

# Lanthanide Modified Cobalt Fischer-Tropsch Catalysts Increases Oxygenate/Olefin Selectivity

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## ABSTRACT

This work investigates the effect of lanthanide (Ln = Ce, Gd, La, Pr, Sm) addition on the structure and reactivity of Co/SiO<sub>2</sub> catalysts for CO hydrogenation (Fischer Tropsch synthesis). *In-situ* XAS of the structure of both Co and Ln containing phases under both activation and FTS conditions were studied, and thus revealing that a mixture containing small CoO/Co<sup>0</sup> nanocrystallites make up the active sites during reaction conditions. Notably, the Ln species were present in the catalyst in the form of dispersed LnOx nanoparticles anchored to the SiO<sub>2</sub> substrate. These species inhibited total reduction of Co, and these partially reduced species coupled with the Co metal nanoparticles altered the mechanism in such a manner that the selectivity to oxygenates - mainly linear primary alcohols - increased. Therefore, overall, the research suggests that modified cobalt catalysts can produce chemical feedstocks for the petrochemicals industry.

## INTRODUCTION

Fischer-Tropsch synthesis (FT) is a collection of chemical reactions that convert syngas (a mixture of carbon monoxide and hydrogen) into hydrocarbons that can be upgraded to diesel, jet fuels, lubricants, and waxes. These reactions occur in the presence of metal catalysts (e.g., cobalt, iron, or ruthenium) at temperatures of 150-300 °C and pressures between 10 and 30 bar. FT serves as an important reaction in both indirect coal liquefaction, gas to liquids (GTL) technology, and even biomass to liquids (BTL).

Researchers are also seeking to use FT technology with modified catalysts to produce feedstock chemicals such as olefins and alcohols, the latter of which can be dehydrated to make alkenes. Therefore, the aim is to use this method as an alternative to producing polyethylene from syngas (H<sub>2</sub>+CO) instead of using oil. In conventional FT, carbon monoxide dissociates on Co, and the carbon then gets hydrogenated into a CH monomer. After that, the hydrocarbon chain growth proceeds by adding the monomer. Then, the chain growth terminates by either adding hydrogen to make an alkane, by losing hydrogen to make an alkene, or by adding molecular carbon monoxide to make alcohol.

On a typical Co catalyst, for Fischer Tropsch to make hydrocarbons, there is a low concentration of oxygen vacancy defects in which water is not activated on the support. Thus, molecularly adsorbed CO species (e.g., formate) do not play a significant role in oxygenate synthesis. For these traditional Co catalysts, the support does not participate to a significant degree in the catalytic cycle.

Here, we explore using lanthanide supports which have oxygen vacancy defects that can activate water and thus form molecularly adsorbed CO species. Our aim is to use these CO species on the support to terminate hydrocarbon chain growth at the interface between Co and the lanthanide.

We vary the oxygen vacancy concentration (monitoring by x-ray absorption near edge spectroscopy) by changing the identity of the lanthanide, and where possible, compare the alcohol + olefin (A + O) selectivity at constant conversion to determine if a correlation exists between increasing oxygen vacancies and A + O selectivity.

## PURPOSE

The purpose of this work is to utilize higher oxygenate/olefin synthesis from syngas as an alternative pathway (i.e., instead of oil) to make chemical feedstocks used to make polymers such as polyethylene found in milk containers, plastic bags, etc.

