

**UTSA**<sup>®</sup>

The University of Texas at San Antonio<sup>™</sup>

**Fischer-Tropsch synthesis: foregoing calcination and utilizing reduction promoters leads to improved conversion and selectivity with Co/silica**

Mohammad Mehrbod

Mechanical Engineering Program, Mechanical Engineering Dept., UTSA

Michela Martinelli, Burtron H. Davis

Center for Applied Energy Research, University of Kentucky

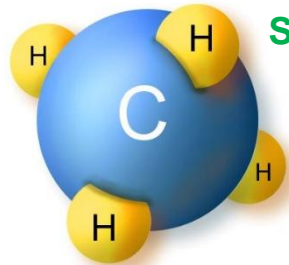
Donald C. Cronauer, A. Jeremy Kropf, Christopher L. Marshall

Advanced Photon Source, Argonne National Laboratory

Gary Jacobs

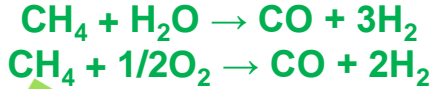
Chemical Engineering Program – Dept. of Biomedical Engineering/ Dept. of Mechanical Engineering, UTSA

March 18, 2017



Natural Gas

Steam Reforming / Partial Oxidation



Coal

Gasification



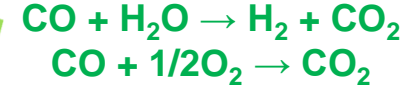
Biomass

FT Catalyst



Hydrogen

Water-gas Shift / Preferential Oxidation



Methanol, Ethanol

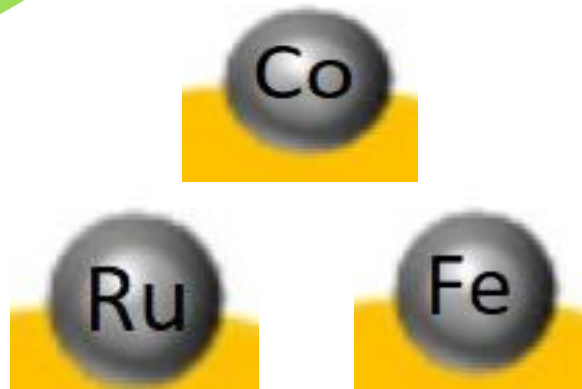
Oxygenate Synthesis



PEM Fuel Cells/SOFC  
Portable Power

Diesel Jet Fuel  
Waxes Lubricants

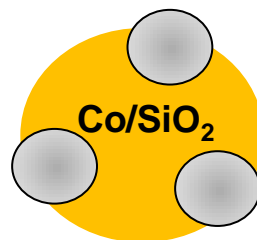
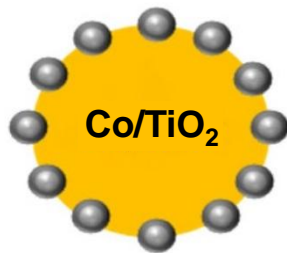
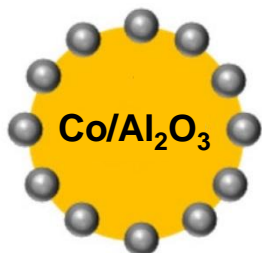
Fischer-Tropsch Synthesis





## Catalyst support and promoter:

- ❑ Cobalt often supported on metal oxide carriers like **alumina** or **titania**.



Problem: The weak interaction between SiO<sub>2</sub> and cobalt oxides on calcined catalysts leads to agglomerated Co<sup>0</sup> after activation. Productivity is lower.

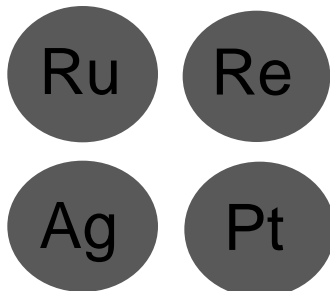
We consider 3 aspect:

Activity (CO conversion per gram of cat.)

Product Selectivity

Stability

## Promoter



Past efforts<sup>1,2</sup> showed that direct reduction of cobalt nitrate led to small, difficult-to-reduce Co species.

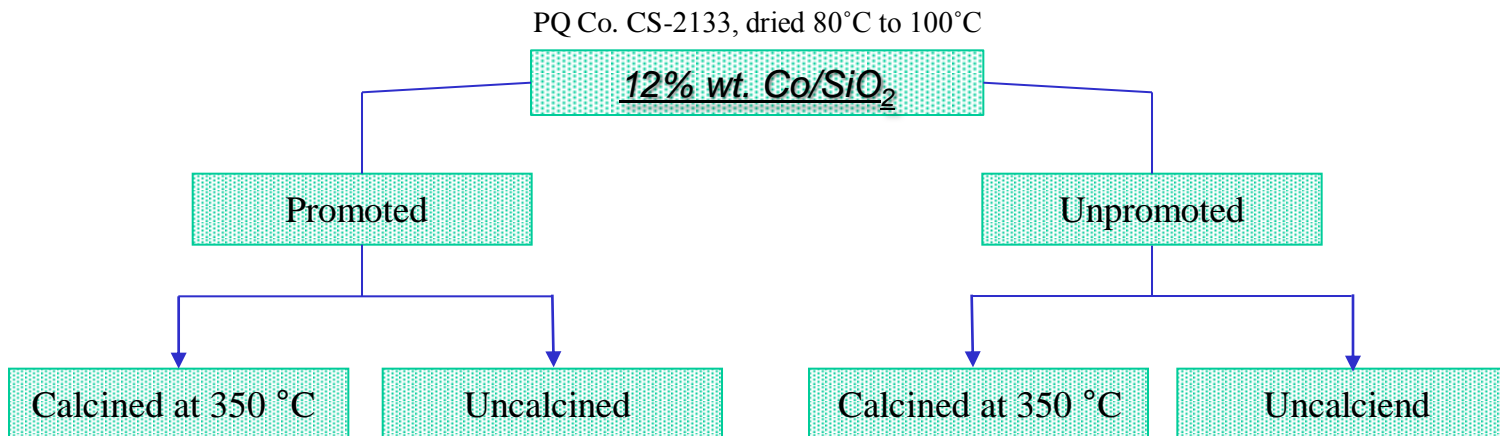
We revisit the possibility of direct cobalt nitrate reduction, but utilize promoters to facilitate activation of the difficult-to-reduce Co species.

1. B.H. Davis, E. Iglesia, DOE Quarterly Report #8, July-September 2000, Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts, Contract DE-FC26-98FT40308, Final Report, June, 30 2004.

2. Li, J.; Jacobs, G.; Das, T.K.; Zhang Y.; Davis, B.H., Applied Catalysis A: General 236 (2002) 67-76.



## Catalyst preparation



To prepare 0.5 wt.% (calcined basis) Pt promoted catalysts, tetraamineplatinum (II) nitrate was added by IWI to the dried  $\text{Co}(\text{NO}_3)_2$ /silica parent batch, and the material was dried again in the rotary evaporator.

Calcined	12%Co/SiO <sub>2</sub>	0.5%Pt-12%Co/SiO <sub>2</sub>	0.276%Ag-12%Co/SiO <sub>2</sub>	0.477%Re-12%Co/SiO <sub>2</sub>	0.259%Ru-12%Co/SiO <sub>2</sub>
Uncalcined	12%Co/SiO <sub>2</sub>	0.5%Pt-12%Co/SiO <sub>2</sub>	0.276%Ag-12%Co/SiO <sub>2</sub>	0.477%Re-12%Co/SiO <sub>2</sub>	0.259%Ru-12%Co/SiO <sub>2</sub>



