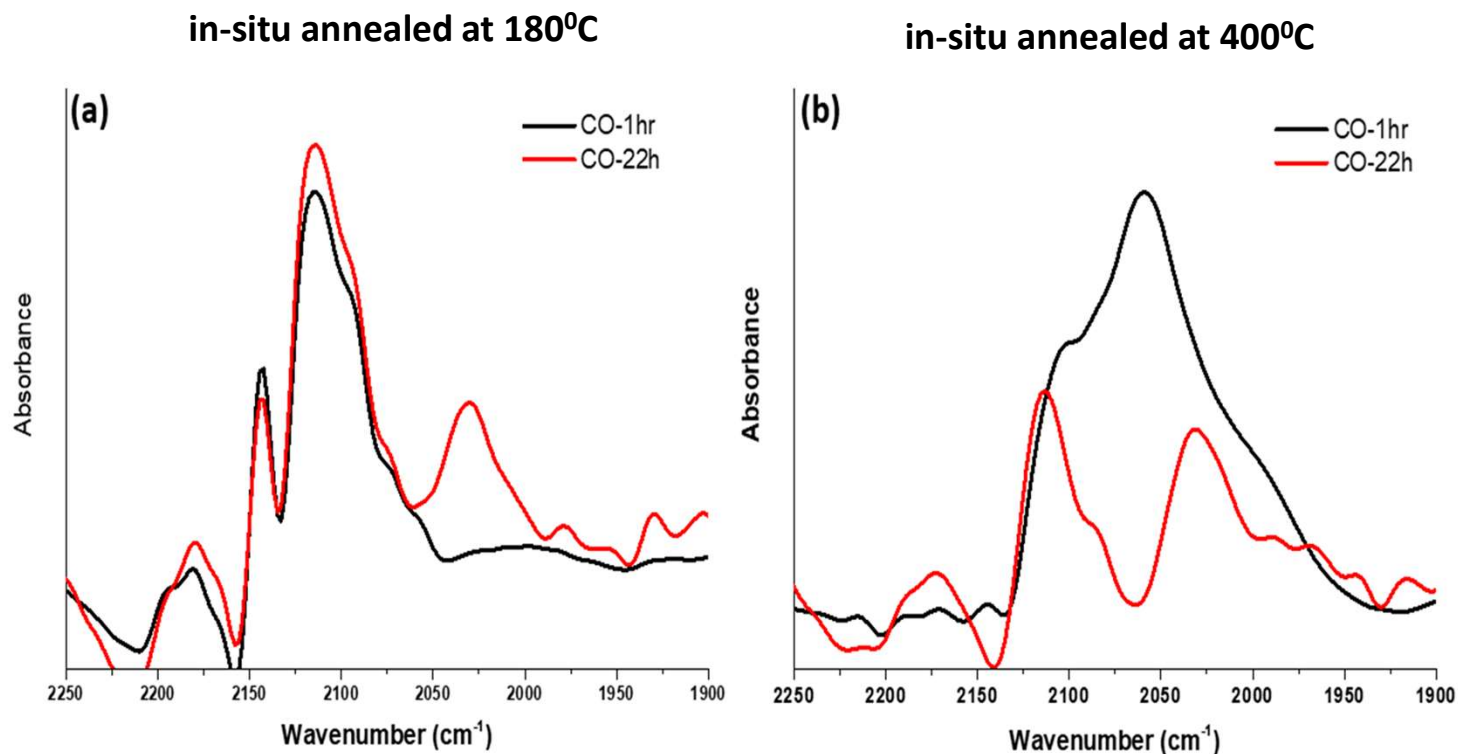
# III. Hypothesis of Au reconstruction



## II. Flow CO at RT for 22 hrs to disprove the hypothesis of CO reduction

**Sample:** 2.2wt% Au/SiO<sub>2</sub>, 1.6 nm

**IR condition:** flow CO at RT for 1 and 22h.



☐ CO reduction over Au<sup>0</sup> to Au<sup>δ-</sup> at room is a very slow process.

