

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/SiO₂ 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/Co⁰ 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 SiO₂ 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 (H₂+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

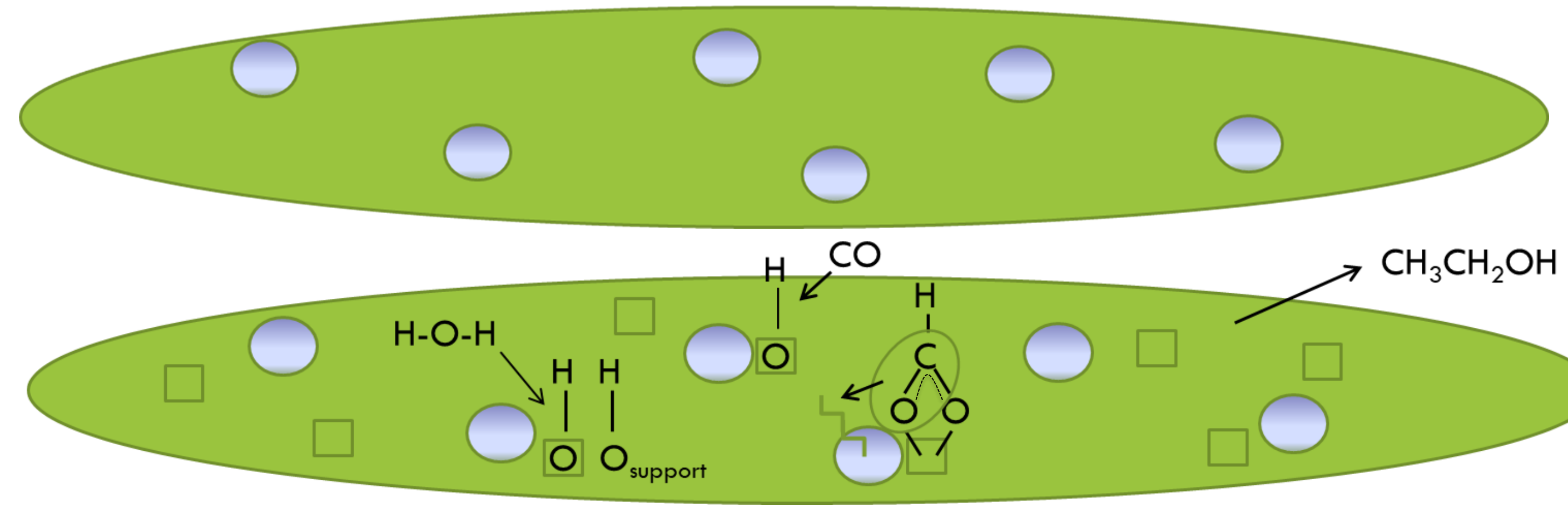
By utilizing higher oxygenate synthesis as an alternative method, we should expect to see an increase in the percentage of oxygenates.



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. The order of the vacancy concentration of reduced defects in the catalyst.

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

↑ O-vacancy concentration

Table 2. Selectivity comparisons at constant conversion among Ln-doped and undoped catalysts.

Catalyst	CO conv. (%)	Selectivity (%)		Product distributions (C-%)#			A+O (C-%)
		CH ₄	CO ₂	Paraffins	Olefins	Alcohols	
15Co/SiO ₂	31.4	6.4	3.2	71.1	20.3	4.8	25.1
15Co/GdO _x SiO ₂	32.0	10.5	2.5	63.4	28.3	5.5	33.8
15Co/CeO _x SiO ₂	20.5	12.1	1.1	57.8	34.7	5.7	40.4
15Co/PrO _x SiO ₂	19.1	13.6	1.1	59.0	30.1	7.1	37.2
15Co/LaO _x SiO ₂	22.7	12.4	0.9	64.1	24.6	10.5	35.1
15Co/SmO _x SiO ₂	20.8	13.5	1.7	64.5	28.6	5.0	33.6