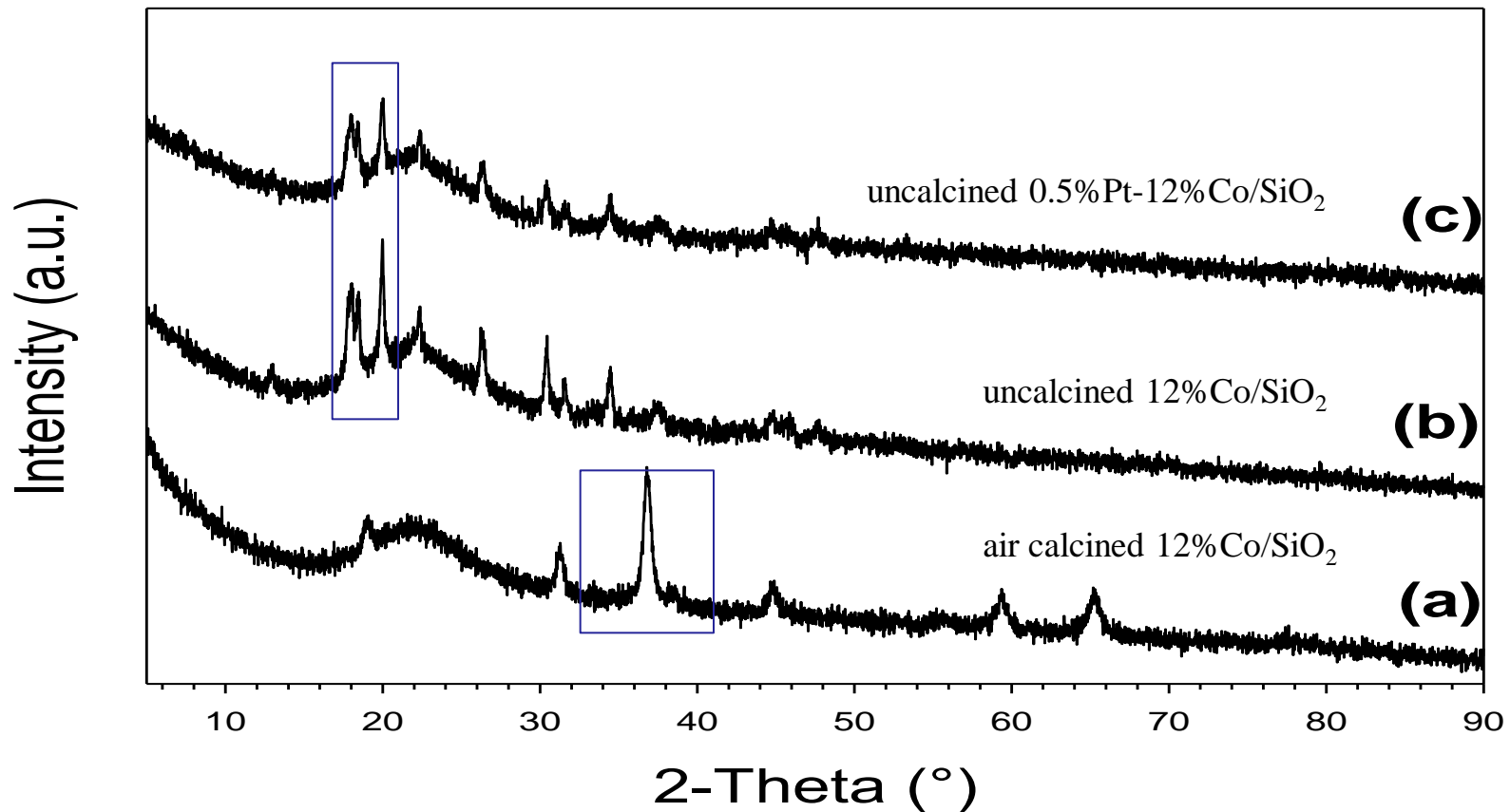
- **BET surface area and porosity measurements**  
*BET surface area and porosity characteristics were measured using a Micromeritics 3-Flex system.*
- **Temperature programmed reduction**  
*TPR profiles of calcined catalysts were recorded using a Zeton-Altamira AMI-200 unit equipped with a thermal conductivity detector (TCD).*
- **Hydrogen chemisorption and percentage reduction by pulse reoxidation**  
*Hydrogen chemisorption was conducted by using temperature programmed desorption (TPD), also measured with the Zeton-Altamira AMI-200 instrument*
- **TPR-EXAFS/ TPR-XANES spectroscopies**  
*In-situ H<sub>2</sub>-TPR XAFS studies were performed at the Materials Research Collaborative Access Team (MR-CAT) beamline at the Advanced Photon Source, Argonne National Laboratory*
- **Catalytic activity**  
*FTS reaction tests were conducted using a 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller*



## BET surface area and porosity measurements

If the support is the main contributor to the area, then after adding 12.3 wt. % Co and assuming no pore blocking, the specific surface area should decrease to 291 m<sup>2</sup>/g for the air calcined Co catalyst and 225 m<sup>2</sup>/g for the uncalcined catalyst.

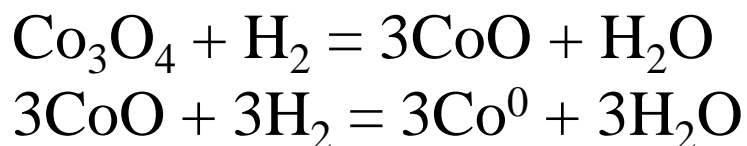
XRD analysis of the catalysts.





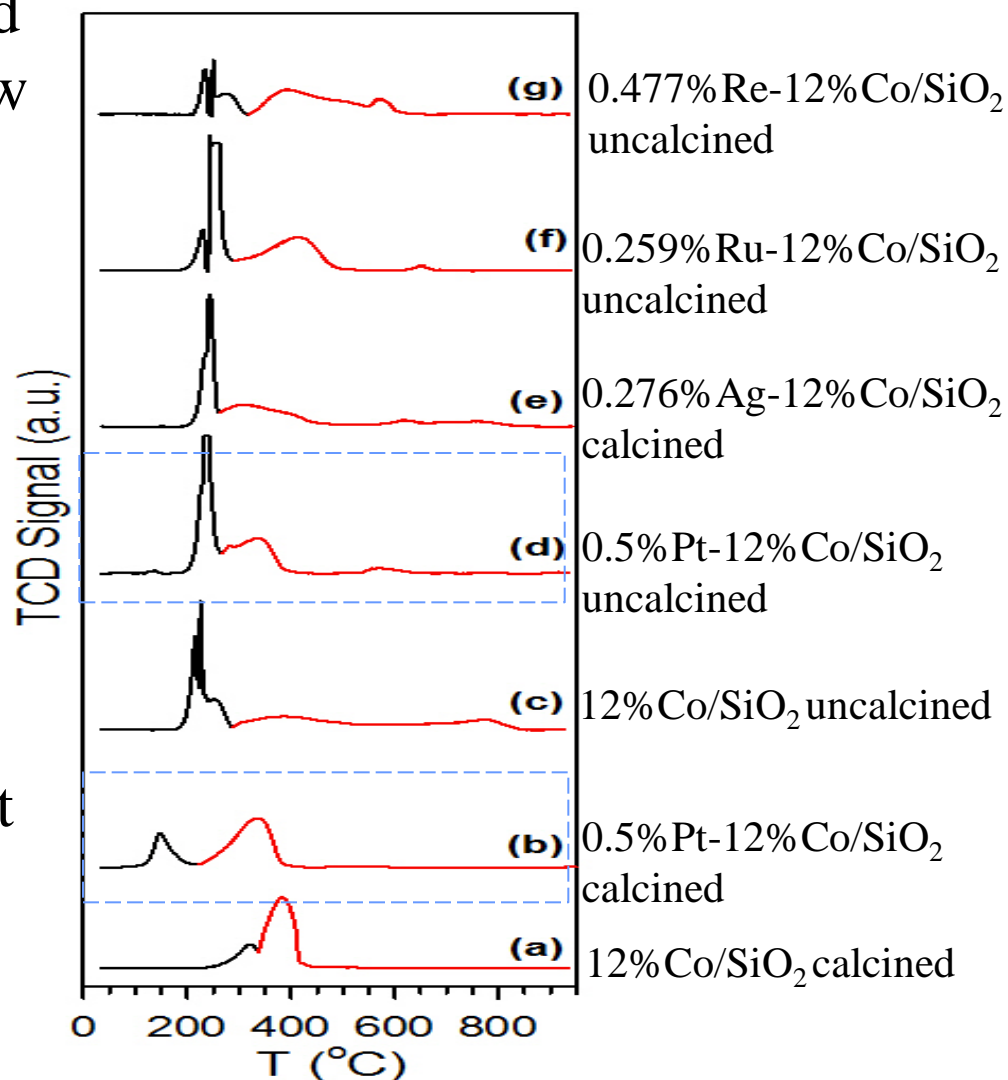
## Cobalt Reducibility:

Figure reveals that the air calcined catalyst reduced at a relatively low temperature



For uncalcined, promoter addition did not shift the peak for nitrate decomposition (black) but did shift the peaks for reduction of cobalt oxides (red) derived from nitrate decomposition.

