

# Direct Reduction of $\text{Co}(\text{NO}_3)_2$ leads to Smaller Metal Nanoparticles for Improved FT Activity

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## ABSTRACT

Fischer-Tropsch synthesis (FT) converts syngas (i.e.,  $\text{H}_2$  and  $\text{CO}$ ) derived from natural gas, biomass, or coal to a distribution of hydrocarbons that can be upgraded to produce diesel and jet fuels, as well as premium lubricants and waxes. For the Gas-to-Liquids (GTL) process, cobalt catalysts are utilized, where activity on a per gram of catalyst basis depends on the surface density of cobalt metal atoms. To increase the Co active site density, cobalt is supported on moderate to high surface area materials, including titania. In comparison with  $\text{H}_2$ -activated air calcined 0.5%Pt-12%Co/ $\text{TiO}_2$  catalysts, where relatively large Co nanoparticles (NPs) formed, direct reduction of uncalcined catalysts (i.e., containing cobalt nitrate) leads to smaller, more strongly interacting Co species. Reduction promoters such as Pt, Re, Ru, and Ag help facilitate their activation, leading to smaller Co NPs and higher Co active site densities.

Based on temperature programmed reduction x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure spectroscopy (EXAFS) measurements,  $\text{Co}(\text{NO}_3)_2$  clusters decomposed to  $\text{CoO}_x$  species, which oxidized to  $\text{Co}_3\text{O}_4$  by  $\text{NO}_x$ , prior to  $\text{H}_2$  reduction to  $\text{CoO}$ , and then  $\text{Co}^0$  NPs.

## BACKGROUND

Calcination is typically performed to decompose the cobalt nitrate precursor, prior to  $\text{H}_2$ -activation. However, it has been found that calcination with certain supports (e.g.,  $\text{SiO}_2$ ) leads to agglomeration of cobalt oxides. Therefore, after activation of the cobalt oxides in hydrogen, large cobalt metal NPs are formed, resulting in lower cobalt surface area, and thus lowering the cobalt active site density that participate in FT catalysis. Direct reduction of  $\text{Co}(\text{NO}_3)_2$  may lead to smaller cobalt NPs; however, due to the support interaction with cobalt there can be a problem in reducing the cobalt oxide species to the metal. Here, we explore using direct  $\text{H}_2$  reduction of  $\text{Co}(\text{NO}_3)_2$  and incorporating reduction promoters such as small amounts of Pt, Rh, Ru, and Ag to facilitate reduction of the strongly interacting cobalt species.

## PURPOSE

The purpose of the project is to test a novel catalyst activation method - direct  $\text{H}_2$ -reduction cobalt nitrate precursor - to achieve higher FT activity on a per gram catalyst basis relative to traditional  $\text{H}_2$ -activated air calcined catalysts. To be successful, this must be achieved without losing desired catalyst selectivity and stability.

## HYPOTHESIS

By utilizing direct reduction of cobalt nitrate precursor on supported  $\text{Co}/\text{TiO}_2$  catalysts, we believe that reduction of strongly interacting cobalt nitrates will lead to smaller, more strongly interacting Co metal NPs. To facilitate reduction, we also aim to test promoters such as Pt, Re, Ru, and Ag. The aim is to increase Co active site density and thus, activity.

## METHODOLOGY

- ❖ **Step 1:** measure the required amount of titania ( $\text{TiO}_2$ ) support
- ❖ **Step 2:** dissolve  $\text{Co}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$  to fill  $\text{TiO}_2$  pores.
- ❖ **Step 3:** impregnate the titania until the point of incipient wetness using a buret and a spinning round-bottom flask.
- ❖ **Step 4:** with each loading of the precursor salt, the catalyst must be dried with a rotary evaporator; repeat as needed due to the solubility limit of cobalt nitrate in water.
- ❖ **Step 5:** divide total  $\text{Co}/\text{TiO}_2$  parent batch into 6 batches.
- ❖ **Step 6:** if a promoter is to be added, dissolve the measured amount in DI water and mix into  $\text{Co}/\text{TiO}_2$  via buret and a spinning round-bottom flask and dry with rotary evaporator
- ❖ **Step 7:** Then package and label correctly to send to the University of Kentucky Center for Applied Energy Research for testing in continuously stirred tank reactors, and to Argonne National Laboratory for synchrotron experiments.

