Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis

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ARTICLE INFO

ABSTRACT

Iron carbides are unmistakably associated with the active phase for Fischer-Tropsch synthesis (FTS). The formation of these carbides is highly dependent on the catalyst formulation, the activation method and the operational conditions. Because of this highly dynamic behavior, studies on active phase performance often lack the direct correlation between catalyst performance and iron carbide phase. For the above reasons, an extensive *in situ* Mössbauer spectroscopy study on highly dispersed Fe on carbon catalysts (Fe@C) produced through pyrolysis of a Metal Organic Framework was coupled to their FTS performance testing. The preparation of Fe@C catalysts via this MOF mediated synthesis allows control over the active phase formation and therefore provides an ideal model system to study the performance of different iron carbides. Reduction of fresh Fe@C followed by low-temperature Fischer-Tropsch (LTFT) conditions resulted in the formation of the ε'-Fe$_{2.2}$C, whereas carburization of the fresh catalysts under high-temperature Fischer-Tropsch (HTFT) resulted in the formation of χ-Fe$_5$C$_2$. Furthermore, the different activation methods did not alter other important catalyst properties, as pre- and post-reaction transmission electron microscopy (TEM) characterization confirmed that the iron nanoparticle dispersion was preserved. The weight normalized activities (FTY) of χ-Fe$_5$C$_2$ and ε'-Fe$_{2.2}$C are virtually identical, whilst it is found that ε'-Fe$_{2.2}$C is a better hydrogenation catalyst than χ-Fe$_5$C$_2$. The absence of differences under subsequent HTFT experiments, where χ-Fe$_5$C$_2$ is the dominating phase, is a strong indication that the iron carbide phase is responsible for the differences in selectivity.

1. Introduction

In the early years surrounding the discovery of the atmospheric-pressure synthesis, Fischer postulated that the primary step before hydrogen addition is the carbon monoxide dissociation, and thus, the formation of carbides as intermediate compounds in the reaction [1,2]. Cobalt, nickel and iron, three metals that display FTS activity, react at 200 °C with carbon monoxide to form carbides, and carbon balances of synthesis reactions and product analysis of the decomposition of spent catalysts indicated that carbides were formed during the synthesis [3]. At this time, catalyst characterization techniques were still emerging, as only fifteen years had passed since the Nobel Prize in Physics was awarded to the Braggs for their work on X-ray diffraction (XRD), and it would be another five before Brunauer and Emmett started publishing on Van der Waals adsorption isotherms. The first iron-phase characterization studies were performed on the high-temperature Fischer-Tropsch (HTFT) catalyst, fused bulk iron catalysts with low surface area, where the iron phase was resolved by magnetization experiments [4]. The temperature-dependent magnetic moments allowed for quantification of the iron phase during FTS, and showed that, after complete reduction, iron was converted in magnetite and Hägg carbide (around 45% and 50%, resp.) with small amounts of metallic iron remaining. The composition of the catalyst changed, as the magnetite phase gradually increased during operation, whereas the Hägg carbide phase decreased and was oxidized and interconverted to another iron carbide phase [5]. This fundamental view on the dynamics of iron catalysts has not changed much up to date.

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The discovery of Mössbauer absorption spectroscopy and the further development of XRD allowed the characterization of small iron nanoparticles on supported catalysts, and several iron carbides were identified over the years [6–17]. In addition, the application of X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XANES/EXAFS) further stimulated the studies into FTS carbide-phase formation. The carbide phases found in literature associated with FTS are ε-Fe$_2$C, ε'-Fe$_{2.2}$C, Fe$_7$C$_3$, χ-Fe$_5$C$_2$, and θ-Fe$_3$C, however, generally, the monoclinic Hägg carbide (χ-Fe$_5$C$_2$) and hexagonal closed packed carbide (ε'-Fe$_{2.2}$C) are the predominant carbide phases found. Debate emerged regarding activity and selectivity of the different iron carbides, now that it became more widely accepted that carbides are the active phase. Thus, many studies have focused on the activation of fresh catalysts in order to optimize their performance and establish the iron phases [18–41]. Particularly, Mössbauer studies coupled with catalytic tests provide good insight into the effect of the activation protocol and operational regime on the carbide phase. However, the focus of these papers was often limited; either the differences in the evolution of the active phase were investigated or the performance of the catalysts acquired through different activation protocols was reported. Hence, the main conclusion usually derived is that one activation method is preferred over the other, for a wide variety of reasons, and that a coexistence of carbide phases could be obtained. Therefore, it is not possible to uniquely determine key performance indicators such as activity and selectivity inherent to a specific iron carbide phase. To properly quantify their intrinsic activity and distinguish the iron carbides, one would need to find a very robust catalyst that can withstand the different activation regimes to maintain identical reducibility, degree of carburization, and catalytic stability.

