



Identification of carbon species on iron-based catalysts during Fischer-Tropsch synthesis

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ABSTRACT

This paper focuses on the use of *in situ* and *ex situ* characterisation techniques to provide evidences of carbon species on a commercial iron-based Fischer-Tropsch synthesis catalyst as well as other indices of potential deactivation mechanisms. *In situ* XANES measurements demonstrate that re-oxidation or transformation of the active iron phase, *i.e.* the Hägg carbide phase, was not a significant deactivation mechanism at the studied conditions. Sintering of Hägg carbide nanoparticles is significant with increasing temperatures and time on stream. The sintering mechanism is proposed to be a hydrothermally-assisted process. *In situ* DRIFTS indicates the presence of different carbon species on the catalyst surface such as aliphatic hydrocarbons from wax products and oxygenate compounds such as alcohols, aldehydes/ketones and carboxylate species. Carboxylate species are resistant towards hydrogenation at 280 °C. The presence of different carbon species on the surface after wax product extraction is evident from TPH-MS measurements. GC-MS analysis shows that the strongly adsorbed carbon species remaining on the catalyst surface from wax products are mainly α -olefins and branched carboxylic species. The interaction of oxygenate compounds, especially carboxylate species with iron oxide, may form stable complexes limiting further iron catalyst carburization. STEM-EDX analysis shows that carbon is preferentially located on iron particles.

1. Introduction

The presence of deactivation mechanisms in Fischer-Tropsch synthesis (FTS) catalysts have been investigated since the first work on these catalysts in the early 1920s [1,2]. However there is still much debate and controversy concerning the main reasons for the eventual loss of catalytic activity [3]. Despite this, there is a consensus regarding the stability and resistance to deactivation of the most common FTS catalysts *i.e.* cobalt-based and iron-based catalysts. The productivity of cobalt-based catalysts at high conversion is currently higher than that of iron-based catalysts. On the other hand, iron-based catalysts are more prone to deactivation as they are further susceptible to carbon deposition, re-oxidation/ transformation of active phases, sintering and catalyst attrition [1,3,4]. Iron-based catalysts are seen as an attractive option for the Biomass-To-Liquid (BTL) process, because of their capacity to manage different syngas feed ratios ($H_2/CO = 0.5 - 2.5$) including syngas rich in CO_2 , since they also catalyse the water-gas-shift (WGS) reaction [1]. In addition, they have the ability to work at higher

temperatures with low methane production, higher sulphur tolerance (< 0.2 ppm) and less expensive catalyst production, which impacts on the cost of the entire process [1,2,4]. Operating the FTS unit with a CO_2 rich feed without purification could result in a simpler, lower cost process [5,6]. Hence, the improvement of current iron-based catalysts is desired. Fundamental research on commercial and model catalysts is crucial to understand deactivation mechanisms during FTS. It may open up possibilities to propose deactivation pathways, decoding their effect on surface chemistry of the catalysts and thus catalytic performance. Based on such research, it may be possible to propose better catalyst formulations, preparation routes and activation procedures as well as deactivation-modelling studies. Due to the complexity of the FTS, the study of deactivation mechanisms requires the use of advanced characterisation techniques. For example; studying of re-oxidation of active phases, which are very sensitive to changes by oxygen from air³, must be done under *operando/in situ* conditions. For that purpose, *in situ* synchrotron techniques such as X-ray absorption fine structure spectroscopy (XAFS) combined with powder X-ray diffraction (XRD) [7–10]

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have been shown to be very useful to study active phases in their working environment. XAFS may be divided in two spectral regions; the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) provide detailed information about the oxidation state and coordination of the absorber atoms [11]. *In situ* XAFS can be employed as a bulk characterisation technique to identify and quantify the different iron oxide and carbide species present during FTS at relevant working conditions [11–17]. *In situ* XRD can bring information related to the crystallinity and sintering [18]. Several carbide species such as ϵ -Fe₂C, ϵ' -Fe_{2.2}C, Fe₇C₃, χ -Fe₅C₂, and θ -Fe₃C have been detected [3]. χ -Fe₅C₂ and θ -Fe₃C [11,12,19–22] are normally the most stable and common species during FTS. High CO conversion rate and hydrocarbon productivity have been associated with χ -Fe₅C₂ (Hägg carbide) while catalyst deactivation due to carbon deposition can be associated with θ -Fe₃C (cementite) [14,23,24]. Iron carbide clusters are usually pyrophoric and are therefore readily transformed into iron oxides when exposed to air [3]. Synchrotron X-ray *in situ* methods in characterising bulk and supported catalysts are excellent tools for studying active site formation/evolution in FTS catalysts [25]. *In situ* XRD is a suitable characterisation technique to measure the degree of sintering since pyrophoric iron carbides [3,12] are preserved without external influence of oxygen from air. Catalyst attrition arising from degradation of catalyst particles into finer particles is mainly observed in slurry and fluidised-bed reactors [26–33], but less pronounced in fixed-bed reactors. Carbon deposition as a potential deactivation mechanism is difficult to investigate due to the accumulation of detrimental carbon species on the catalyst surface being masked by the presence of hydrocarbon wax products. Although it is hard to differentiate between them, polymeric carbon has been identified as the most deleterious of carbon species [34]. It is believed that this carbon is formed from the polymerisation of CH_x and has an alkyl group structure making it less reactive. The resilient carbon species on spent cobalt-based catalysts have been characterised by many *ex situ* techniques; they are mainly composed of aliphatic hydrocarbons like α -olefins and oxygenates such as carboxylic acids, aldehydes, ketones and alcohols. Oxygenates showed special affinity to the acid sites of the support [35,36]. Moreover, it has been reported that carboxylic acids can cause atomic carbon formation on cobalt-based catalysts during FTS as a result of strongly adsorbed carboxylate species on the support [37]. In addition, once adsorbed, they can accumulate on catalyst surface and generate steric hindrance [36], probably leading to a decay in catalytic activity. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has recently been used to determine the nature/reactivity of surface carbon species under FTS conditions on cobalt-alumina catalysts, suggesting the presence of aliphatic species related to wax products and oxygenate species associated with formate and carboxylate [38,39]. Results also indicate strong interaction of oxygenate compounds, especially carboxylate species, with oxidic sites and the catalyst support. Beyond the previously mentioned, very little information can be found in the open literature about the use of *in situ* and *ex situ* characterisation techniques to investigate deactivation mechanisms on iron-based FTS catalysts. Hence, this work makes use of several *in situ* and *ex situ* characterisation techniques to provide insight into potential deactivation mechanisms on a commercial iron-based catalyst under relevant operating conditions.