## RESULTS

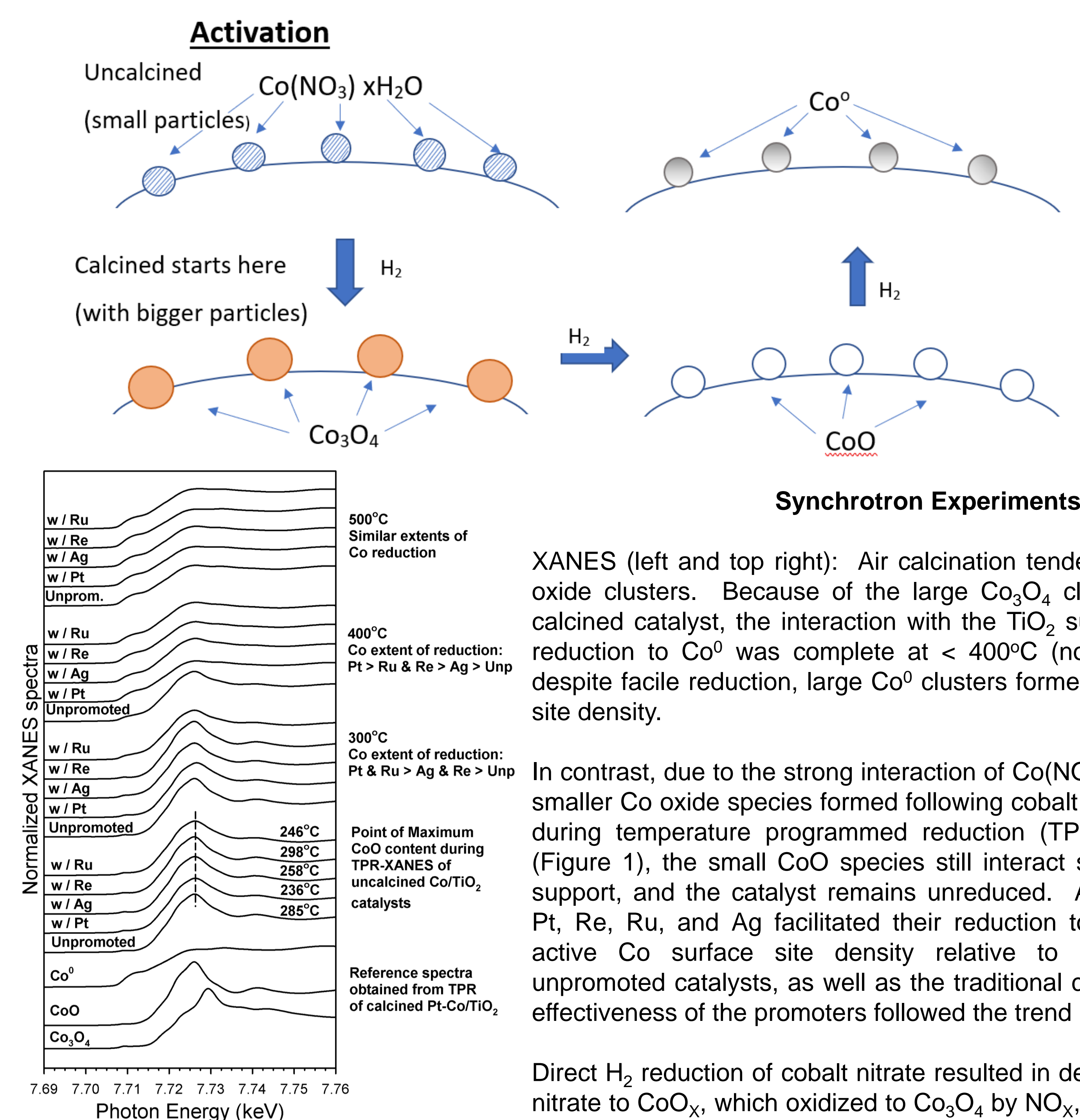


Figure 1. XANES spectra during  $\text{H}_2$  TPR.