The discovery and development of a new type of iron catalyst produced through the decomposition of highly porous, crystalline, and dispersed iron clusters in carbon matrices, or metal-organic frameworks (MOFs) was recently reported by our group [42–44]. The Fe@C catalysts have a high loading of monodispersed nanoparticles and show high degree of carburization during *in situ* Mössbauer experiments following the MOF pyrolysis (Table 1). Moreover, the resulting Fe@C catalysts display exceptional activity and stability under high temperature Fischer-Tropsch (HTFT) conditions due to the embedding of iron in the carbon matrix formed after MOF decomposition. These catalysts provide an ideal model system because of the control over the particle size and iron phase by tuning the degree of carbonization through the pyrolysis temperature [44]. It has been observed that with increasing particle size a higher χ-Fe$_5$C$_2$ over ε'-Fe$_{2.2}$C ratio is formed as determined by Mössbauer spectroscopy. Additionally, *in situ* Mössbauer experiments following the pyrolysis of the Fe-BTC precursor and its carburization confirmed that ε'-Fe$_{2.2}$C is indeed a stable phase under HTFT conditions for particles below ~3 nm. However, after reduction and subsequent activation under HTFT conditions, controlling and isolating the hexagonal carbide phases under HTFT is tedious. The low carbon chemical potential under HTFT does not allow the formation of single phase ε'-Fe$_{2.2}$C when starting from the fully oxidized iron nanoparticles.

In this study, the previous HTFT work and abundant literature data on iron catalyst activation are applied to produce different iron carbides in order to compare their performance at steady state operation over 100 h. To demonstrate the intrinsic carbide performance, χ-Fe$_5$C$_2$ and ε'-Fe$_{2.2}$C phases are prepared from the same MOF-derived Fe@C catalysts using syngas activation and hydrogen reduction followed by low-temperature Fischer-Tropsch (LTFT) experiments. The catalyst phase during activation and LTFT is derived from *in situ* Mössbauer spectroscopy and the activation and LTFT experiments are carried out in parallel in fixed-bed reactor operation, both starting from catalysts produced by pyrolysis of the same MOF at 500 and 600 °C (hereafter Fe@C-500 and Fe@C-600, respectively). TEM analysis of the fresh and spent catalysts is performed to ensure proper structure-activity relations are obtained by maintaining nanoparticle dispersion. While this study does not aim to elucidate the active sites and intermediates present on the highly dynamic surface of the bulk carbide phases, it unequivocally demonstrates the effect of the carbide bulk phase on the activity and selectivity of the catalysts.

2. Experimental

Fe@C-500 and Fe@C-600 were synthesized by our earlier reported MOF mediated synthesis approach [42–44], where approximately 1.0 g of as-received Fe-BTC Basolite F300 was placed inside a crucible and subjected to pyrolysis at 500 or 600 °C for 8 h in a horizontally located quartz tubular reactor under a nitrogen gas hourly space velocity of 4.5 h^{-1}. The resulting nanoparticles were passivated in 5% oxygen in nitrogen at room temperature, however, they were extremely prone to oxidation, witnessed by a conversion over 92% of the reduced iron phase into maghemite (γ-Fe$_2$O$_3$). The following key experimental procedures are addressed in a concise manner to display the similarities in the characterization and testing. For full technical details, the reader is referred to the Supplementary material and references therein. The catalytic performance tests (Fig. S1) [45] and *in situ* Mössbauer experiments (Fig. S2) [44] were carried out in stainless steel tubular reactors of 4 mm and 15 mm internal diameter, respectively. The catalysts were pretreated either by atmospheric hydrogen reduction or pressurized syngas activation, denoted herein as reduction and carburization, respectively. Reduction comprises feeding pure hydrogen at an atmospheric pressure while ramping the temperature to 400 °C at a rate of 2 °C min^{-1}, allowing reduction for 3 h at a space velocity based on catalyst weight (*WHSV*) of approximately 90 dm$^3_{H2}$ g$_{Fe}^{-1}$ h^{-1}. The activated catalyst is cooled down to FTS reaction temperature of 230 °C under hydrogen flow. The pressure was subsequently increased to 20 bar, and carbon monoxide introduction followed during a period of 1 h to obtain a H$_2$/CO ratio of unity with a *WHSV* of 55 dm$^3_{H2/CO}$ g$_{Fe}^{-1}$ h^{-1}. Carburization comprises feeding equimolar syngas at 15 bar while ramping the temperature to 340 °C at a rate of 2 °C min^{-1}, effectively carburizing the catalyst for a period of 140 h at a *WHSV* of 120 dm$^3_{H2/CO}$ g$_{Fe}^{-1}$ h^{-1}. The activated catalyst is cooled down to FTS reaction temperature of 230 °C under syngas flow. The pressure was subsequently increased to 20 bar and the *WHSV* decreased to 55 dm$^3_{H2/CO}$ g$_{Fe}^{-1}$ h^{-1}. The weight hourly space velocities for activation and FTS were increased by a factor 2.0 for

Table 1
Fe@C catalyst characterization* after passivation; T_{pyro} denotes the pyrolysis temperature in °C.

T_{pyro}/°C	w_{Fe}/%	d_p/nm	γ-Fe$_2$O$_3$/%	Fe/C$_{surf}$/-	S_{BET}/m^2 g^{-1}	V_P/cm^3 g^{-1}
500	37.8	3.6	95	0.021	281	0.30
600	43.8	6.0	92	0.016	339	0.32

* Iron loading in wt% (w_{Fe}), average iron nanoparticle size (d_p), percentage of bulk iron oxide phase (γ-Fe$_2$O$_3$), iron to carbon ratio on the surface (Fe/C$_{surf}$), BET area (S_{BET}) and total pore volume (V_P) per gram of catalyst.