Direct Reduction of Co(NO₃), leads to Smaller Metal Nanoparticles for Improved FT Activity Annabelle G. Martino, Mohammad Mehrbod, Michela Martinelli, PhD, Burtron H. Davis, PhD, Donald C. Cronauer, PhD A. Jeremy Kropf, PhD, Christopher L. Marshall, PhD, Gary Jacobs, PhD

ABSTRACT

Fischer-Tropsch synthesis (FT) converts syngas (i.e., H₂ and 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 H_2 activated air calcined 0.5%Pt-12%Co/TiO₂ 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, $Co(NO_3)_2$ clusters decomposed to CoO_X species, which oxidized to Co_3O_4 by NO_x , prior to H_2 reduction to CoO, and then Co^0 NPs.

BACKGROUND

Calcination is typically performed to decompose the cobalt nitrate precursor, prior to H_2 -activation. However, it has been found that calcination with certain supports (e.g., 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 $Co(NO_3)_2$ 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 H_2 reduction of $Co(NO_3)_2$ 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 H_2 -reduction cobalt nitrate precursor - to achieve higher FT activity on a per gram catalyst basis relative to traditional H₂-activated air calcined catalysts. To be successful, this must be achieved without losing desired catalyst selectivity and stability.

HYPOTHESIS

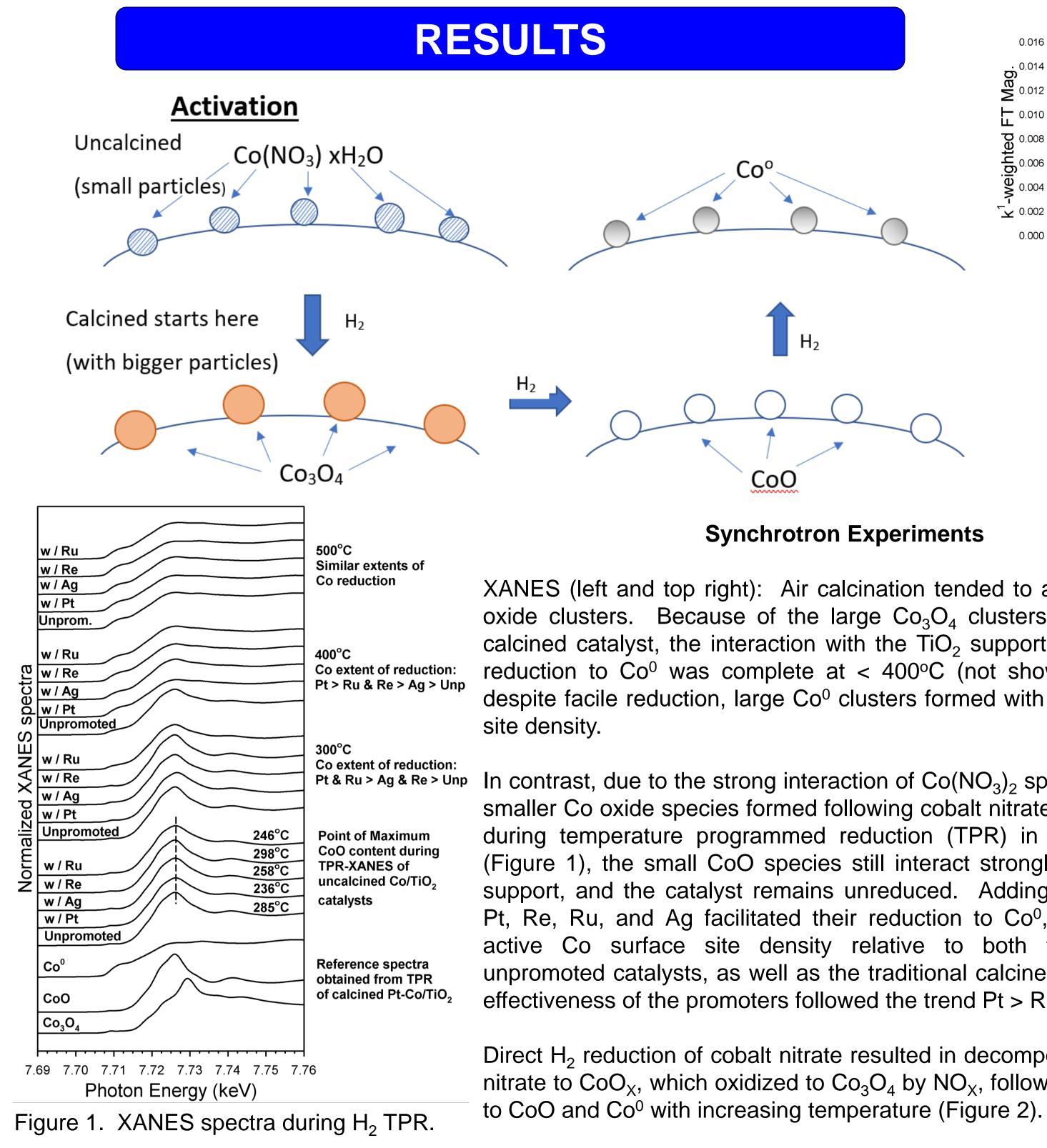
By utilizing direct reduction of cobalt nitrate precursor on supported Co/TiO₂ catalysts, we believe that reduction of strongly interacting cobalt nitrates will lead to smaller, more strongly interacting Co metal NPs. To facilitate reduction, we also aim to test promoters such as Pt, Re, Ru, and Ag. The aim is to increase Co active site density and thus, activity.