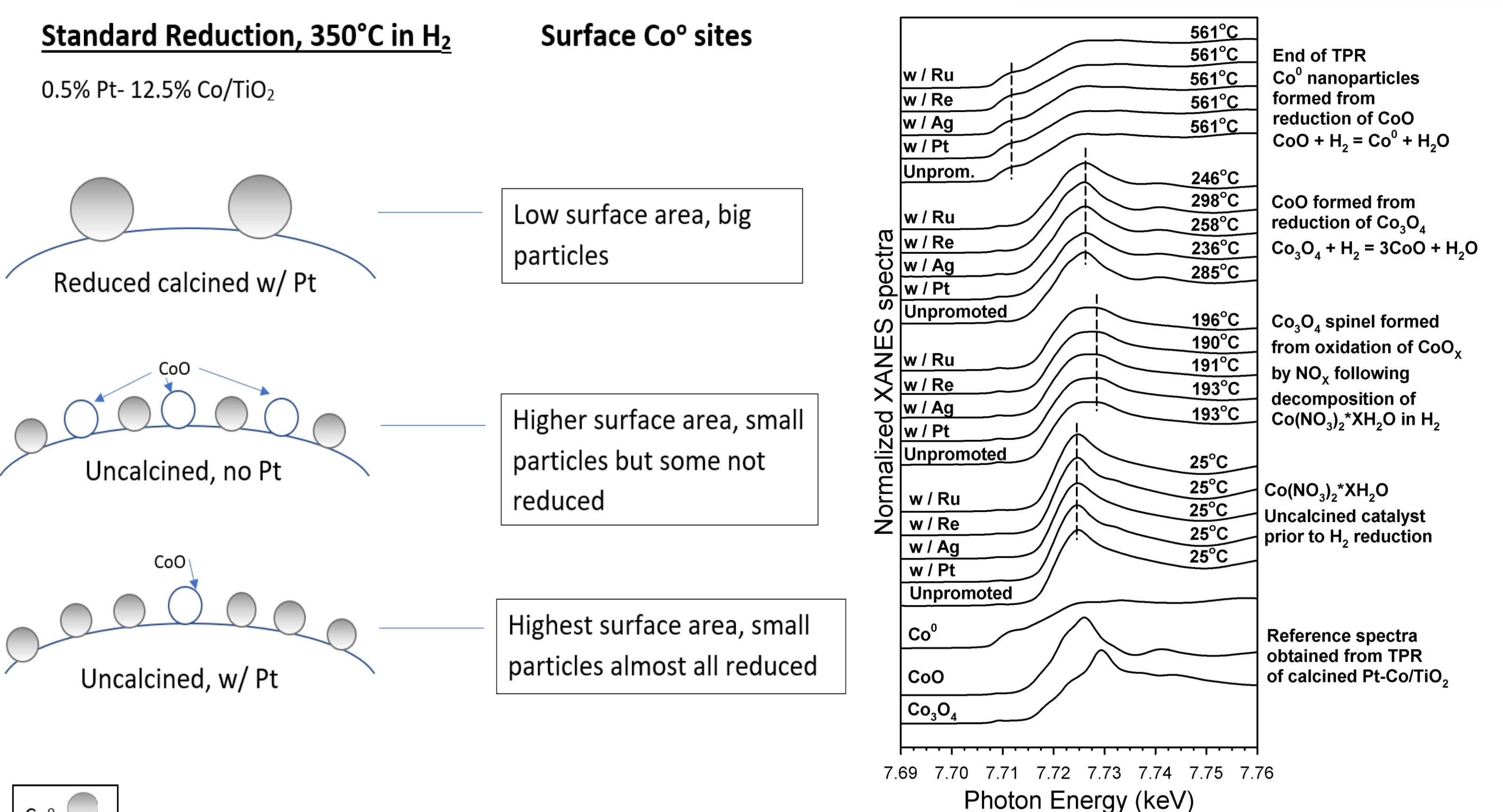


Figure 2. Chemical species observed during direct reduction of cobalt nitrate as function of temperature.

