



The impact of pre-reduction thermal history on the metal surface topology and site-catalytic activity of Co/SiO₂ Fischer–Tropsch catalysts

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ABSTRACT

For *ex-nitrate* Co/SiO₂ Fischer–Tropsch synthesis (FTS) catalysts, the influence of the early thermal treatments during catalyst synthesis on the ultimate catalytic properties is studied without overlapping of particle size effects ($d(\text{Co}) > 15$ nm). The *bulk* and surface properties of the Co₃O₄ crystallites in the oxidic catalyst precursors depend on the previous thermal history and are decisive for the oxide reduction kinetics. Even after a homogeneous reduction treatment (673 K, H₂ flow), catalysts with different pre-reduction thermal histories showed dissimilar TOF (per surface Co⁰ atom) under FTS conditions (493 K, 2.0 MPa). As revealed by CO-TPSR and CO-FTIR, the different surface-specific activities relate to differences in the surface topology of the Co⁰ nanoparticles which likely result from the varying reduction kinetics. By tracking the effects of the earlier thermal treatments on the properties of the Co species, this work evidences that the pre-reduction thermal history not only determines metal dispersion and reducibility, but also the ultimate TOF. Such “memory effect” underscores the significance of a rational design of the entire synthesis and activation procedures to achieve Co-based Fischer–Tropsch catalysts with improved activity.

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1. Introduction

The Fischer–Tropsch synthesis (FTS) of hydrocarbons from synthesis gas (*syngas*) is a highly attractive catalytic route to convert carbon resources alternative to petroleum into liquid hydrocarbons. The FTS is at the core of the gas-to-liquids (GTL) processes which convert *syngas* derived from abundant natural gas reservoirs into high quality liquid fuels. The GTL process has been operated at a commercial scale since the 1990s and new units of unprecedented magnitude are currently being designed and started worldwide. In addition, biomass-to-liquids (BTLs) processes which produce renewable fuels from lignocellulosic biomass-derived *syngas* have reached demonstration and pre-commercial scale [1]. Cobalt is the catalyst of choice to maximize the production of long-chain hydrocarbons (mostly waxes) as precursors for ultra-clean synthetic diesel and specialty lubricants [2–4]. The use of Co FTS catalysts was already described in the original works by Fischer and Tropsch [5]. Despite this early and currently commercial application of Co catalysts, this catalytic system is presently receiving an unprecedented research

interest. Considerable progress has been made in establishing relationships between the catalytic performance and the catalyst structure at the meso- and nano-scales. The porosity of the catalytic support and related mass-transport phenomena [6–8] as well as the size [9–12] and crystalline structure [13] of the catalytic Co⁰ nanoparticles (NPs) have deserved particular attention as study variables. The emerging fundamental knowledge is essential in guiding the design and synthesis of new generations of Co catalysts with improved performance [14], while studying catalyst formulations and synthesis procedures in close resemblance to those applied industrially facilitates translation into technical realization.

Commercial Co FTS catalysts are commonly prepared by impregnation of a porous carrier (SiO₂, Al₂O₃, or TiO₂) with an aqueous solution of a metal precursor. Cobalt nitrate is preferred owing to its high solubility in water, allowing single-step high metal loadings, and its easy decomposition into reducible Co oxides. After impregnation and drying, the dried impregnate is submitted to a thermal treatment (*calcination*), generally in air, in order to decompose the Co precursor and generate supported Co oxide nanocrystallites. Finally, the oxidic catalyst precursor is *in-reactor* reduced, normally under flow of H₂, in order to *in situ* generate the catalytically active Co⁰ species. This sequence of thermal treatments constitutes the catalyst *thermal history* and is well known to have a significant impact on the ultimate catalytic performance. Hence, several studies have previously focused in determining the optimal activation conditions.

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Metallic cobalt displays two main crystallographic structures, hexagonal-close-packed (*hcp*) and face-centered-cubic (*fcc*). The phase transition *hcp* → *fcc* for *bulk* Co⁰ lies in the temperature range of 688–703 K [15], that is, within the range of temperatures typically required for the reduction of supported Co FTS catalysts (573–773 K). Therefore, the H₂-reduction treatment which precedes catalysis has been classically considered as potentially determinant for the crystalline structure and the catalytic activity of the resulting Co⁰ NPs. Previous reports exist on the influence of the gas composition [16,17], the heating rate [18], and the final applied reduction temperature (T_{red}) [19,20] on the microstructure and the catalytic activity of the resulting Co⁰ NPs. Some studies have postulated a higher intrinsic catalytic activity for *hcp*-Co⁰ [16,21,22].

The pre-reduction thermal history, particularly the (air-)calcination treatment, has also been the matter of study in previous works. Several parameters such as the gas atmosphere composition [23,24], the gas–solid hydrodynamics [24], the heating rate, and the final applied calcination temperature (T_{cal}) [13,23] have been shown to influence the final catalytic performance. Yet, another protocol, typically termed as *direct reduction*, has been proposed which combines decomposition of the metal precursor into oxide species and subsequent reduction in a single-step under flow of H₂ [2]. However, unlike the reduction treatment, the effects arising from the calcination stage have been traditionally rationalized exclusively in terms of metal dispersion and reducibility. Thus, the calcination conditions were considered to determine the size and reducibility of the resulting Co oxide nanoparticles and therefore the density of surface-exposed Co⁰ atoms after the subsequent reduction step. In addition to catalyst synthesis, air calcination treatments play also a central role in catalyst regeneration procedures [25]. The intrinsic catalytic activity is commonly expressed as site-activity or *turnover frequency* (TOF) and is formally determined per surface Co⁰ atom. To date, no differences in the nature of the Co⁰ sites or TOF owing to varying calcination conditions have been considered. The main reason is that the calcined catalyst precursor is always further submitted to the H₂ reduction treatment before is set to its catalytically active state. Indeed, examination of the scientific and the patent literature evidences that the conditions of catalyst calcination, and most particularly, the calcination temperature (T_{cal}) seems to be arbitrarily chosen within 573–873 K. In other cases, a minimum calcination temperature comes dictated by the decomposition temperature of the Co precursor [26] or the need for removal of organic moieties employed in specific preparative routes [27–29].