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METHODOLOGY

- \therefore Step 1: measure the required amount of titania (TiO₂) support
- **Step 2**: dissolve $Co(NO_3)_2$ in H_2O to fill TiO₂ pores.
- impregnate the titania until the point of incipient ✤ Step 3: wetness using a buret and a spinning round-bottom flask.
- ✤ <u>Step 4</u>: 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 Co/TiO₂ parent batch into 6 batches.
- ✤ <u>Step 6</u>: if a promoter is to be added, dissolve the measured amount in DI water and mix into Co/TiO₂ via buret and a spinning round-bottom flask and dry with rotary evaporator
- Step 7: Then package and label correctly to send to the $\frac{2}{10}$ University of Kentucky Center for Applied Energy Research for testing in continuously stirred tank reactors, and to Argonne National Laboratory for synchrotron experiments.





Synchrotron Experiments

XANES (left and top right): Air calcination tended to agglomerate Co oxide clusters. Because of the large Co_3O_4 clusters present in the calcined catalyst, the interaction with the TiO₂ support was weak and reduction to Co^0 was complete at < 400°C (not shown). However, despite facile reduction, large Co⁰ clusters formed with low Co surface

In contrast, due to the strong interaction of $Co(NO_3)_2$ species with TiO_2 smaller Co oxide species formed following cobalt nitrate decomposition during temperature programmed reduction (TPR) in H₂. At 400°C (Figure 1), the small CoO species still interact strongly with the TiO_2 support, and the catalyst remains unreduced. Adding promoters like Pt, Re, Ru, and Ag facilitated their reduction to Co⁰, increasing the active Co surface site density relative to both the uncalcined unpromoted catalysts, as well as the traditional calcined catalyst. The effectiveness of the promoters followed the trend Pt > Ru & Re > Ag.

Direct H₂ reduction of cobalt nitrate resulted in decomposition of cobalt nitrate to CoO_X , which oxidized to Co_3O_4 by NO_X , followed by reduction