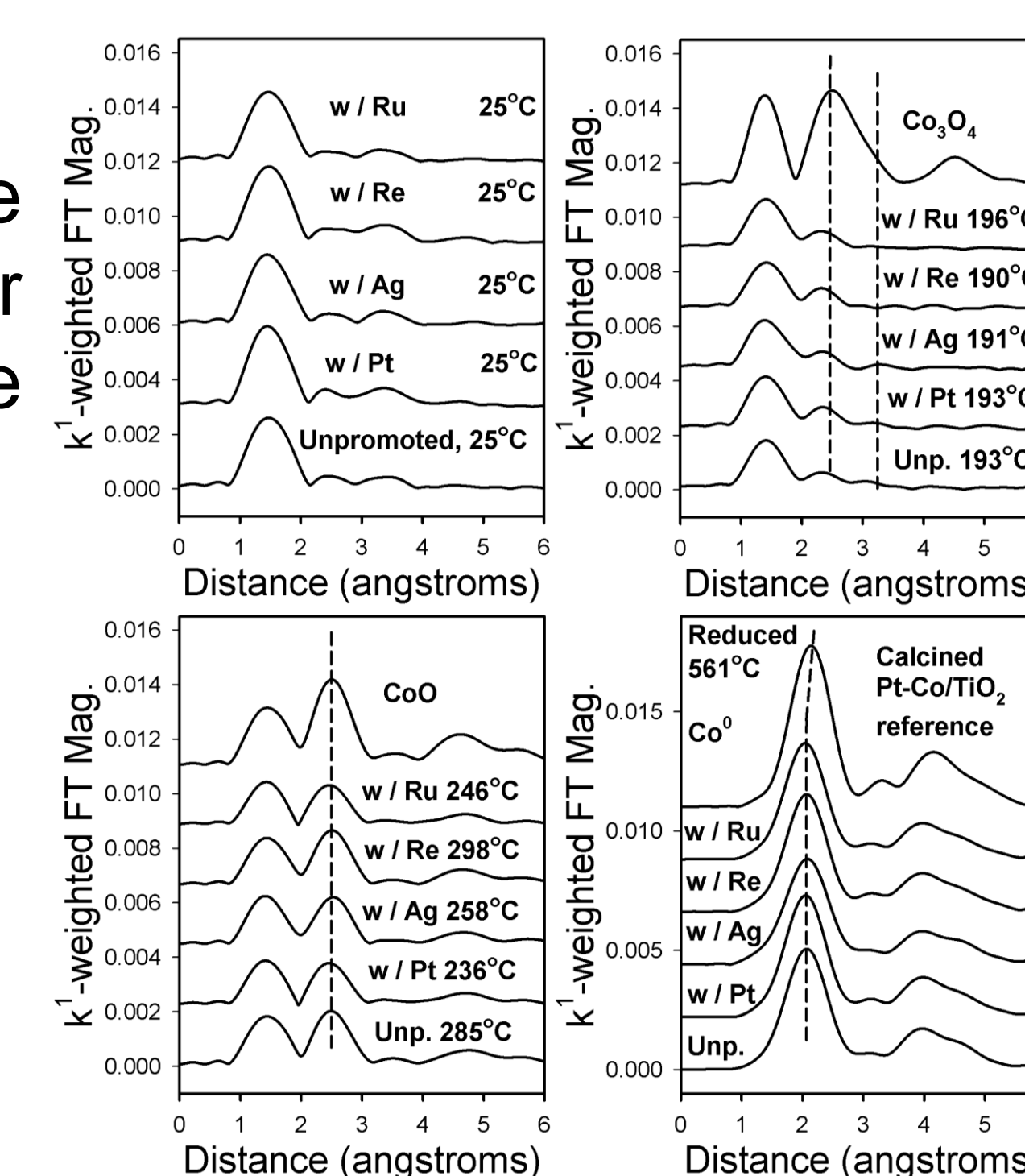


Figure 3. EXAFS spectra of chemical species during  $\text{H}_2$ -TPR and fittings of activated catalysts. The much lower  $N_{\text{Co-Co}}$  (Co-Co coordination number) of catalysts after direct reduction of cobalt nitrate confirms smaller cobalt NPs than activated calcined catalyst.

## CONCLUSIONS

- ❖ XANES experiments confirmed that smaller, more strongly interacting Co species with the titania support, were formed by direct cobalt nitrate reduction as compared to activation of traditional air calcined catalysts.
- ❖ Adding reduction promoters facilitated reduction of these smaller, more strongly interacting Co species, resulting in smaller Co metal NPs as compared to activated air calcined catalysts.
- ❖ Promoter effectiveness followed the order  $\text{Pt} > \text{Re}, \text{Ru} > \text{Ag}$ .
- ❖ EXAFS experiments showed that the Co-Co metal coordination number was much lower for Co NPs prepared by direct cobalt nitrate reduction compared with reduced air-calcined catalysts; this confirms that smaller Co NPs were formed, boosting the Co active site density significantly.

## REFERENCES

Mehrbod, M.; Jacobs, G.; Martinelli, M.; Davis, B.H.; Cronauer, D.C.; Kropf, A.J.; Marshall, C.L., "Fischer-Tropsch synthesis: Improved conversion and selectivity with Co/silica foregoing calcination and utilizing reduction promoters," 255<sup>th</sup> American Chemical Society National Meeting & Exposition, New Orleans, Louisiana, USA March 18 – 22, 2018.