



In situ magnetometer study on the formation and stability of cobalt carbide in Fischer–Tropsch synthesis



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ABSTRACT

While carbides are always present in iron-based Fischer–Tropsch synthesis, very little is known about the presence and the role of carbides in cobalt-based CO hydrogenation. Cobalt carbide, Co₂C, has been reported in catalysts where operational upsets occurred and it is associated with low catalyst activity and increased methane selectivity. In this study, a novel *in situ* magnetometer was used to study the formation and the stability of cobalt carbide during the Fischer–Tropsch synthesis at fully relevant conditions. The formation of cobalt carbide was confirmed by means of *in situ* XRD and synchrotron XRD measurements. Cobalt carbide is relatively stable at typical reaction conditions, but a rapid decomposition into hcp cobalt occurs in hydrogen above 150 °C. Cobalt carbide formation is inversely proportional to the H₂/CO ratio and the reaction temperature. However, the amounts of cobalt carbide formed are small and the impact on deactivation at realistic Fischer–Tropsch conditions should generally be negligible.

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1. Introduction

Cobalt-based catalysts are preferred over their iron counterparts for Fischer–Tropsch synthesis in gas-to-liquids processes [1] due to their higher selectivity to paraffinic products, lower water gas shift activity, and longer lifetime. Due to the high costs of cobalt and noble metal promoters, extended catalyst lifetime is required to make the process economically feasible [2]. In order to improve lifetime of a cobalt catalyst for such processes, an understanding of the deactivation mechanisms is important. In the recent years, carbon deposition has received a lot of attention as a mechanism for deactivation of cobalt-based Fischer–Tropsch catalysts [2–5]. Most of these studies have focussed on the role of surface carbon. There does not seem to be much consensus in the literature regarding the formation of bulk cobalt carbide at realistic Fischer–Tropsch synthesis conditions.

It is generally accepted that bulk cobalt carbide can form when exposing a cobalt catalyst to pure CO at typical temperatures for the low temperature Fischer–Tropsch synthesis which might occur during an upset. For example, work at Syntroleum [6] on a Co/Al₂O₃ catalyst showed the formation of bulk carbide during the Fischer–Tropsch synthesis (216 °C and 37 bar), when the

catalyst was exposed to pure CO for a period of 8 h (due to failure of a H₂ flow meter). The performance of the catalyst was severely affected when the standard synthesis gas with a H₂/CO ratio of 2 was reintroduced; the CO conversion had dropped by more than half, and the methane selectivity had doubled in comparison with the performance prior to the upset. A similar behavior at upset conditions has also been reported by researchers at Sasol [3]: the exposure of a cobalt catalyst to pure CO at an even shorter period of 2 h and representative pressures and temperatures of the low temperature Fischer–Tropsch synthesis could result in catalyst deactivation through the formation of bulk cobalt carbide.

However, there have been few reports documenting the formation of bulk cobalt carbide during normal or realistic operating conditions. Jacobs et al. [7] employing synchrotron XRD, detected a small amount of Co₂C that may have been formed during the Fischer–Tropsch synthesis (220 °C; 18 bar; H₂/CO = 2). Karaca et al. [8] conducted *in situ* synchrotron XRD evaluation of an alumina supported Co catalyst and showed that the exposure of Co catalysts to syngas for longer times (H₂/CO = 2; P = 20 bar, T = 220 °C, initial CO conversion = 60%) led to a partial carburization and small particles of Co₂C were detected after exposure of the catalyst to syngas for a period of after 8–10 h.

While there is evidence for the carbides contributing to activity for FTS on iron catalysts, bulk cobalt carbide is considered to be a deactivating species in cobalt catalysts [9]. Early work at the

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Bureau of Mines on Co/ThO₂/Kieselguhr catalysts showed that bulk carbide was not an intermediate in the Fischer–Tropsch synthesis nor was it catalytically active [10]. Excessive amounts of carbides, produced upon CO exposure prior to the reaction, were found to severely inhibit the FTS activity. In some cases, a fourfold increase in activity was noticed after the hydrogenation of the carbide at around 150–200 °C which yielded an hcp cobalt phase and methane [11]. The transition of cobalt carbide, obtained via carburization of a prereduced CoPt/Al₂O₃ catalyst, to metallic cobalt has recently also been monitored with *in situ* X-ray absorption spectroscopy measurements by Kwak et al. [12]. In agreement with earlier work [11], cobalt carbide was found to decompose at around 160–200 °C and the resulting catalyst displayed improved FT activity. Ducreux et al. [13] observed the formation of Co₂C on alumina- and titania-supported cobalt-based Fischer–Tropsch catalysts by *in situ* XRD techniques and related its presence with a deactivation process. Recent work by Mohandas et al. [14] also showed that Co₂C, synthesized from carburization of Co₃O₄, initially displayed poor activity for the Fischer–Tropsch synthesis with methane and CO₂ as the main carbon-containing products. The performance of the catalyst improved with time due to the decomposition of the carbide to metallic cobalt under Fischer–Tropsch conditions.