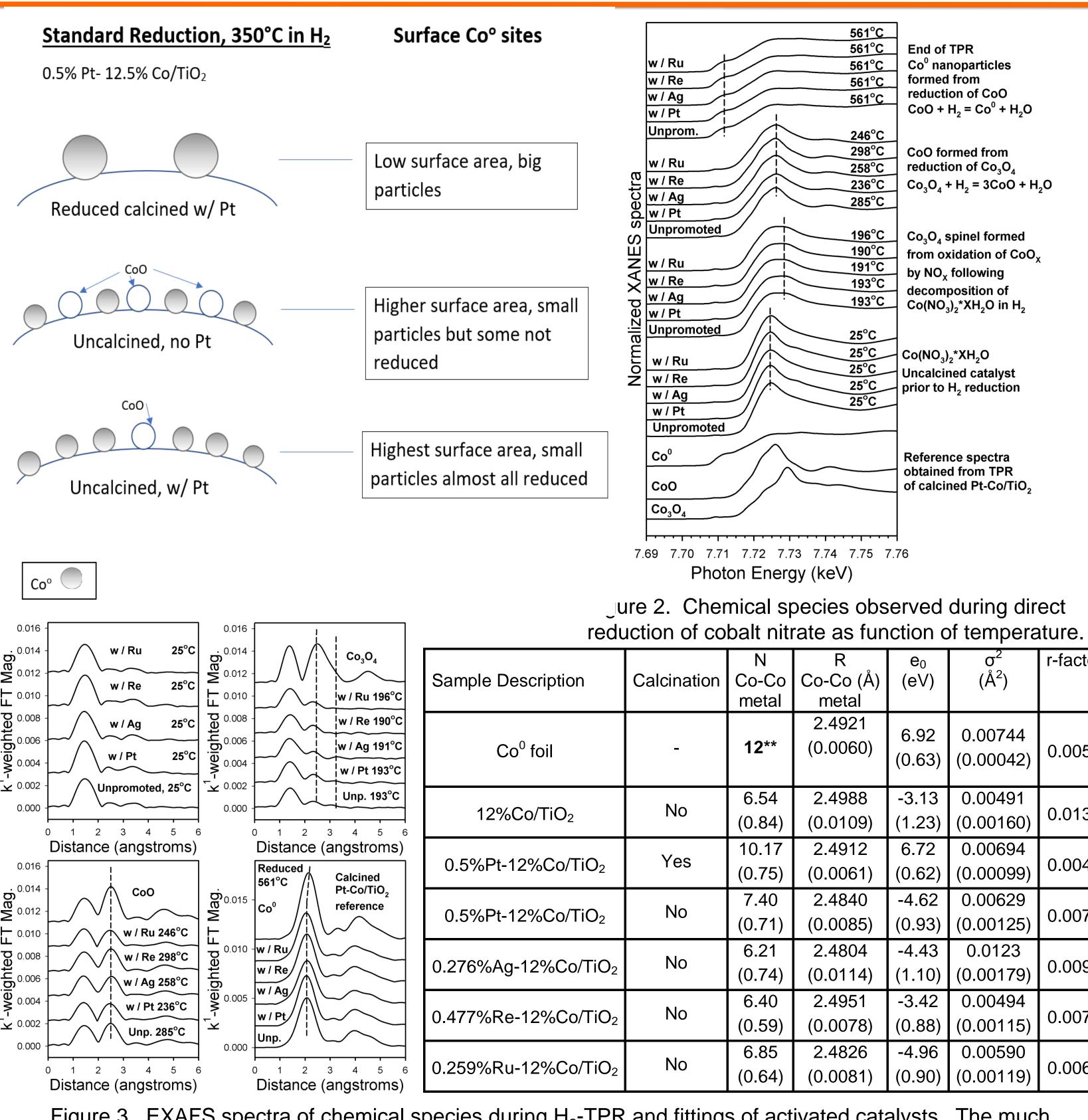


Figure 3. EXAFS spectra of chemical species during H₂-TPR and fittings of activated catalysts. The much lower N_{Co-Co} (Co-Co coordination number) of catalysts after direct reduction of cobalt nitrate confirms smaller cobalt NPs than activated calcined catalyst.

active site density significantly.

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," 255th American Chemical Society National Meeting & Exposition, New Orleans, Louisiana, USA March 18 – 22, 2018.

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ample Description	Calcination	N Co-Co	R Co-Co (Å)	e ₀ (eV)	σ ² (Å ²)	r-factor
		metal	metal			
Co ^o foil	-	12**	2.4921 (0.0060)	6.92 (0.63)	0.00744 (0.00042)	0.0059
12%Co/TiO ₂	No	6.54 (0.84)	2.4988 (0.0109)	-3.13 (1.23)	0.00491 (0.00160)	0.0135
0.5%Pt-12%Co/TiO ₂	Yes	10.17 (0.75)	2.4912 (0.0061)	6.72 (0.62)	0.00694 (0.00099)	0.0045
0.5%Pt-12%Co/TiO ₂	No	7.40 (0.71)	2.4840 (0.0085)	-4.62 (0.93)	0.00629 (0.00125)	0.0073
276%Ag-12%Co/TiO ₂	No	6.21 (0.74)	2.4804 (0.0114)	-4.43 (1.10)	0.0123 (0.00179)	0.0093
477%Re-12%Co/TiO ₂	No	6.40 (0.59)	2.4951 (0.0078)	-3.42 (0.88)	0.00494 (0.00115)	0.0070
259%Ru-12%Co/TiO ₂	No	6.85 (0.64)	2.4826 (0.0081)	-4.96 (0.90)	0.00590 (0.00119)	0.0069

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.

 \Rightarrow Promoter effectiveness followed the order Pt > Re, Ru > 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

REFERENCES