## HYPOTHESIS

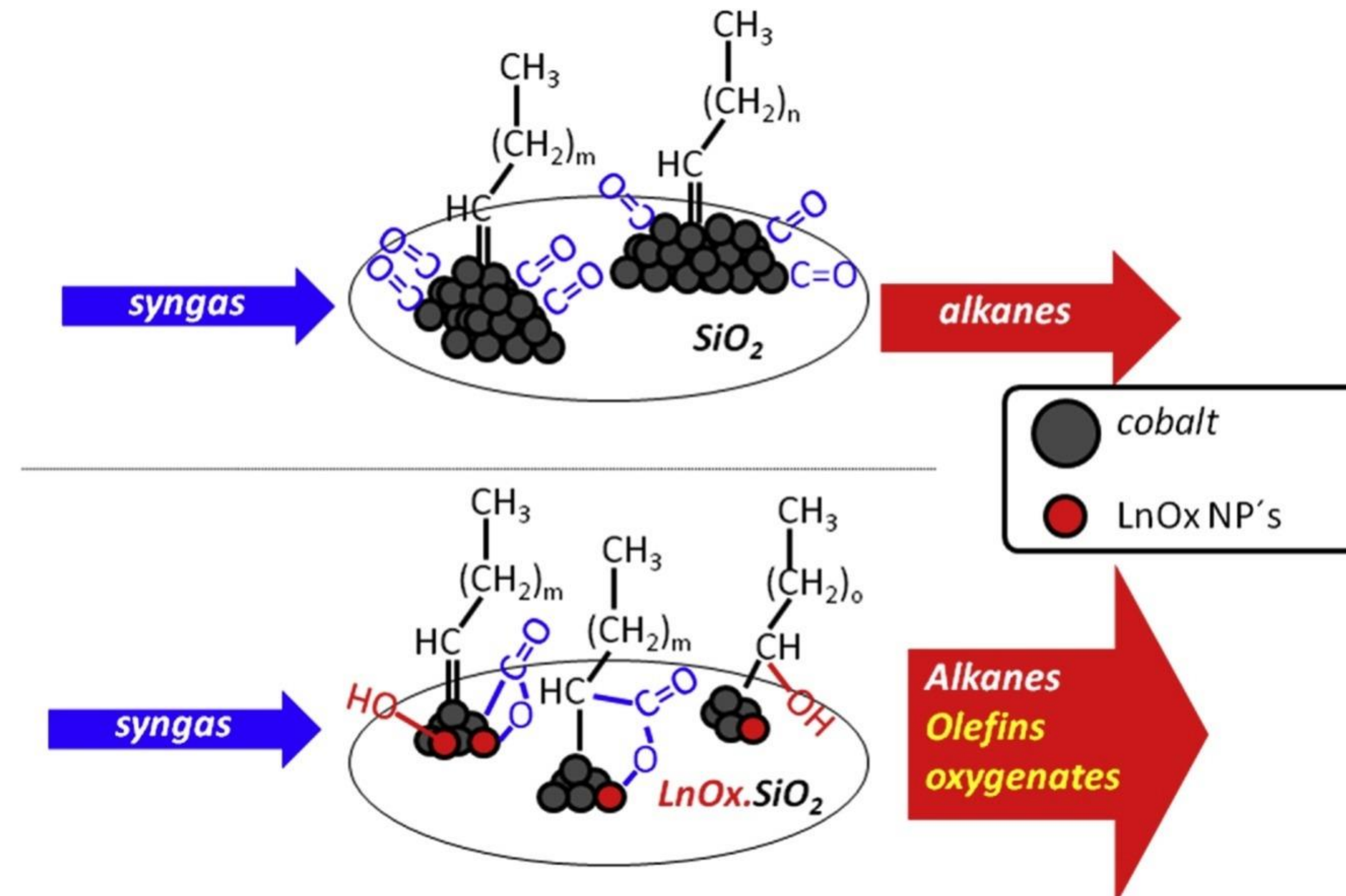
By utilizing higher oxygenate synthesis as an alternative method, we should expect to see an increase in the percentage of oxygenates.



Right: Brazilian Synchrotron (LNLS)

## METHODOLOGY

To determine the concentration of reduced defects (e.g., oxygen vacancies and their associated bridging hydroxyl groups) we used XANES and EXAFS spectroscopies. Then, we correlated the concentration of defects to the oxygenates. Previously it was shown that when varying the interface between the active support (one with vacancies) and the Co metal, the oxygenate selectivity increased. After that, we use silica doped with different lanthanides that have different concentrations of vacancies to determine if O-vacancies control the selectivity of oxygenates being made.