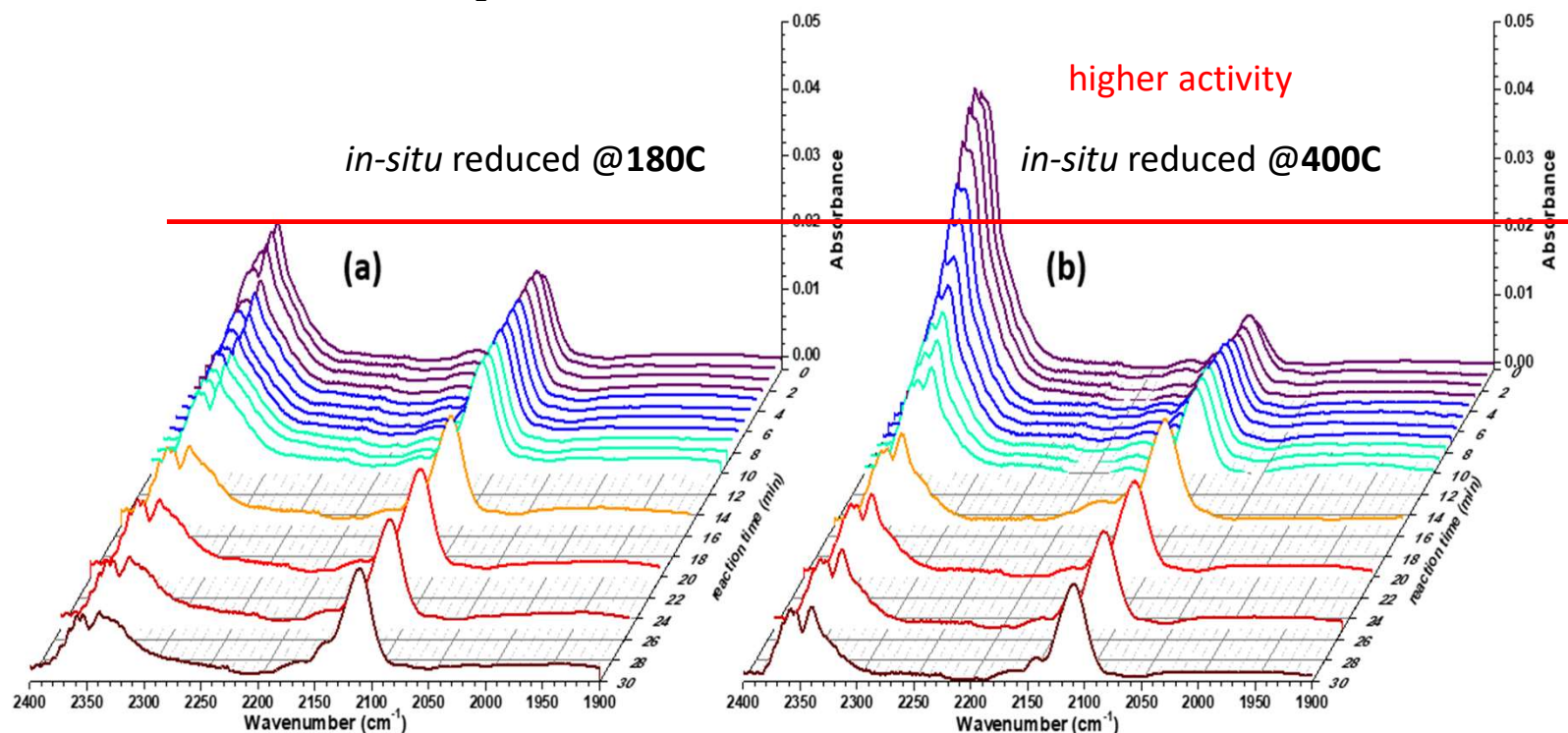


# Room temperature CO oxidation monitored by IR

**Sample:** 2.2wt% Au/SiO<sub>2</sub>-SEA;

**Pretreatment:** In-situ reduced in IR cell @ 180°C (a), 400°C (b), cool down to RT ;

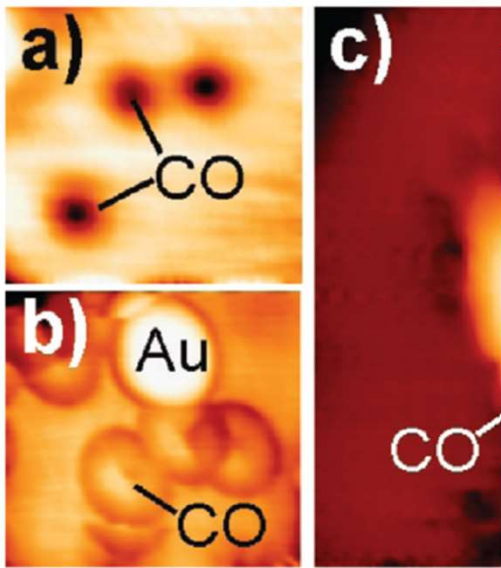
**Reaction condition:** flow 1%CO+10%O<sub>2</sub> into IR cell at RT.