2. Experimental

2.1. Commercial catalyst and carbide references

The catalyst used in this study was a Fe-based co-precipitated catalyst provided by Johnson Matthey. The catalyst is composed of Fe₂O₃, SiO₂, CuO, K₂O and Na₂O. Before *in situ* characterisation, the catalyst was crushed and sieved to particles between 38–106 μ m diameters. The spent catalyst for *ex situ* characterisation was recovered after the sample was pre-treated under pure CO for 7 h at 210 °C and then exposed to

FTS at 280 °C, H₂/CO = 2, 20 bars and GHSV \sim 600 LKg_{cata}⁻¹ h⁻¹ in a fixed bed reactor, and maintained for 120 h. For carbon characterisation, the hydrocarbon wax-product was extracted from the spent catalyst via Soxhlet extraction, using similar methodology to what has been reported elsewhere [35,40]. For the identification of carbide species present in the spent catalysts, two carbide references were synthesised using the procedure reported by de Smit et al. [12]:

- Hägg carbide (χ -Fe₅C₂) reference: A commercial sample of Fe₂O₃ (Sigma-Aldrich, 99% < 5 microns) was reduced in pure CO at 350 °C for 4 h (ramping rate of 4 °C min⁻¹) at atmospheric pressure.
- Cementite carbide (θ -Fe₃C) reference: A commercial sample of Fe₂O₃ (Sigma-Aldrich, 99% < 5 microns) was reduced in pure CO at 450 °C for 4 h (ramping rate of 4 °C min⁻¹) at atmospheric pressure.

2.2. *In situ* XANES /XRD/MS combined set-up

The *in situ* XANES /XRD measurements were collected at the Swiss-Norwegian beam lines (BM01B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The crystallinity and composition of the different iron phases were monitored by *in situ* XRD and XAFS, respectively. Around 6 mg of the catalyst precursor was placed inside a capillary reactor (1.0 mm outer diameter) giving a bed length of about 10 mm. This type of capillary reactor has shown quasi plug flow reactor performance especially designed for X-ray applications [41]. The reactor was mounted in a stainless steel bracket and sealed with high temperature epoxy glue. The sample was pre-treated *ex situ* with pure CO at 210 °C for 7 h at ambient pressure and kept sealed in He atmosphere. The measurements were carried out at 230 °C, 250 °C and 280 °C, 18 bar, gas hourly space velocity (GHSV) \sim 15,000 LKg_{cata}⁻¹ h⁻¹, syngas 64% vol. H₂, 32% vol. CO and Ar 4% vol. Firstly, He was introduced to achieve the working pressure (18 bar) with the pressurization taking approximately 1 h. After ensuring no leaks, the temperature was increased from room temperature to 230 °C using a ramp rate of 5 °C min⁻¹ under syngas (\sim 6 h for each temperature step). XRD and XANES data were alternately collected together with on-line MS data. A cycle of measurements took around 1 h, *i.e.* one X-ray diffractogram (25 min) and six XANES spectra (5 min). The ion chambers were optimised for iron K-edge energy (7112 eV) detection. Qualitative and quantitative analysis were carried out on the XANES part of the XAS spectra. The experimental set-up and the protocol of *in situ* measurements are described in detail elsewhere [42].

2.3. *In situ* DRIFTS measurements

DRIFTS experiments were performed at ambient pressure with a Praying Mantis™ high-temperature DRIFTS reaction cell from Harrick Scientific Corporation with ZnSe windows. A detailed description of the reaction cell and the experimental set-up can be found elsewhere [42]. The sample was diluted with KBr (3:1) in order to obtain a good signal to noise ratio. The contribution from the gas-phase was subtracted using the syngas spectrum collected over pure KBr at the different reaction temperatures. Initially, the fresh catalyst was heated to 230 °C under He atmosphere, then the syngas was introduced (1 mL m⁻¹ H₂, 0.5 mL m⁻¹ CO, H₂:CO 2:1) while collecting spectra for approximately 3 h at each temperature. The system was operated at atmospheric pressure and the GHSV was about 1200 LKg_{cata}⁻¹ h⁻¹. The analysis was performed mainly in the alkane and oxygenate regions to detect potential accumulation of such species on the catalyst surface with time on stream.

2.4. *Ex situ* characterisation techniques

The XRD patterns of the fresh and spent samples were obtained by using a Bruker D8 Advance DaVinci instrument with a Cu anode ($\lambda = 1.54 \text{ \AA}$). The samples were run for 120 min in the range

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