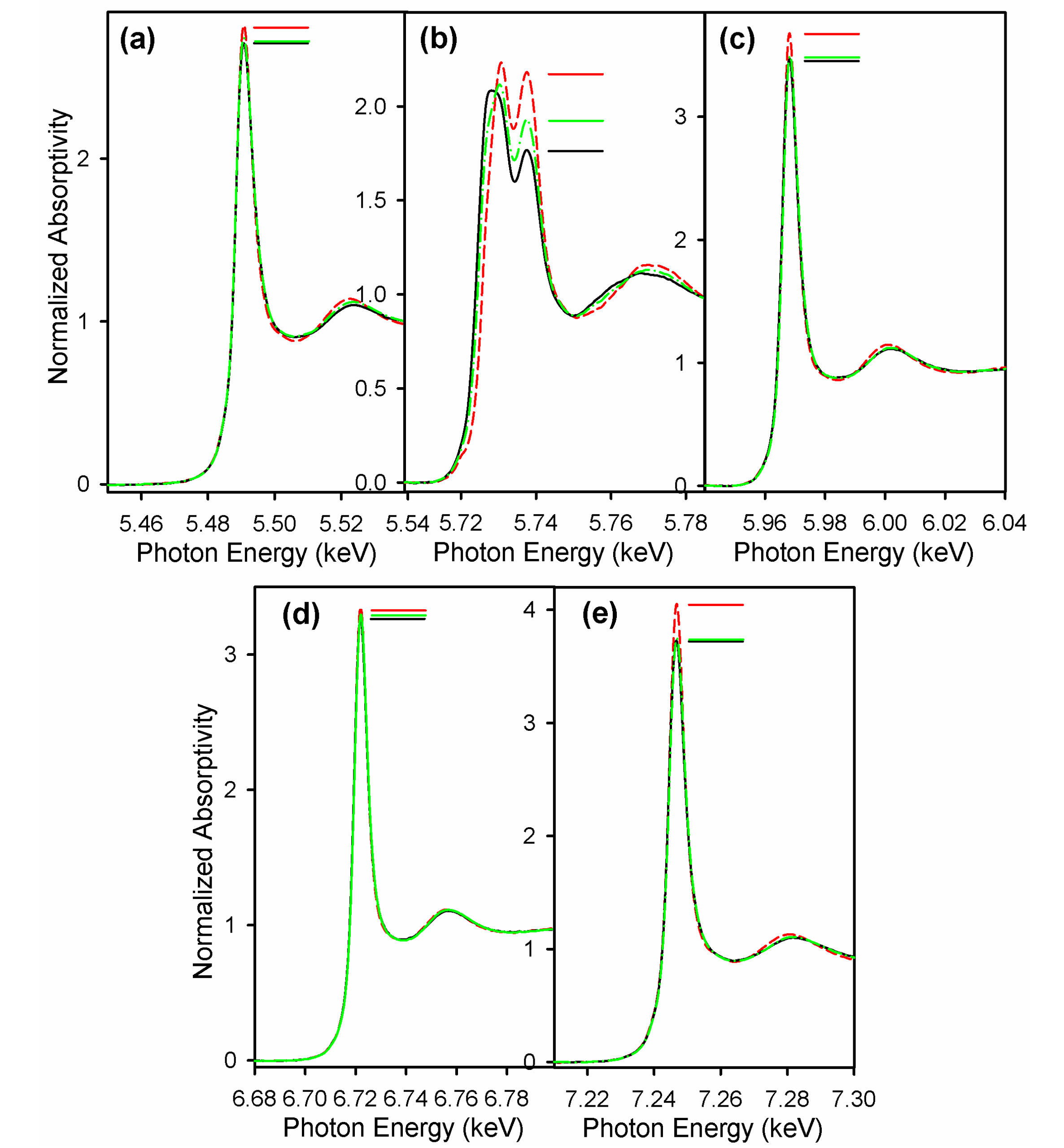


Figure 3. XANES snapshots of Ln L_{III} edges (red dashed) before activation, (black) after activation in H₂/He at 350°C, and (green) following exposure to syngas mixture for 1 h.

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 CeO₂ supported Pt-Co catalysts," *Applied Catalysis A: General* 393 (2011) 17-23.