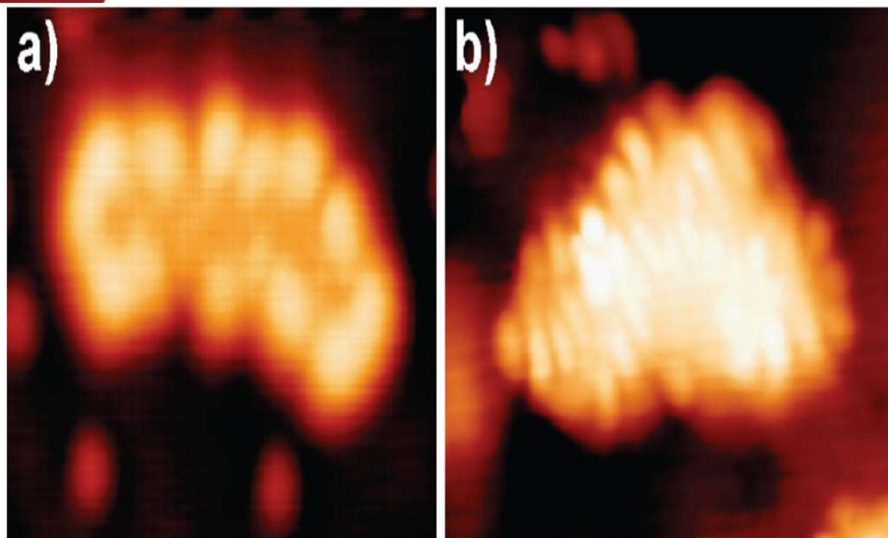
- ❑ Au sample in-situ reduced at 400°C showed higher performance in RT CO oxidation;
- ❑ Activity decreased sharply after several minutes of the reaction.

IR spectra were recorded at room temperature with background and gas CO correction.

### III. Hypothesis of Au reconstruction



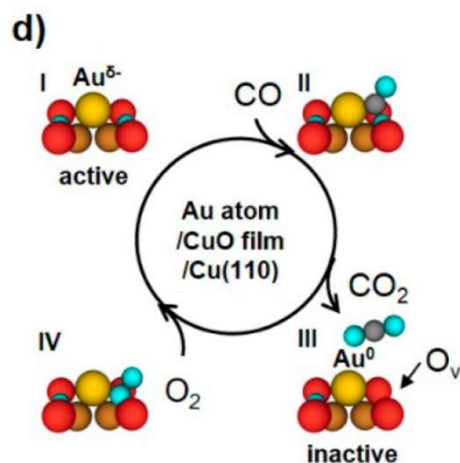
**Figure 1.** STM topographic images of Ag(001) imaged with (a) a metallic and 150 mV, 3pA). The CO(tip)–CO(sample) appearance of the adsorbates in (b). (c) STM image of a CO-saturated Au island taken with a CO-covered tip ( $4 \times 4 \text{ nm}^2$ , 100 mV, 3pA). CO-induced contrast is only revealed at the perimeter of the Au island.



**Figure 3.** STM topographic images of (a) a bare and (b) a CO-saturated Au island on 2 ML MgO/Ag(001) ( $7.0 \times 5.5 \text{ nm}^2$ , 150 mV). Whereas the bare island is surrounded by a bright rim, indicating charge accumulation at the perimeter, the CO-covered island exhibits charge-density waves in the interior. The standing electron waves are due to electron displacement from the island boundary upon CO adsorption.

- ❑ CO adsorbed on gold island perimeter (with electrons), instead of on the center (adsorbate-free);
- ❑ CO adsorption can modify the charge distribution within the Au islands.