TPR profiles of uncalcined and calcined catalysts





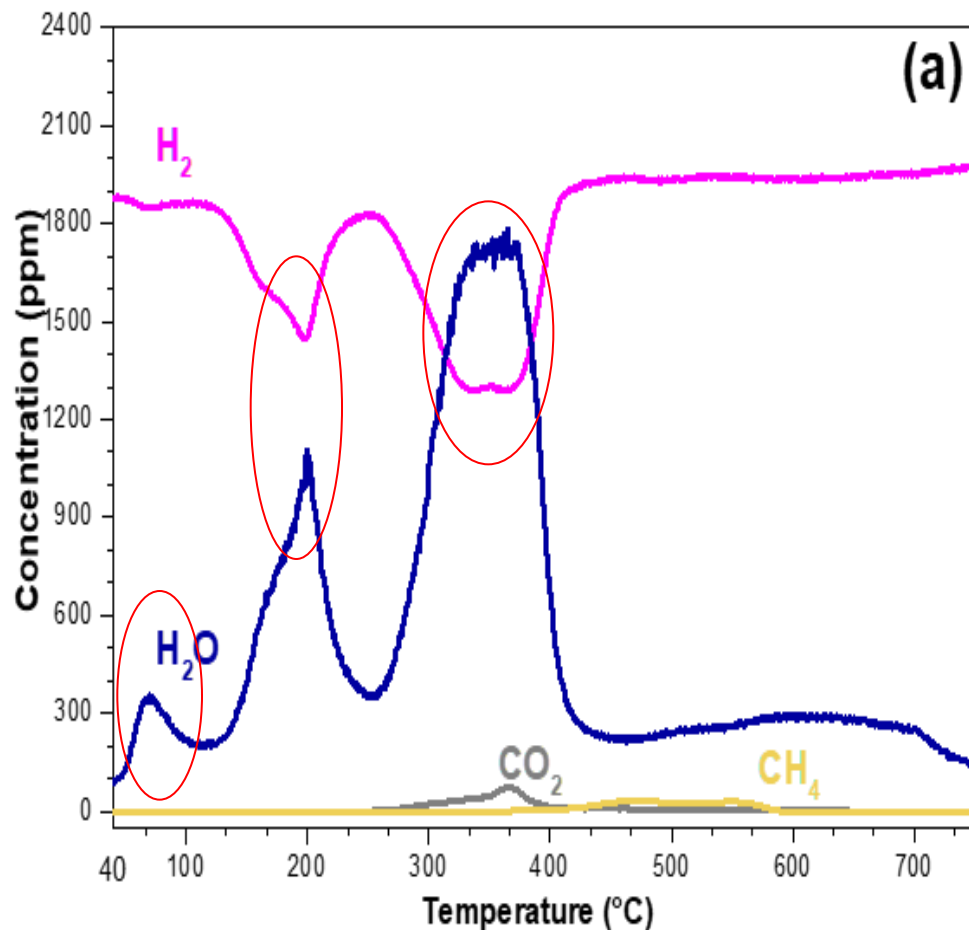
## Cobalt Reducibility:

### H<sub>2</sub>-TPR Mass Spectrometry

- ❖ The hydrogen has two consumption peaks, associated with H<sub>2</sub>O production for the calcined sample

These peaks are due to the two reduction steps from Co<sub>3</sub>O<sub>4</sub> to Co involving CoO as an intermediate, as previously discussed

There is a small peak on H<sub>2</sub>O profile at temperatures lower than 100°C. This is probably due to some adsorbed water on the catalyst.



**0.5%Pt-12%Co/SiO<sub>2</sub> calcined**



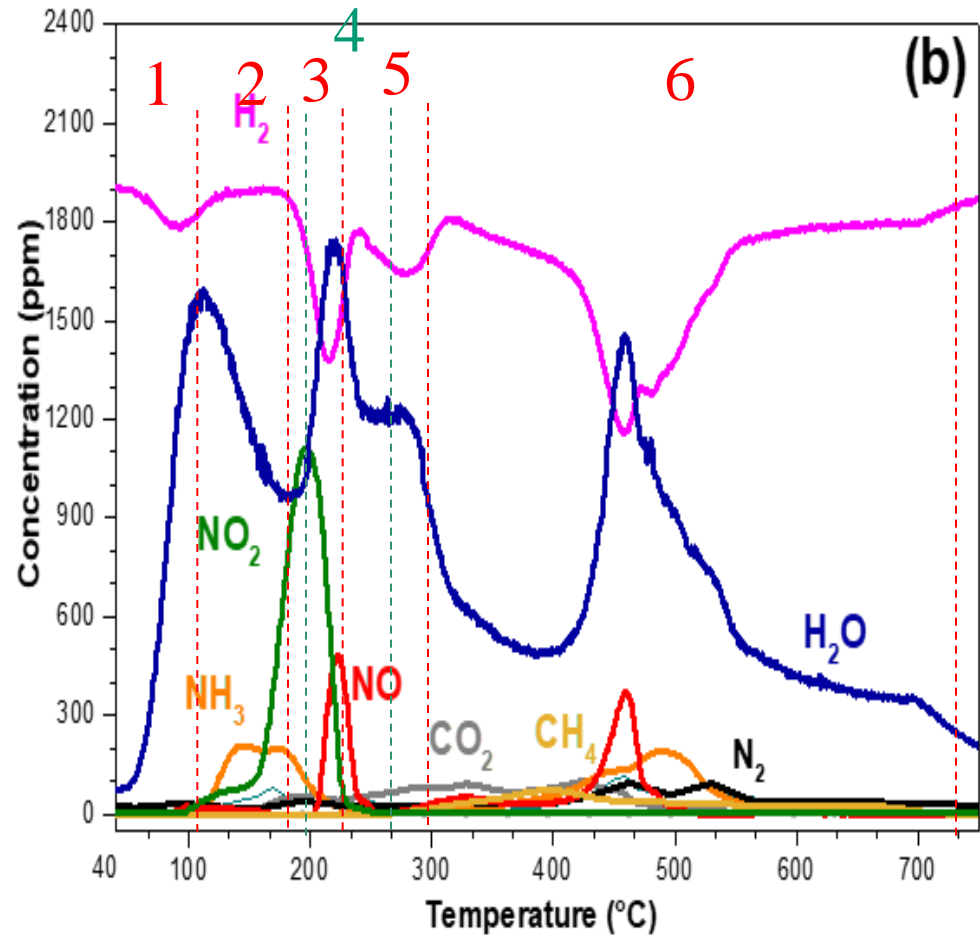


## Cobalt Reducibility:

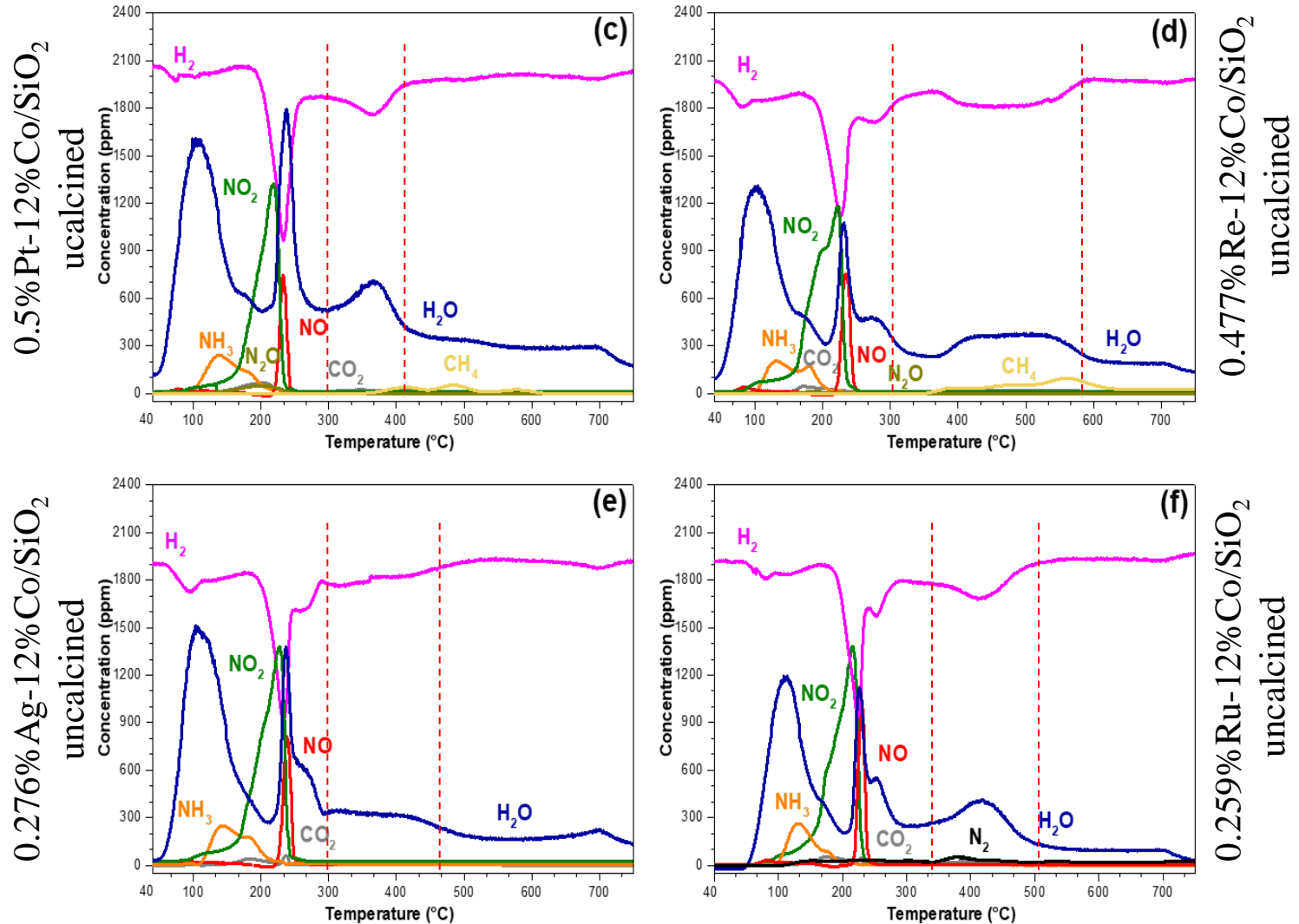
### TPR Mass Spectrometry

At temperatures lower than 180 °C, there are at least six major events, whereby:

6- Between 300 °C and 750 °C, there is a series of hydrogen uptakes with corresponding evolution of H<sub>2</sub>O peaks, these are assigned to reduction of CoO species