Various techniques have been used to characterize the presence and stability of cobalt carbide in cobalt-based Fischer–Tropsch catalysts with *ex situ* XRD [2] being the most commonly used one. Cobalt carbide is regarded metastable and is not usually observed using *ex situ* techniques. There are a few documented cases of using magnetic measurements to characterize or detect cobalt carbide. Hofer et al. [15] first studied the decomposition of cobalt carbide using a magnetic balance, while Pankina et al. [16] and Mirodatos et al. [17] used *ex situ* magnetic measurements coupled with temperature-programmed hydrogenation (TPH) to infer the presence of carbides in spent catalysts. More recently, Braconnier et al. [18] studied the rates of carburization and decarburization of supported catalysts using an *in situ* magnetometer. However, to our knowledge, there are no reports of studying the stability and effects of cobalt carbides in an *in situ* magnetometer at relevant Fischer–Tropsch conditions, i.e. at relevant temperature and pressure with simultaneous catalyst performance evaluation.

The stability and formation of cobalt carbide appears to be an important topic in the context of catalyst deactivation in cobalt-based Fischer–Tropsch synthesis. In this study, the formation of cobalt carbide on a Co/Pt/Al₂O₃ catalyst and its impact on activity and selectivity was investigated using an *in situ* magnetometer, which was jointly developed by the University of Cape Town and Sasol [19]. The aim was to develop a method to identify cobalt carbides using the magnetic setup. In the first part, we studied the stability of purposefully made carbides and their effect on the performance in the Fischer–Tropsch synthesis at realistic conditions, and secondly, we attempted to identify carbides in end of run samples of catalyst tested at different conditions (i.e., without purposeful pre-carbiding). The aim of our study was to determine whether cobalt carbide formation is a significant deactivation mechanism under realistic Fischer–Tropsch synthesis conditions.

2. Experimental

2.1. Catalyst preparation

A 20 wt% Co/Al₂O₃ catalyst, promoted with 0.05 wt% platinum, was prepared by slurry impregnation of a γ -alumina support (Puralox 2/150, Sasol Germany) with an aqueous cobalt nitrate

solution, also containing the platinum promoter. After impregnation and drying, the catalyst intermediate was calcined at 250 °C in air. To achieve the required cobalt loading, two sequential impregnation and calcination steps were performed [20].

2.2. *In situ* magnetic measurements

In situ magnetic measurements were taken by the Weiss extraction method in an electromagnet providing fields up to 20 kOe (2.0 T) at the University of Cape Town, South Africa [19]. The setup can be operated at high temperatures (600 °C and higher) and importantly also at high pressures (50 bar and higher) under fixed bed flow conditions so that tests can be conducted at fully relevant industrial conditions. Contrary to many other “*in situ*” methods, which often do not allow for catalyst bed flow through (“plug flow conditions”) or which are limiting in terms of temperature and pressure ratings this setup can be used for true *in situ* material characterization while meaningful kinetic data of the catalyst performance can be obtained. The amount of reduced cobalt present in the catalyst was determined by comparing the saturation magnetization obtained with the specific saturation magnetization of bulk cobalt. The degree of reduction in this study is defined as the percentage of metallic cobalt of the amount of cobalt loaded. Metallic cobalt is strongly magnetic, i.e. ferromagnetic [21], at reaction conditions, whereas Co₃O₄ and CoO are paramagnetic at reaction temperature with Néel temperatures of 30 K and 290 K, respectively [21,22]; their magnetic moments can therefore be neglected in comparison with that of the metal. The cobalt carbide relevant to this study, Co₂C, is ferromagnetic; however, it also displays a very low and negligible magnetic susceptibility compared to cobalt [15] (see also Section 3.2). A decrease of magnetization of a working FT cobalt catalyst can therefore be interpreted as either oxide and/or carbide formation and, in certain cases, confirmatory experiments and/or methods may be required in order to allow drawing definite conclusions regarding phase changes.

In addition to information regarding phases, magnetic characterization can be used to derive crystallite size related information. The mass fraction, γ , of cobalt in magnetic domains larger than the critical minimum diameter (D_c) is calculated from the remnant magnetization and the saturation magnetization ($\gamma = 2 * M_{rem}/M_{sat} * 100$). Dalmon and Martin [23–25] have reported D_c for cobalt to be approximately 15–20 nm at room temperature. Bean and Livingstone [26,27] gave theoretical values of 8 nm for hcp cobalt and 28 nm for fcc cobalt at room temperature. Note that D_c corresponds to single domain size for spherical particles. In this study, the saturation magnetization was measured at maximum field strength (20 kOe), which was followed by a measurement at 0 kOe to determine the remnant magnetization (measuring time 2 min). A detailed description of the setup for *in situ* magnetic measurements has recently been given by Fischer et al. [28].

2.3. *In situ* and *ex situ* XRD

The crystalline phase changes during the reduction and carburization of the catalyst and hydrogenation of the carbide were also determined using *in situ* powder X-ray diffraction analysis with a Panalytical X'Pert Pro multipurpose diffractometer with Co K α radiation ($\lambda = 1.78897 \text{ \AA}$) equipped with an *in situ* reaction chamber (XRK 900, Anton Paar). The catalyst (0.2 g of calcined Co/Pt/Al₂O₃) was packed into a stainless steel holder and treated firstly with hydrogen in a temperature-programmed manner. The catalyst sample was reduced in H₂ with a flow rate of 100 ml/min (STP). The sample was heated at 1 °C/min to a temperature of 425 °C, which was maintained for 7 h. The sample was then cooled to 150 °C under helium with a flow rate of

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