Nevertheless, close inspection of published catalytic data suggests a non-negligible impact of the pre-reduction thermal history on the ultimate surface-specific activity under FTS conditions. Enache et al. [13] reported increased TOF values for *ex-nitrate* Co catalysts activated by *direct reduction* as compared to air-calcined materials and ascribed the higher activity of the former to a higher contribution of *hcp* and “*poorly crystalline*” Co⁰ phases. Chu et al. [30] found a 56% decrease in the Co-time-yield (CTY) when T_{cal} was increased from 613 K to 773 K for Co/Al₂O₃ catalysts. Although no TOF values were given, it is apparent that the reported differences in metal dispersion and degree of reduction hardly explain on their own this activity decrease, unless an additional effect of the air calcination temperature on TOF is considered. Similarly, Co/ITQ-2 catalysts submitted to high temperature (773 K) air calcination treatments have been found by Prieto et al. [11] to exhibit TOF values 2–3 times lower than previously reported Co/SiO₂, Co/Al₂O₃, and Co/CNF catalysts activated via air calcination at lower temperatures ($T_{\text{cal}} \leq 623$ K) or *direct reduction*, having similar Co⁰ particle sizes. Indeed, the significance of the pre-reduction thermal history for the ultimate TOF is supported by a detailed scrutiny of previously published catalytic data for an extended ser-

ies of Co catalysts activated through various protocols [2,8,10,11,31,27,32,33–37] (see Supplementary information, section SI-2, for details).

This background certainly calls for a systematic study on the influence of the pre-reduction thermal history on the final structural and catalytic features of Co-based FTS catalysts. The derived knowledge is presumed highly valuable for a rational design of the activation and regeneration thermal treatments for this catalytic system of eminent industrial relevance. Here, we report a detailed study on the impact of the use of air calcination and the applied calcination temperature on the surface Co⁰ site nature, density, and TOF for 20%Co/SiO₂ FTS catalysts. An exhaustive characterization of the supported Co species throughout their entire thermal history is carried out in order to track the effects of the earliest thermal activation treatments down to the final catalytic state. In doing this, it is crucial to avoid overlapping with Co⁰ particle size effects (PSE) on TOF, which become noticeable for $d(\text{Co}^0) < 8\text{--}10$ nm [10,11,38]. In consequence, a low surface area and wide-pore SiO₂ support together with high cobalt loadings are employed in the present study to ensure Co particle sizes >10 nm. In addition, SiO₂ is a relatively inert support, as compared to Al₂O₃ or TiO₂ alternatives, which limits the cobalt-support interaction, enabling high Co reduction degrees. This is prerequisite to address fundamental aspects of the metallic phase without masking effects related to metal-support mixed compounds.

2. Experimental

2.1. Synthesis of Co/SiO₂ catalysts

To prepare the series of Co/SiO₂ catalysts, the silica support (*Silica gel spherical* from Fluka, B.E.T. surface of 146 m² g⁻¹, pore diameter of 19.0 nm) was previously dried at 373 K overnight. The dried support was then impregnated to incipient wetness with an aqueous solution containing the required amount of Co(NO₃)₂·6H₂O (Aldrich) to attain a 20%Co weight loading. The impregnated solids were subsequently dried at 333 K for 12 h. Three portions of the dried impregnate were calcined in flowing synthetic air at 573, 698, and 823 K, respectively. In all cases, the temperature was ramped to 573 K and maintained for 3 h to allow a homogeneous decomposition of the Co nitrate precursor and crystallization of the resulting Co oxide phase. Afterward, the temperature was increased to the final calcination temperature (when higher than 573 K) which was then held for 3 h. In all cases, heating rates of 2 K min⁻¹ and a constant gas space velocity of 1500 cm³ g⁻¹ h⁻¹ were employed. The obtained catalysts were labeled as Co/SiO₂-*x*, where *x* = 573, 698, or 823 depending on the final calcination temperature. High annealing temperatures can simultaneously alter the properties of the SiO₂ support, e.g., via (partial) irreversible de-hydroxylation or shrinkage of the porous structure, and these modifications might have catalytic implications. In order to decouple these potential secondary effects from those exclusively related to the Co phases, an additional catalyst was prepared following a so-called *dual calcination* protocol. In this case, the SiO₂ support was air-calcined at the highest employed calcination temperature (823 K) as previously described for the Co/SiO₂-823 sample. Afterward, the treated support was impregnated, dried, and finally air-calcined at the lowest applied calcination temperature (573 K), as detailed for Co/SiO₂-573. This catalyst was denoted Co/SiO₂-*dc*, where *dc* stands for *dual calcination*. Finally, another aliquot of the dried precursor was not calcined, to be *in-reactor* activated by a direct H₂-reduction treatment at 673 K. This catalyst is referred to as Co/SiO₂-*dr*, where *dr* stands for *direct reduction*. The dried impregnate as well as the air-calcined materials were stored in a glove box (<1 ppm O₂, <1 ppm H₂O) until their characterization.

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