



Fundamental issues on practical Fischer–Tropsch catalysts: How surface science can help



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ABSTRACT

The present article highlights the contribution of surface science and molecular modeling to the understanding of Fischer–Tropsch catalysis, in particular related to carbon-induced Co Fischer–Tropsch catalyst deactivation. The role of atomic and graphitic carbon in surface restructuring is discussed. Both forms of surface carbon stabilize surface roughness, while molecular CO promotes mobility of Co surface atoms. In a proposed chain growth mechanism on Co(0001) chain elongation proceeds via alkylidyne + CH. The resulting acetylenic species is hydrogenated to alkylidyne, the route to further growth. (Cyclo-)polymerization of acetylenic species produces (aromatic) forms of polymeric surface carbon, a slow side reaction.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is classified as a carbon-insensitive reaction [1], which suggests that carbon deposition is not important. Carbon-insensitive reactions are defined as catalytic reactions where carbon deposition is reversible, as (i) hydrogen is present in the reactant stream and (ii) the FTS catalyst is a hydrogenation catalyst. In other words, removal of surface carbon is possible under reaction conditions. This does not exclude carbon deposition from the description of FTS catalyst deactivation. If the net carbon formation rate is positive carbon build-up can still occur. A prime example is deactivation of Fe-based FTS catalysts. In this case carbon deposition is very significant, and is held responsible for most of the issues related to catalyst stability [2].

Carbon build-up on cobalt LT-FTS catalysts is just a fraction of that on Fe catalysts, but even small quantities of carbon, typically 1–3 wt%, represent a full monolayer coverage, even when considering the high dispersion of the supported cobalt nanoparticles [3]. Hence, despite the small unreactive carbon content, carbon deposition cannot a priori be dismissed as a deactivation mechanism for Co low temperature FTS (LT-FTS) catalysts.

The present article aims to summarize the current fundamental understanding on carbon as a deactivation mechanism on cobalt-based LT-FTS catalysts, with particular focus on the role of carbon in (i) restructuring the catalyst surface and (ii) the structure and formation mechanisms of detrimental carbon on a cobalt catalyst during FTS, the latter in direct relation to the FTS chain growth mechanism.

2. Materials and methods

The reader is referred to the supplementary information for details of the experimental and theoretical methods used.

3. Results and discussion

3.1. Surface restructuring: the role of surface carbon

The surface structure of supported cobalt catalyst particles under working conditions is inaccessible with the present state-of-the-art techniques. Hence, one needs to rely on theoretical calculations and surface science experiments on single crystal surfaces of cobalt. The most important indication of (severe) surface roughening under FTS came from the work of Wilson and de Groot [4]. Recently new STM work has been presented by Navarro et al. [5]. Their approach, in situ STM and surface X-ray diffraction at 300–600 mbar and 210–220 °C, confirmed rapid surface restructuring during exposure to synthesis gas.

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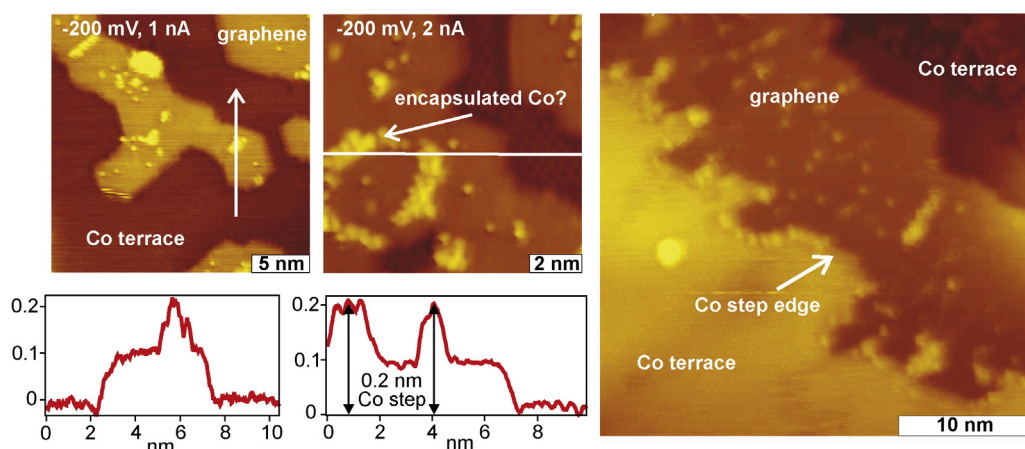


Fig. 1. STM image of graphene islands on a Co(0001) surface, grown between 100 and 360 °C. Graphene contains specific defects, with a height of 0.2 nm with respect to the surrounding cobalt terrace (left). In addition (right), cobalt step edges have become irregular, indicating that Co atoms originating from step edges have migrated and became trapped by defects in the imperfect graphene island.

Adapted from Ref. [15].