12%Co/SiO<sub>2</sub> uncalcined

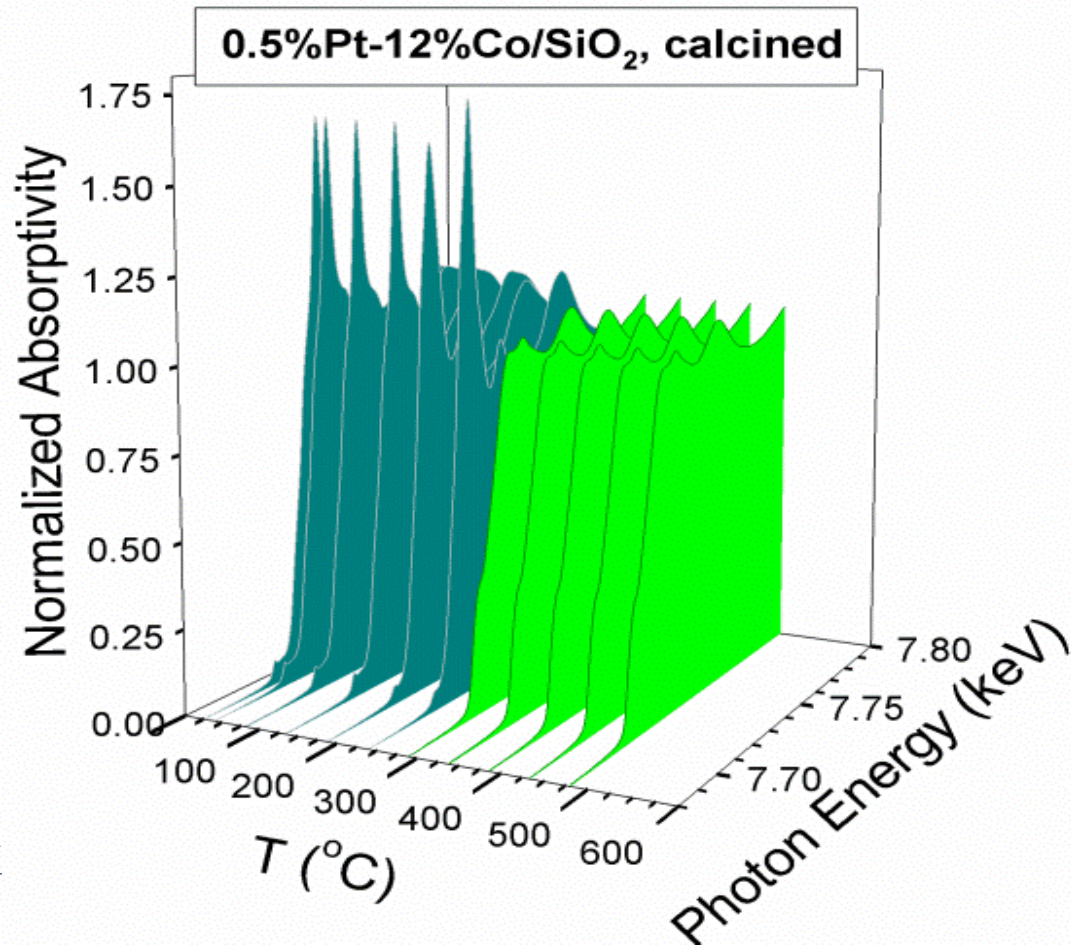


The ranking of promoter effectiveness for CoO reduction from TPR-MS is: Pt > Re > Ru > Ag > unpromoted



## TPR XANES

This calcined catalyst starts with a line shape resembling the cobalt oxide spinel structure of  $\text{Co}_3\text{O}_4$ , with conversion to  $\text{CoO}$  being achieved below  $250^\circ\text{C}$ . Next, because of the larger weakly interacting  $\text{Co}$  clusters,  $\text{Co}^0$  metal is rapidly formed by  $\sim 300^\circ\text{C}$  (final dark blue spectrum to first green spectrum for  $\text{CoO}$  to  $\text{Co}^0$ )



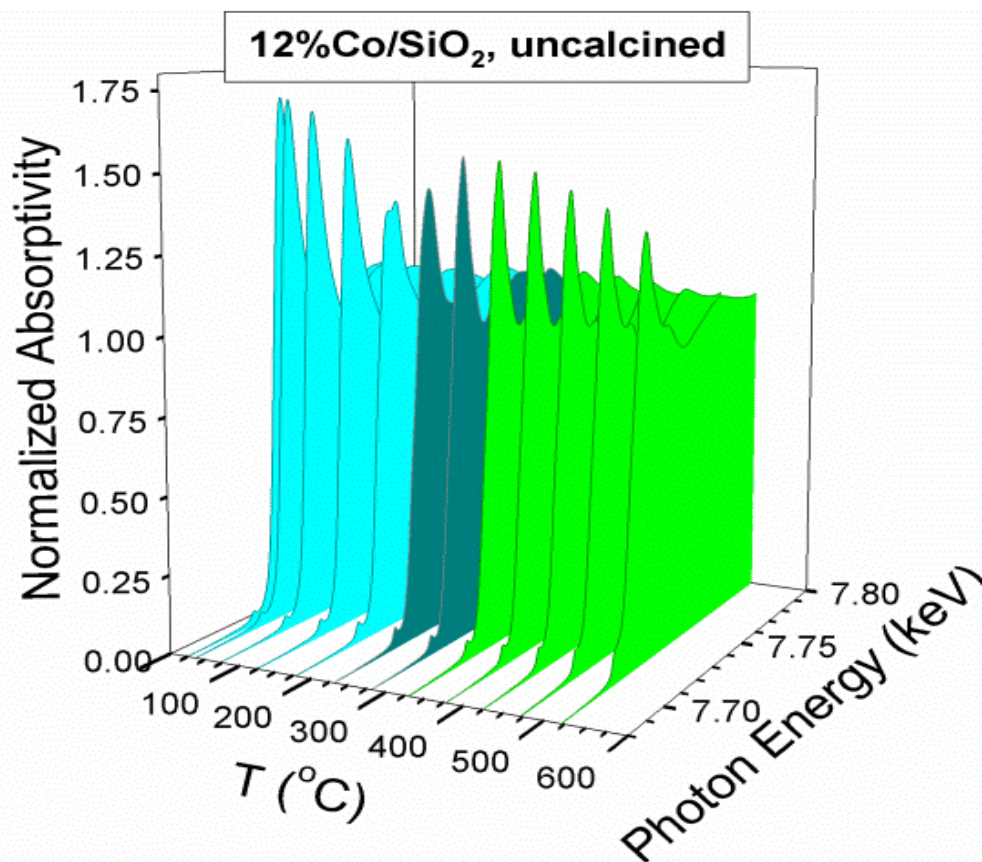


## TPR XANES

With the uncalcined catalysts,  $\text{Co}(\text{NO}_3)_2$  slowly converts to  $\text{CoO}_x$  decomposition products that are oxidized to a spinel (e.g.,  $\text{Co}_3\text{O}_4$ ) – final light blue spectrum.

Afterwards, a typical two step reduction of  $\text{Co}_3\text{O}_4$  was observed, with  $\text{CoO}$  as the intermediate (final dark blue spectrum).

Relative to the calcined catalyst, reduction of cobalt oxides occurs over a wider range, indicating smaller, interacting Co oxide species.