### III. Room temperature CO oxidation reaction-mechanism



- ❑ **Au atoms with a lower coordination number can bind CO and  $\text{O}_2$  molecules more strongly** (CO bonds at corners and edge sites more strongly than at facet sites, Au step edges both O and  $\text{O}_2$  adsorption and  $\text{O}_2$  don't bind to flat facet of gold NPs)
- Smaller gold NPs can adsorb more CO and  $\text{O}_2$  molecules;

- ❑ **Negatively charged gold species can adsorb  $\text{O}_2$  more strongly than neutral ones.**
- ❑ Molecular oxygen obtains two electrons from the Au cluster to form a superoxol state ( $\text{O}_2^-$ ) which can react with a co-adsorbed CO molecule. **(Anionic Au is needed to adsorb and activate  $\text{O}_2$ )**
- ❑ Active sites of the Au catalysts are the surface and/or perimeter interface Au atoms which have different charge densities from the bulk metal.

Sample: Au/A300-SEA

Pretreatment: in-situ reduced in IR cell @ 400C

Saturated Au surface by CO, then flow CO+O<sub>2</sub> into IR cell at RT.

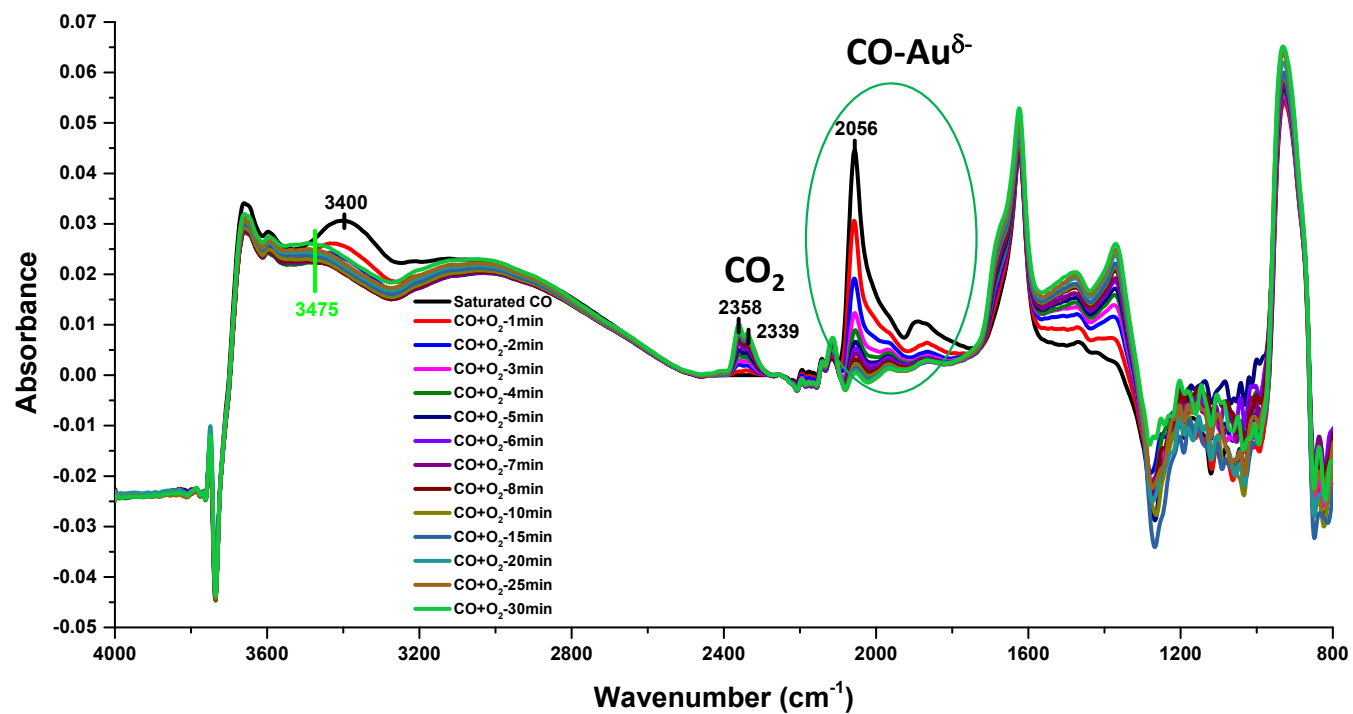


Figure 12. IR spectra over Au/A300-SEA-H-400 in CO and O<sub>2</sub> atmosphere after CO saturation.