## RESULTS

- 1) Concentration of reduced defects – the vacancy concentration in catalysts follows the trend of Ce > Gd > Pr > La > Sm
- 2) Having the lanthanide gives you higher alcohols plus olefins selectivity, as shown in the 30% CO conversion comparison between unpromoted and Gd-promoted Co/Silica. At 20% CO conversion, the alcohols plus olefins selectivity follow precisely the trend in oxygen vacancy defects: Ce > Pr > La > Sm.

**Table 1.** FT reaction data under the following conditions: T = 220 °C; syngas pressure = 1.99 MPa; H<sub>2</sub>/CO molar ratio = 2, and space velocity = 2.0 SL/h/g.

Catalyst	TOS (h)	CO conv. (%)	Selectivity (C-%)		Product distributions (C-%) <sup>a</sup>			A + O (C-%)	A/O
			CH <sub>4</sub>	CO <sub>2</sub>	Paraffins	Olefins	Alcohols		
15Co/SiO <sub>2</sub>	307.5	31.4	13.6	3.2	71.1	20.3	4.8	25.1	0.24
15Co/GdO <sub>3</sub> /SiO <sub>2</sub>	453.8	32.0	27.3	2.5	63.4	28.3	5.5	33.8	0.19
15Co/LaO <sub>3</sub> /SiO <sub>2</sub>	89.7	22.7	11.3	0.9	64.1	24.6	10.5	35.1	0.42
15Co/CeO <sub>3</sub> /SiO <sub>2</sub>	211.5	20.5	14.7	0.6	57.8	34.7	5.7	40.4	0.16
15Co/PrO <sub>3</sub> /SiO <sub>2</sub>	90.5	19.1	19.6	1.1	59.0	30.1	7.1	37.2	0.23
15Co/SmO <sub>3</sub> /SiO <sub>2</sub>	386.3	20.8	26.2	1.7	64.5	28.6	5.0	33.6	0.17

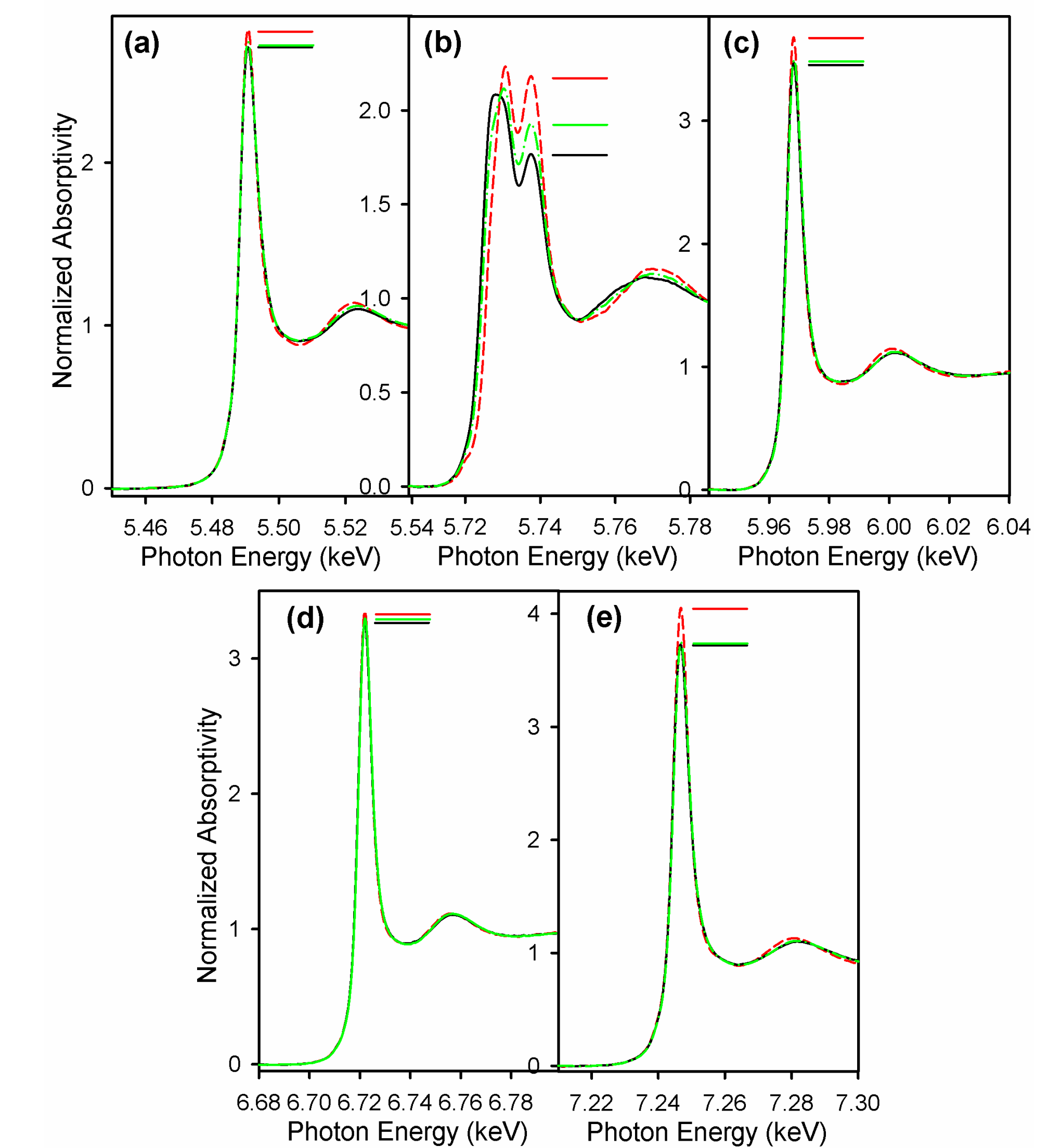
<sup>a</sup> CO<sub>2</sub> free.