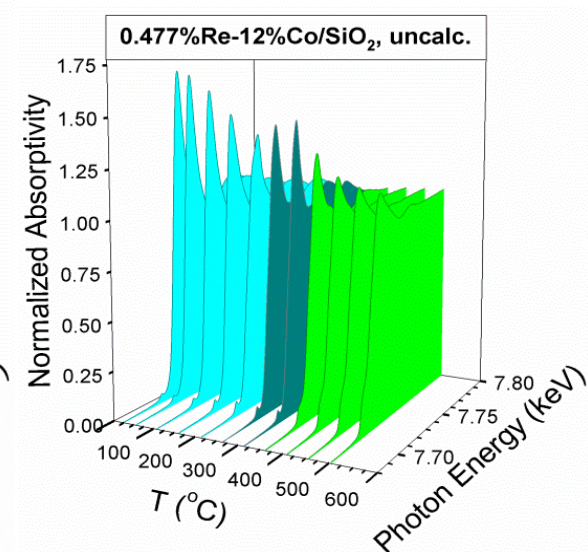
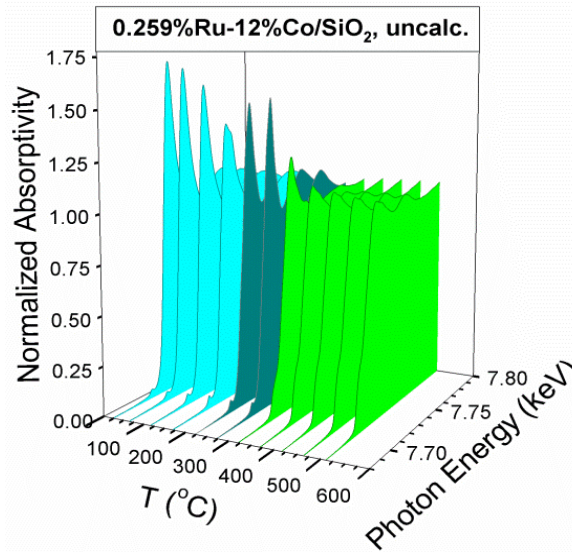
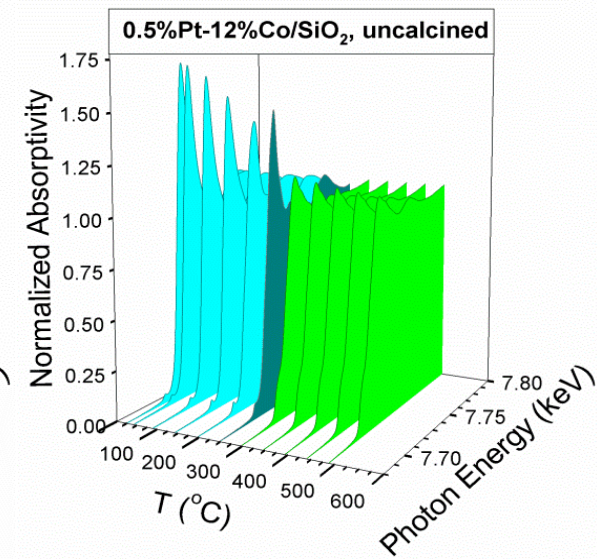
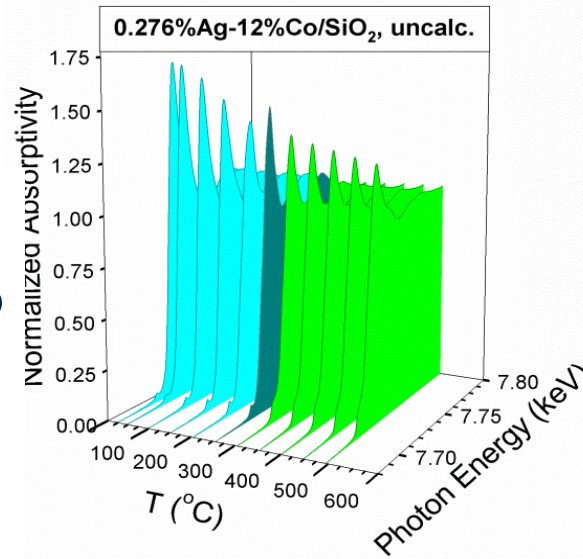




## TPR XANES

CoO converted to Co<sup>0</sup>  
(final dark blue spectrum to green spectra) with vastly different final extents of reduction by 500 °C depending on the presence or absence of promoter, as well as the promoter identity

Pt > Re, Ru > Ag



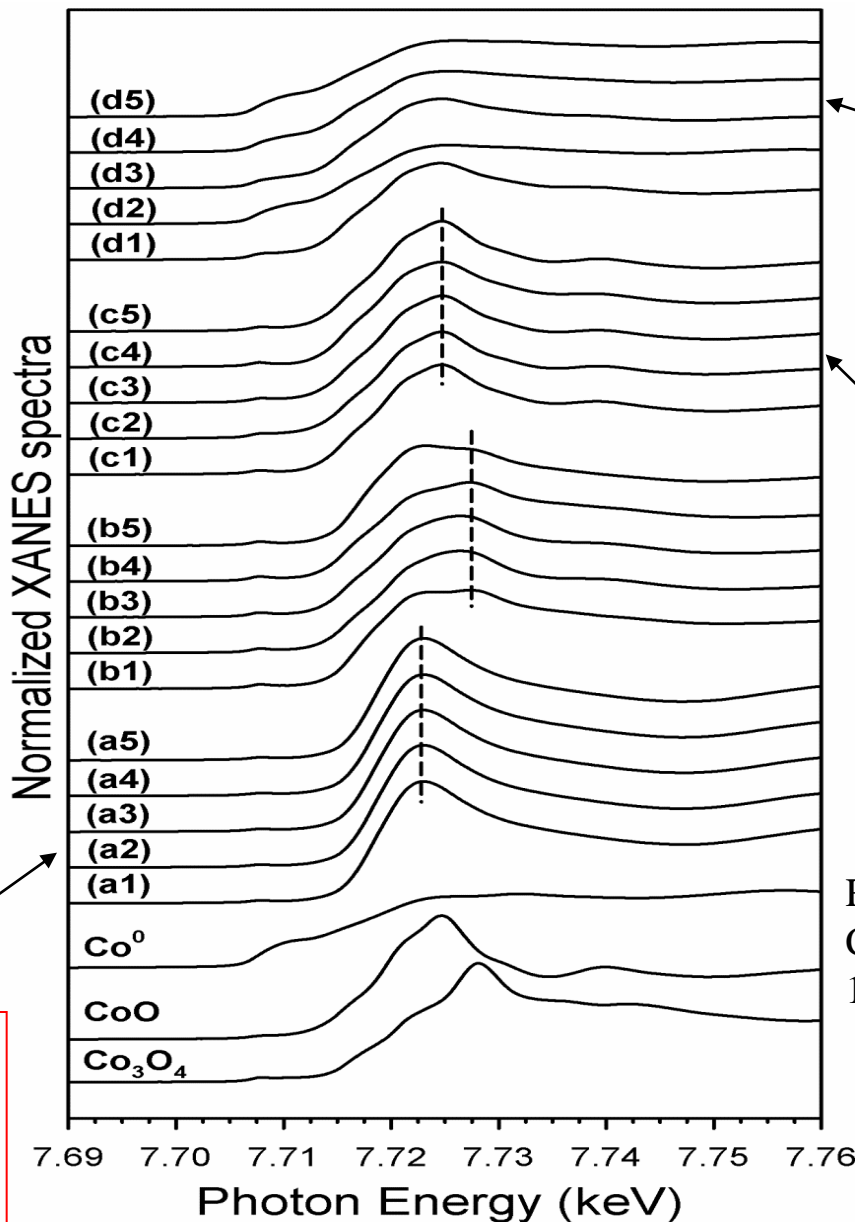


## TPR XANES

(1) uncalcined unpromoted catalyst, and uncalcined catalysts promoted with (2) Pt, (3) Ag, (4) Re, and (5) Ru

The point of maximum spinel (e.g.,  $\text{Co}_3\text{O}_4$ ) following cobalt nitrate decomposition

$\text{Co}(\text{NO}_3)_n \cdot n\text{H}_2\text{O}$  in the initial spectra of uncalcined catalysts



