

# The influence of thermal history on the site nature and intrinsic catalytic properties of Co/SiO<sub>2</sub> Fischer-Tropsch catalysts

Agustín Martínez\*, Gonzalo Prieto and Raúl Murciano  
Instituto de Tecnología Química, Avd. Los Naranjos s/n, Valencia 46022 (Spain)  
\*amart@itq.upv.es

## Introduction

Cobalt-catalyzed Fischer-Tropsch synthesis (FTS) is the preferred catalytic way to convert natural gas or biomass derived syngas into high-quality clean diesel fuels. Despite the early application of Co-based catalysts for long-chain hydrocarbons synthesis, we are currently witnessing an unprecedented research interest on these systems from a more fundamental standpoint. Thus, the impact of kinetically relevant mass transports, the chemical nature and texture of catalytic carriers, promoters and Co<sup>0</sup> particle size on catalytic activity, selectivity and stability have deserved particular attention in the last two decades [1]. The emerging knowledge is channeling scientists into plausible ways to controllably attain improved Co-based catalysts. Turning catalyst preparation art into a science while preserving an acceptable level of simplicity (for large-scale industrial application) seems an obvious strategy.

Co-based FTS catalysts are widely prepared by aqueous impregnation of a porous carrier (mostly SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) with an inorganic precursor, with nitrate being the most commonly applied. Afterwards, the catalyst is optionally submitted to air-calcination (at temperatures often arbitrarily chosen in the range of 573-873 K) leading to Co<sub>3</sub>O<sub>4</sub>, before undergoing an *in-reactor* H<sub>2</sub>-reduction required to generate the active Co<sup>0</sup> sites. Although the influence of calcination conditions (gas environment, final temperature, etc.) on the final catalytic properties have been explored [2], not detailed analysis on the different site population leading to different catalytic rates has been reported up to now.

Here we report a detailed study on the influence of the use (or not) and the temperature of air-calcination for 20%Co/SiO<sub>2</sub> catalysts on their site nature, density and intrinsic activity in FTS. Catalysts displaying medium metal dispersions ( $d(\text{Co}^0) > 10$  nm) are used to avoid masking effects from the recently reported particle-size TOF dependence [3].

## Materials and Methods

A series of 20%Co/SiO<sub>2</sub> catalysts has been prepared by incipient wetness impregnation of a low surface area (146 m<sup>2</sup>/g) and large pore size (19.0 nm) SiO<sub>2</sub> (Fluka) with a Co(NO<sub>3</sub>)<sub>2</sub> aqueous solution. Equal portions of the dried (333 K) precursor were calcined in flowing air at increasing temperatures 573-823 K while other aliquot was directly reduced in H<sub>2</sub>. Catalysts were characterized by ICP, XRD (including *in situ* reduction monitoring), H<sub>2</sub>-TPR, H<sub>2</sub> chemisorption, CO-TPSR, XPS, and LRS, among other techniques. FTS was performed at T=493 K, P=2.0 MPa, H<sub>2</sub>/CO=2, and quasi-differential conversion levels (<10%). Catalysts are *in situ* reduced at 673 K for 10 h prior to feeding syngas through the reactor.

## Results and Discussion

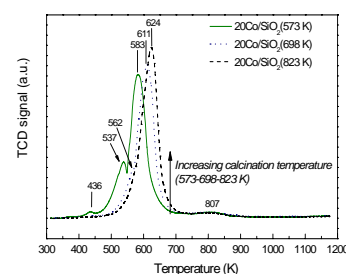
Increasing calcination temperature (573-823 K) leads to an increase in  $d(\text{Co}_3\text{O}_4)$  as ascertained by XRD and to drastic changes in the reduction behavior of this spinel oxide which

progressively switches from a two-step ( $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ ) to a single-step reduction with raising calcination temperature, as evidenced by H<sub>2</sub>-TPR (Fig. 1). Metal particle size ( $d(\text{Co}^0)$ ) in reduced catalysts continuously increases with increasing calcination temperature in the range 21-29 nm (Fig. 2). The directly reduced (uncalcined) catalyst displays the lowest  $d(\text{Co}^0)$ =16.2 nm. *In situ* XRD-monitored H<sub>2</sub>-reduction confirms the different reductive kinetics observed by H<sub>2</sub>-TPR for the calcined catalysts and shows that reduction evolves through CoO for the uncalcined sample. After reduction at 673 K, all catalysts show, however, high extent of reduction (ER > 95%) and *fcc* as the predominant metal cobalt phase.

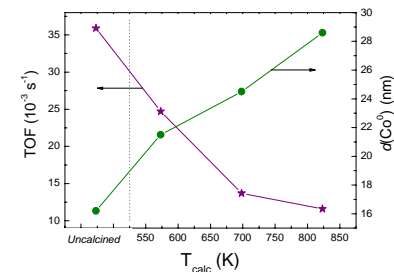
Surprisingly, despite the homogeneity in ER and Co<sup>0</sup> crystallinity, up to a 3-fold difference in cobalt site-activity (TOF) is found depending on the thermal history of the catalyst (Fig. 2). In line with this, CO-TPSR performed on *in situ* pre-reduced catalysts reveals significant changes in the temperature-resolved hydrogenation of CO which are related to marked differences in the nature and relative proportion of different metal surface sites.

## Significance

Rationalizing the links between the *in situ* Co<sup>0</sup> site-characterizations and the changes in the FTS intrinsic activities, determining up to 460% variations in the specific (per Co mass) overall rates, allows to understand the profound effects of the thermal history and points to a simple and scalable way to optimize the performance of Co-based FTS catalysts.



**Figure 1.** H<sub>2</sub>-TPR profiles for 20%Co/SiO<sub>2</sub> catalysts calcined at different temperatures in the range 573-823 K.



**Figure 2.** Co<sup>0</sup> particle size and TOF dependence with calcination temperature. The directly reduced (uncalcined) sample is also shown.

## References

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3. G. L. Bezemer, et al., *J. Am. Chem. Soc.* 128, 3956 (2006).