Wilson et al. [4] highlighted the role of mobile sub-carbonyl species, which were observed experimentally by others in their laboratory [6,7]. Such species can account for the high mobility of surface cobalt atoms at FTS temperatures, and would make restructuring *kinetically* possible. In fact, CO-induced mobility of cobalt has been found at room temperature on Co(10–12) and Co(11–20), surfaces that expose low-coordinated Co atoms [8,9]. CO chemisorption itself cannot provide a significant *thermodynamic* driving force for roughening of the close-packed surface: TPD data on Co(0001) vs. Co(10–10), a more open surface, show that CO does not bind significantly stronger to surface atoms with a lower coordination number [10,11]. Wilson and de Groot reported a significant quantity of atomic carbon after exposure to realistic FT synthesis conditions, and suggest that carbon pins down mobile sub-carbonyl species. Our investigations focused on the role of surface carbon (of any type) in surface roughening.

Theoretical calculations by Ciobîcă et al. showed that atomic carbon can reconstruct both the fcc-Co(100) and fcc-Co(111) surfaces [12], (the so-called clock-reconstruction), in analogy to the corresponding surfaces of Ni, on which this reconstruction was found experimentally [13,14]. Our recent experimental study confirmed that 0.5 ML atomic carbon can indeed induce the predicted surface reconstruction on Co(0001), but no indications were found for ad-island formation [15]. A carbon coverage of 0.2 ML, on the other hand, does not cause surface reconstruction. Under FTS conditions, where surface hydrogen is available, and with the information that *bulk* cobalt carbide decomposition in the presence of hydrogen occurs below typical FTS temperatures (<210 °C) [16], it is unlikely that carbon concentrations of 0.5 ML will be reached on the flat, close-packed terraces of active particles.

This does not exclude the possibility suggested by Wilson and de Groot [4], in which atomic carbon is suggested to pin down mobile sub-carbonyl species. Atomic carbon prefers a specific, high coordination environment with a square geometry (and even reconstructs the Co surface to create it [12,15]). DFT calculations show that C bound at the bottom of an A-type step edge (triangular step geometry, see Fig. 2) is 40 kJ mol⁻¹ more stable than on the flat terrace. When bound at the bottom of a B-type step (square step geometry) carbon is 74 kJ mol⁻¹ more stable than on the terrace. When a mobile cobalt (sub-carbonyl) species meets a carbon atom on the surface it is strongly bound, as it increases the coordination of carbon. This immobilized ad-atom can then act as a nucleus for growth of an ad-island. The strong preference of carbon for B-type steps leads to formation of (experimentally observed) triangular surface

structures, a geometry in which one type of step edges (presumably of the B-type) is exposed.

Atomic carbon is not the only form of surface carbon that can pin down mobile Co species. Navarro et al. [5] proposed a different mechanism for Co surface roughening during FTS, with a prominent role for (defective) graphene [5], which formed very fast under their experimental conditions. Our STM experiments [15] led to the hypothesis that defects in graphene trap mobile Co ad-atoms. In those experiments, performed in the absence of CO, mobile ad-atoms were brought about thermally (by heating to 360 °C, higher than typical FTS temperatures). Low-coordinated (i.e. step edge) atoms on single crystal surfaces are known to become mobile at relatively low temperature [15,17–19], a phenomenon that one relies on when annealing the defective single crystal surface after sputtering. This notion explains the experimental observations shown in Fig. 1: (left) graphene islands contain encapsulated Co atoms, and (right) step edges of cobalt have become irregular, i.e. cobalt atoms have been removed from it. In other words: at ~360 °C, mobile Co atoms, which originate from step edges, bind practically irreversibly to defects in the graphene island.

Under FTS conditions both molecular CO and surface carbon are seen as essential ingredients for surface roughening: CO is required for *kinetic* reasons, providing high surface atom mobility at FTS temperatures, but the *thermodynamic* driving force for

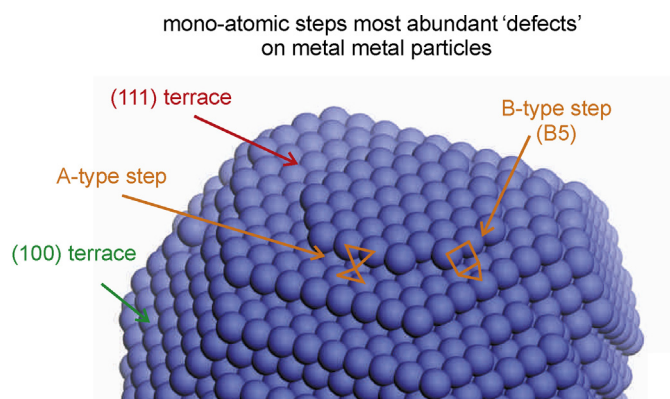


Fig. 2. Atomic model of a ~4.6 nm Co particle (4603 atoms), terminated predominantly by (111) and (100) facets. A significant portion of defects is present, in particular ad-islands terminated by mono-atomic step edges.

Courtesy: P. van Helden.

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