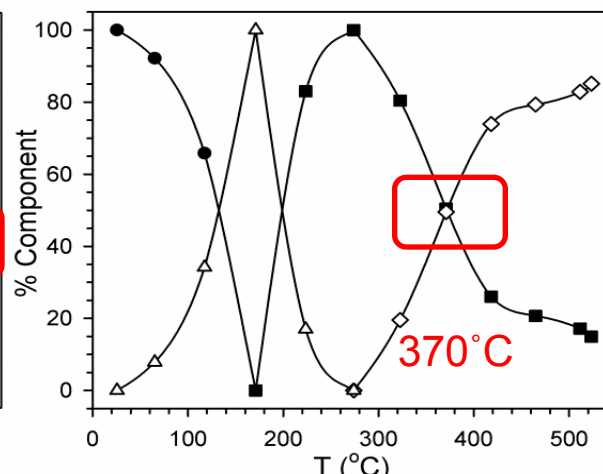
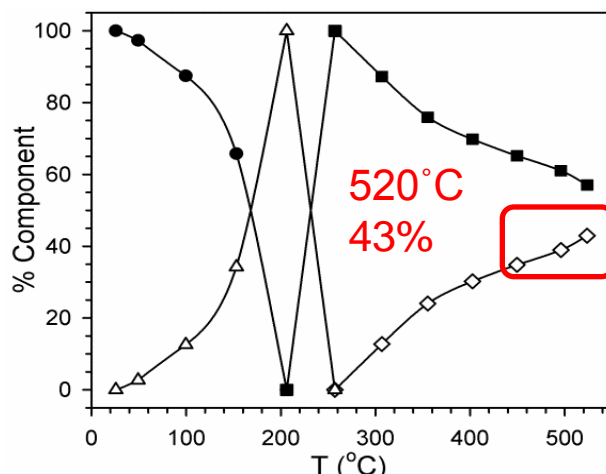
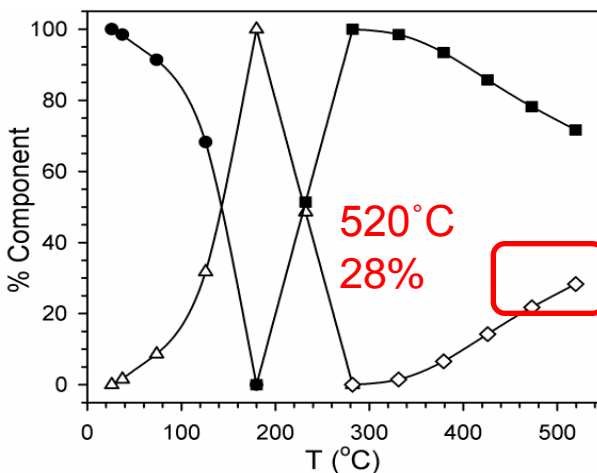
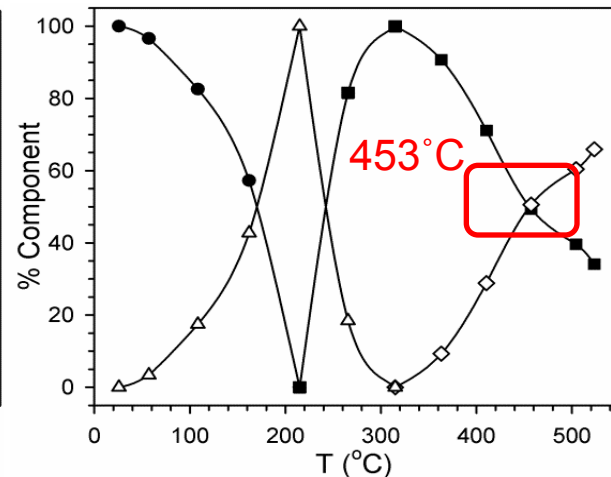
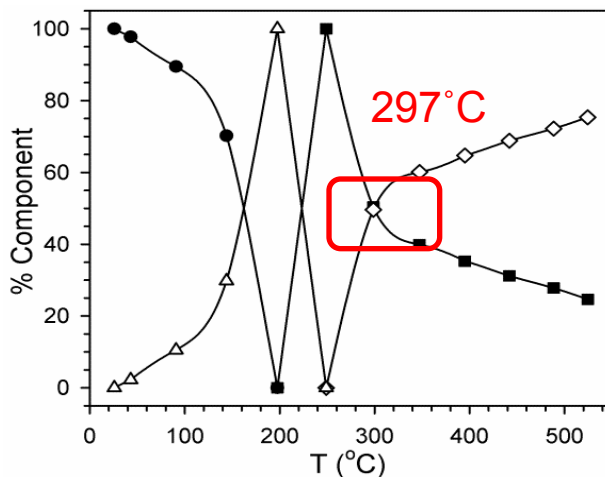
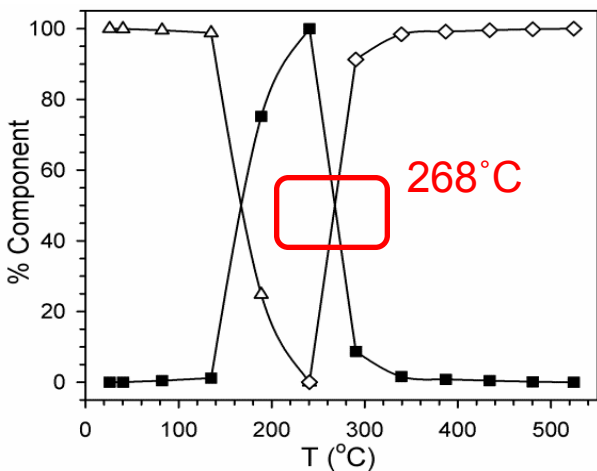
The point of maximum  $\text{Co}^0$  content

The point of maximum  $\text{CoO}$  following reduction of the spinel

Reference spectra  
Calcined  
12%  $\text{Co}/\text{SiO}_2$



## Temp. vs Composition



(b) 12%Co/SiO<sub>2</sub> uncalcined

(d) 0.276%Ag-12%Co/SiO<sub>2</sub> uncalcined

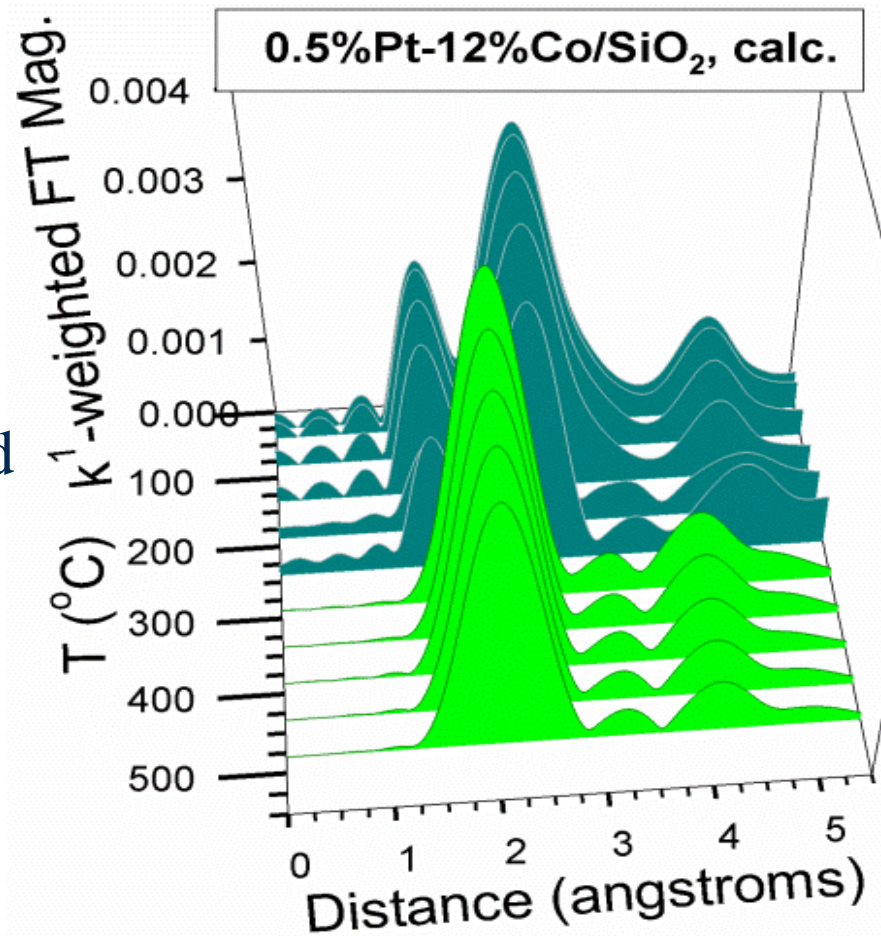
(f) 0.259%Ru-12%Co/SiO<sub>2</sub> uncalcined



## TPR EXAFS

With the calcined catalyst,  $\text{Co}_3\text{O}_4$  is converted to  $\text{CoO}$  (final dark blue spectrum), with resulting slight shifts in the distances of Co-O and Co-Co coordination.

$\text{CoO}$  is a short-lived intermediate, and with a slight increase in temperature, a large peak for Co-Co metal coordination is formed (Green).



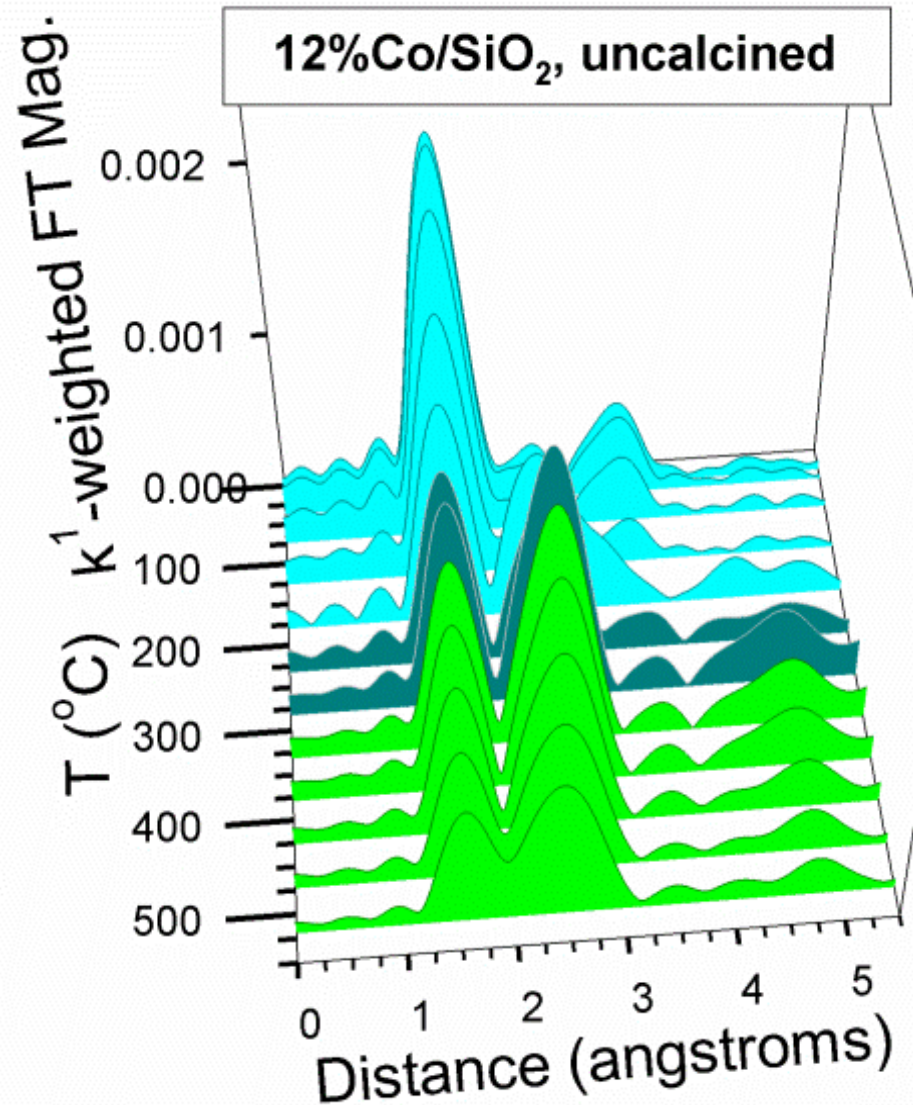




## TPR EXAFS

With the uncalcined unpromoted catalyst, cobalt nitrate slowly converts to  $\text{CoO}_x$  that oxidizes to a spinel (e.g.,  $\text{Co}_3\text{O}_4$ ) (first dark blue spectrum). The spinel converts to  $\text{CoO}$  (final dark blue spectrum).