**Table 2.** Shift in peak maxima position and attenuation of peak maxima height following activation relative to initial catalyst spectrum prior to activation.

Catalyst	Peak Maximum Energy relative to initial (eV)	Peak Maximum Height relative to initial (%)
Ce Peak B	-2.7	93.3
Ce Peak C	BDL	81.0
Gd	-0.3	91.9
La	-0.4	96.3
Pr	BDL	94.3
Sm	BDL	97.5

**Table 3.** Shift in peak maxima position and attenuation of peak maxima height following syngas treatment at 220 °C relative to initial catalyst spectrum prior to activation

Catalyst	Peak Maximum Energy relative to initial (eV)	Peak Maximum Height relative to initial (%)
Ce Peak B	-0.3	94.7
Ce Peak C	BDL	92.6
Gd	BDL	92.5
La	-0.5	97.4
Pr	BDL	95.1
Sm	BDL	98.3



**Figure 3.** XANES snapshots of Ln LIII edges (red dashed) before activation, (black) after activation in H<sub>2</sub>/He at 350 °C, and (green) following exposure to syngas mixture for 1 h. La (a), Ce (b), Pr (c), Sm (d) and Gd (e) doped Co/SiO<sub>2</sub> catalysts.

## SUMMARY

- ❖ We modify the catalyst by using an active support to make oxygenates.
- ❖ We vary the Ln support type to control the density of available reduced defect sites (e.g., oxygen vacancies), which are proposed to be involved in the catalysis of oxygenate/olefin synthesis.
- ❖ Using a constant conversion comparison, the trend in oxygenate + olefin selectivity followed the concentration of reduced defect in the Ln-modified support.
- ❖ The significance of this method is to utilize a different natural resource as an alternative to make chemical feedstocks used to synthesize polymers such as polyethylene – found in milk containers, trash cans, grocery bags, etc.

## REFERENCES

Gnanamani, M.K.; Ribeiro, M.C.; Ma, W.; Shafer, W.D.; Jacobs, G.; Graham, U.M.; Davis, B.H., "Fischer-Tropsch synthesis: metal-support interfacial contact governs oxygenates selectivity over CeO<sub>2</sub> supported Pt-Co catalysts," *Applied Catalysis A: General* 393 (2011) 17-23.