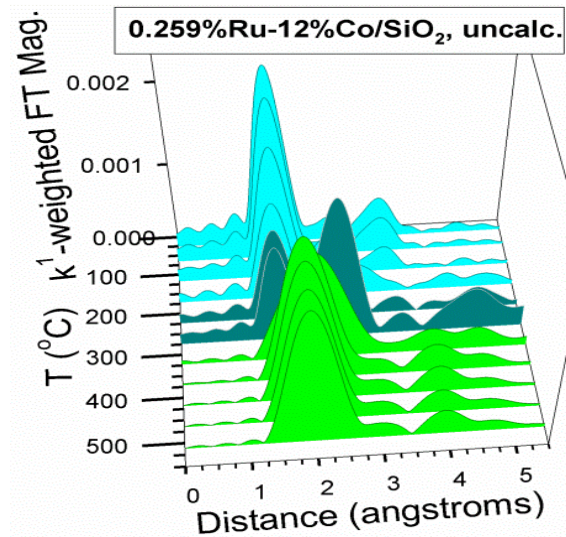
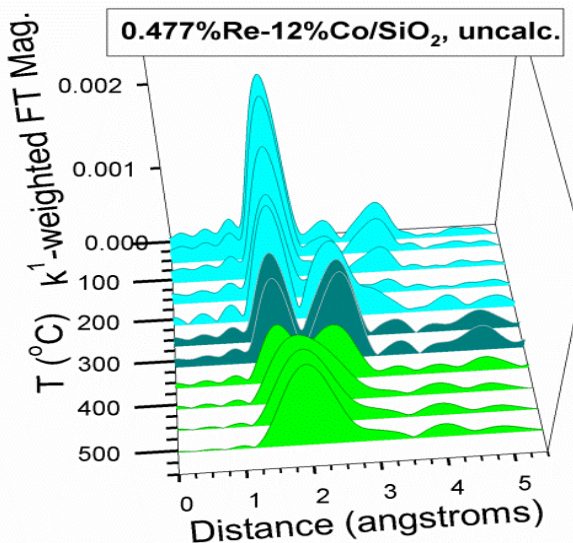
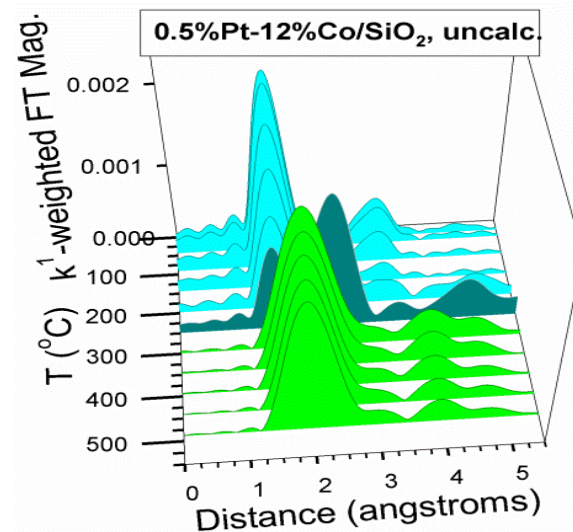
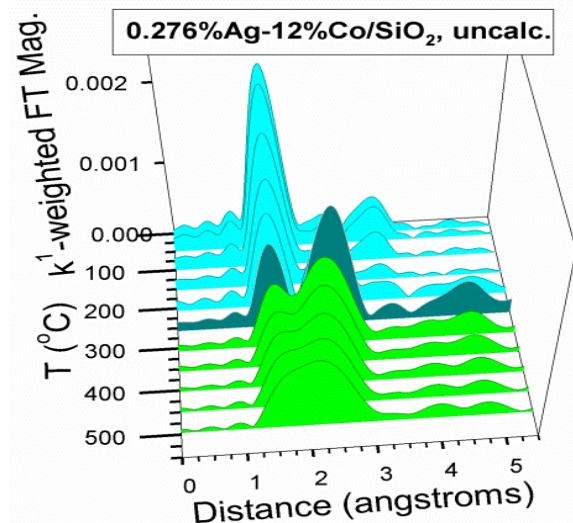
Once formed,  $\text{CoO}$  converts very slowly to the metal (green spectra). Even at  $500^\circ\text{C}$ , Co-O coordination is still observed.





## TPR EXAFS

By adding the promoter, the major difference is that significant Co-Co metal coordination peaks begin to form at lower temperature as expected from the TPR and TPR-XANES results, including Pt-promoted 300°C, Re-promoted ~400°C, Ru-promoted ~370°C.

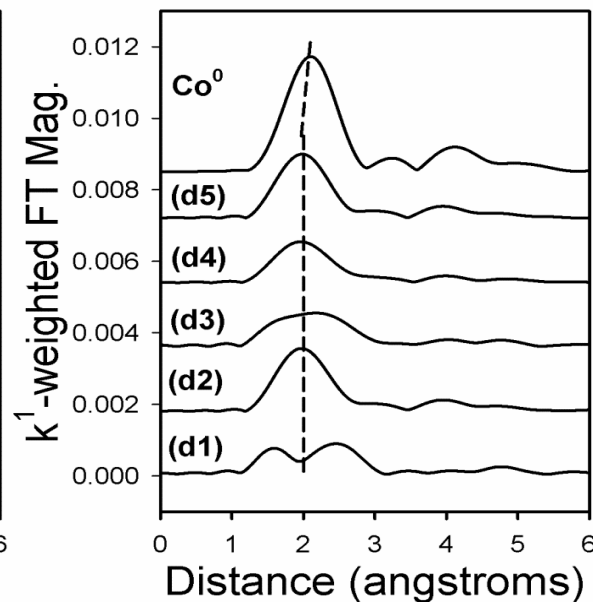
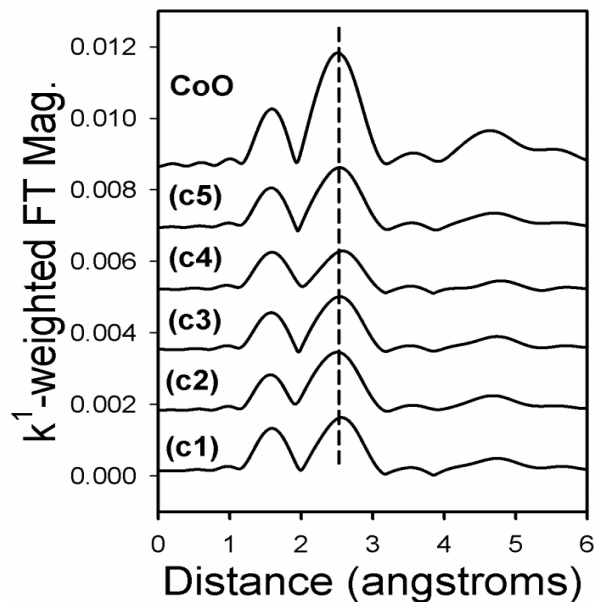
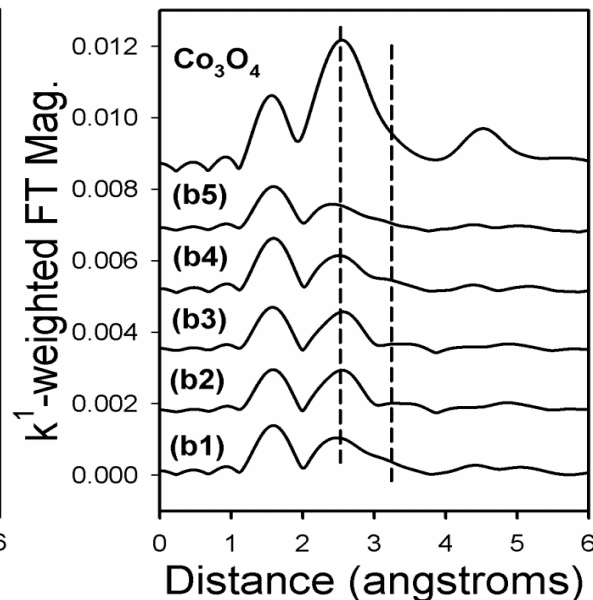
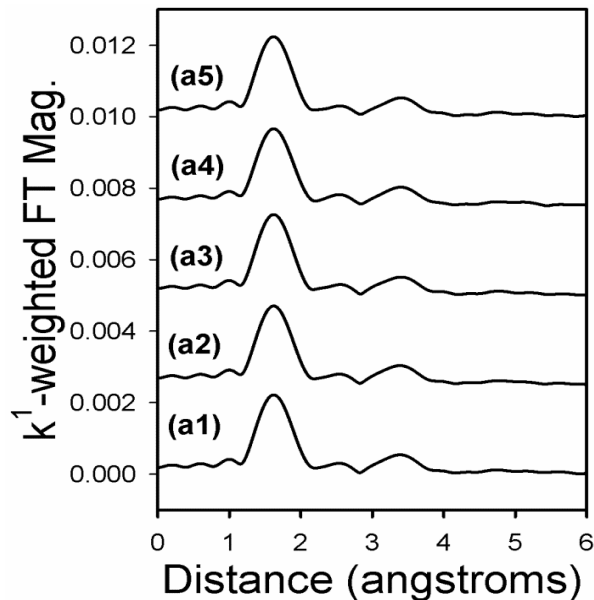




## TPR EXAFS

(1) uncalcined unpromoted catalyst, and uncalcined catalysts promoted with (2) Pt, (3) Ag, (4) Re, and (5) Ru

(a)  $\text{Co}(\text{NO}_3)_n \cdot n\text{H}_2\text{O}$  in the initial spectra (b) the point of maximum spinel following cobalt nitrate decomposition, (c) the point of maximum  $\text{CoO}$  and (d) the point of maximum  $\text{Co}^0$  content.





## Cobalt particle size differences

Results of hydrogen chemisorption and pulse re-oxidation.

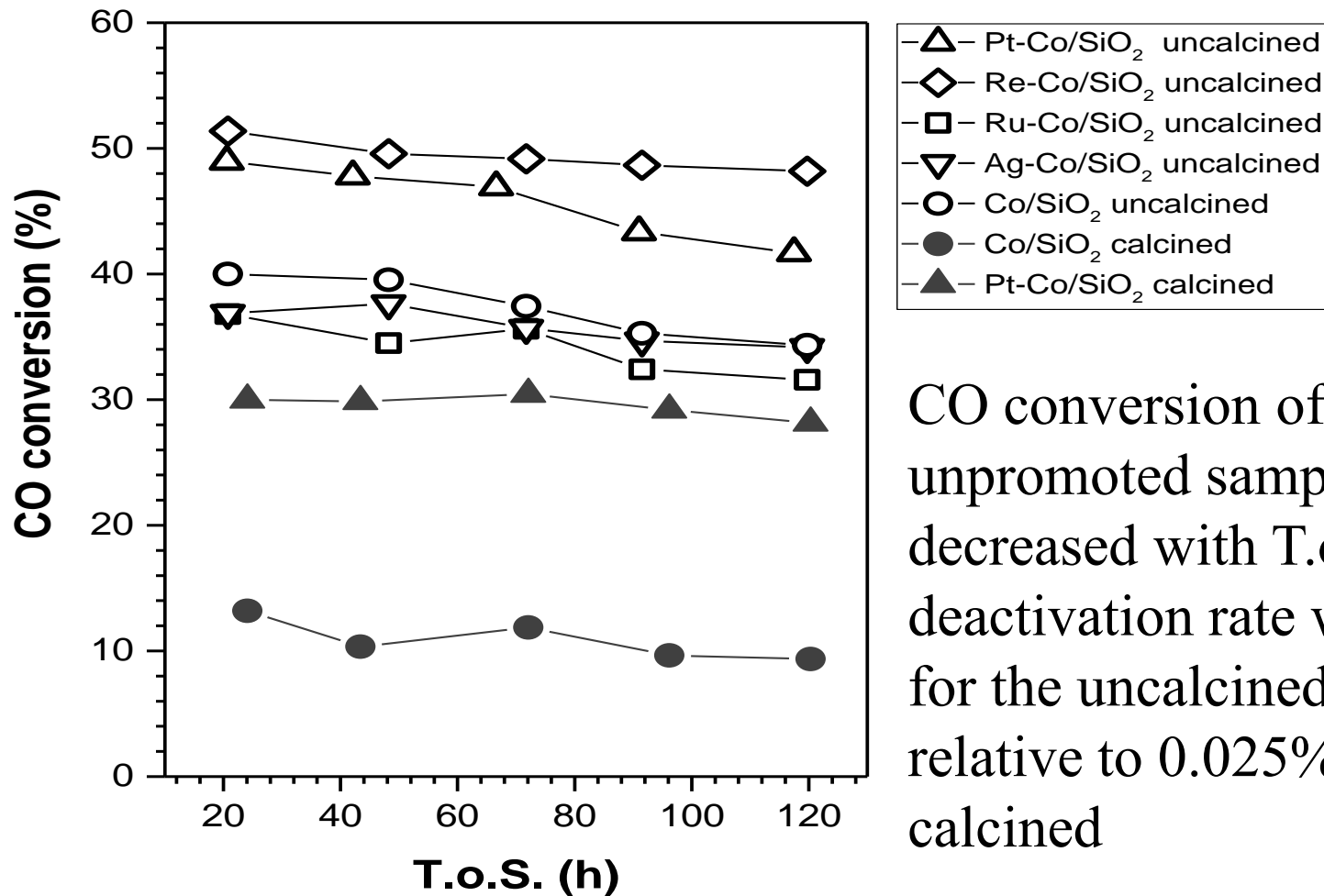
Sample ID	H <sub>2</sub> desorbed per g <sub>cat</sub> [ $\mu\text{mol/g}_{\text{cat}}$ ]	Uncorr. Disp. [%]	Uncorr. Diam. [nm]	% Red. [%]	Corr. Disp. [%]	Corr. Diam. [nm]
12%Co/SiO <sub>2</sub> calcined	10.8	0.98	104.9	49.8	1.98	52.2
0.5%Pt-12%Co/SiO <sub>2</sub> calcined	19.3	1.91	54.0	51.4	4.29	24.0
0.5%Pt-12%Co/SiO <sub>2</sub> uncalcined	39.2	3.85	26.8	37.0	11.5	8.9

This table provides an estimate of the average Co metal particle size and extent of reduction obtained from hydrogen chemisorption with pulse reoxidation.



CO conversion and product selectivity for the tested catalysts (process conditions: T = 220°C, P= 300 psi, H<sub>2</sub>/CO= 2 mol/mol, SV = 6 slph per g<sub>cat</sub>).

Catalyst	CO Conv[%]	Selectivity [%]			
		CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5+</sub>	CO <sub>2</sub>
<b>12%Co/SiO<sub>2</sub> calcined</b>	13.3	12.5	12.7	73.4	1.4
<b>12%Co/SiO<sub>2</sub> uncalcined</b>	40.2	7.3	8.0	84.4	0.3
<b>0.5%Pt-12%Co/SiO<sub>2</sub> calcined</b>	30.0	10.1	10.7	78.8	0.4
<b>0.5%Pt-12%Co/SiO<sub>2</sub> uncalcined</b>	48.9	8.0	10.2	81.5	0.3
<b>0.276%Ag-12%Co/SiO<sub>2</sub> uncalcined</b>	36.8	8.7	14.6	76.4	0.3
<b>0.477%Re-12%Co/SiO<sub>2</sub> uncalcined</b>	51.3	6.8	11.7	81.2	0.3
<b>0.259%Ru-12%Co/SiO<sub>2</sub> uncalcined</b>	36.8	9.3	9.1	81.2	0.4



CO conversion of the unpromoted samples decreased with T.o.S., and the deactivation rate was 0.05%/h for the uncalcined catalyst relative to 0.025%/h for the calcined

Evolution with Time On Stream of carbon monoxide conversion for uncalcined and calcined samples process conditions: T = 220°C, P= 300 psi, H<sub>2</sub>/CO= 2 mol/mol, SV = 6 slph per g<sub>cat</sub>.



- ✓ Foregoing calcination and utilizing direct reduction of cobalt nitrate led to the formation of smaller and more strongly interacting cobalt oxide nanoclusters in interaction with silica support as intermediates of the activation process to  $\text{Co}^0$  nanoparticles; this was demonstrated by TPR, TPR-MS, TPR-XANES, and TPR-EXAFS experiments using hydrogen.
- ✓ These intermediate cobalt oxides included a spinel (e.g.,  $\text{Co}_3\text{O}_4$ ) formed from oxidation of  $\text{Co}^{2+}$  species by  $\text{NO}_2$ , which in turn converted to  $\text{CoO}$  prior to formation of the metal.
- ✓ To improve the reducibility, metal promoters such as Pt, Re, Ru, and Ag were added.



- ✓ The best catalysts were Re and Pt promoted 12%Co/SiO<sub>2</sub> catalysts utilizing direct reduction of the nitrate, where conversions in a CSTR were up to 3.8 times higher and 71% higher than unpromoted and Pt promoted air calcined catalysts, respectively.
- ✓ At the same time, methane production was lower (6.8 and 8.0% for Re and Pt promoted catalysts by direct reduction versus 12.5 and 10.1% for unpromoted and Pt promoted air calcined catalysts) and C<sub>5+</sub> selectivity was higher (81.2 and 81.5% for Re and Pt promoted catalysts by direct reduction versus 73.4 and 78.8% for unpromoted and Pt promoted air calcined catalysts).



**Thanks**