The importance of passivation in the study of iron Fischer–Tropsch catalysts

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In the study of iron catalysts, careful passivation is necessary for study of microstructure by ex situ analytical techniques. The passivation procedure used in our study consists of heating the sample in He at the reaction temperature, cooling to room temperature and introducing small amounts of O_2 (< 1%) in a flowing He stream. A properly passivated sample shows no more than a few nm of surface Fe_3O_4 on α-Fe, when examined in a high resolution TEM. Proper passivation is also characterized by an exotherm of no more than 2–3 K. We show that a Fischer–Tropsch catalyst carbided in CO will show substantial amounts of magnetite, if exposed to air without proper passivation. Such surface oxidation may cause errors in determining the relative amounts of the magnetite and carbide phases in Fischer–Tropsch catalysts, which are important for proper identification of the catalytically active phase.

Keywords: Fischer–Tropsch synthesis catalysts; Fe catalysts; passivation of high resolution transmission electron microscopy

The Fischer–Tropsch synthesis (FTS) for the production of liquid hydrocarbons from synthesis gas has become important as the planet faces exhaustion of its petroleum reserves in the near future. The use of coal to manufacture synthesis gas is attractive in view of its vast reserves. However, synthesis gas manufactured from coal typically has a low H_2/CO ratio (≈ 0.7) while the stoichiometry of the reaction requires an H_2/CO ratio ≈ 2.0. Iron catalysts can make up this deficit with their high water–gas shift activity. Furthermore, iron catalysts can synthesize fuel range liquid hydrocarbons at elevated pressures (10–15 atm). In recent years, there have been several studies attempting to characterize iron Fischer–Tropsch catalysts with a view to understanding the phase transformations in the catalyst as a result of exposure to various activation and reaction treatments, and to identify the active catalytic phase.

These catalysts are usually synthesized as hematite (α-Fe_2O_3) and must be subjected to an activation treatment before they become active for the Fischer–Tropsch synthesis. During the activation and subsequent reaction, several phases are known to coexist. These include metallic iron, iron oxides and iron carbides. The formation and distribution of these phases depends on the reaction conditions, reaction times and state of the catalyst (reduced/unreduced, supported/unsupported, etc.). In 1982, Teichner and co-workers [1,2] proposed that magnetite was the active phase. This assertion was questioned in 1986 by Dictor and Bell [3], who concluded that the active phase is a mixture of χ- and ε'-carbides and some metallic α-Fe. The debate over whether magnetite is the active phase has been revived in recent years by Kuivila et al. [4] who suggest that magnetite is the active phase. Their conclusion was based on the observation that the active catalyst shows magnetite on the surface, as detected by X-ray photoelectron spectroscopy (XPS), while Ar ion etching exposes carbide which they conclude must lie underneath the surface magnetite. The difficulties in identifying the active phase are further exemplified in a recent paper by Huang et al. [5] who found on the one hand that the magnetite catalyst was inactive when it was initially exposed to syngas. However, after the catalyst was activated in CO and reached its peak activity, magnetite was the only crystalline phase detected by X-ray diffraction (XRD). Therefore these authors concluded that while magnetite was not necessarily the active phase, the active phase may exist as a surface phase on the magnetite crystals.

Most of these studies involve the use of ex situ characterization techniques such as XRD, Mössbauer spectroscopy and XPS where the catalysts are exposed to air after removal from the reactor. If sufficient attention is not paid to passivating the catalyst carefully before removal from the reactor, the active phase of the iron could get oxidized. As we show in this note, lack of adequate passivation can cause transformation of the carbide phase to magnetite leaving magnetite as the only detectable phase in the catalyst.

The details of the experimental procedures and characterization equipment are given elsewhere [6]. We have used a binderless, precipitated iron catalyst that was obtained from the Department of Energy, Pittsburgh

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Energy Technology Center (PETC). The catalyst is spray-dried Fe_2O_3–CuO–K_2O prepared by United Catalysts Incorporated [6,7]. Activation and reaction studies were performed in a differential fixed-bed reactor with product analysis done using a Varian 3400 gas chromatograph. Several characterization techniques were employed to study the catalyst. These included high resolution transmission electron microscopy (HRTEM), XRD, XPS and elemental analysis. In order to passivate the catalyst, the sample was purged in He at the reaction temperature and cooled to room temperature. A very small amount of O_2 was introduced in the flowing He (< 1% O_2 in He). The passivation of the catalyst was marked by the appearance of a small exotherm, typically 2–3 K. After the exotherm died down, the O_2 content was gradually increased to a final concentration of 20% O_2 in He in order to simulate atmospheric conditions. If the passivation was done correctly, the increase in O_2 content did not lead to any further rise in temperature. At the end of this step, it was safe to pull out the catalyst out of the reactor for subsequent characterization. Fig. 1 shows a transmission electron micrograph of a sample activated in CO (space velocity 4000 h^{-1}) at 543 K for a period of 10 h and examined after careful passivation as described above. The carbide phase is clearly visible on the catalyst surface as well as in the bulk. The phase is identified from its lattice fringes ~ 2 Å, seen clearly in fig. 2, its X-ray diffraction pattern [6] and also by XPS (after the surface carbon is etched away) [7]. While the 2 Å fringes, by themselves, do not uniquely identify the carbide phase, it is a combination of the characterization techniques that lead us to conclude that the particles shown in fig. 2 are iron carbide crystallites. The magnetite phase (which also has a 2 Å lattice plane) starts off with larger crystals giving spot patterns whereas the carbide being smaller in size ends up giving ring patterns. The ring patterns arise from the randomly oriented particles present within the region whose diffraction pattern is obtained. Furthermore, when the sample transforms completely into the carbide, a diffuse ring at ~ 2 Å is seen which is consistent with the diffraction patterns reported in the JCPDS data base for iron carbide. The combination of TEM evidence as well as that from XRD and XPS makes the identification of these particles unambiguous.

Figs. 1 and 2 show that the iron carbide particles are always surrounded by a film of carbon. When the samples were carefully passivated, this carbon overlayer served to protect the underlying carbide and no magnetite was detected in conjunction with the carbide phase. The inset diffraction pattern in fig. 1 shows a prominent ring corresponding to the carbide phase, as well as spots corresponding to magnetite which remained unconverted. The diffraction pattern of fig. 2 shows spots cor-

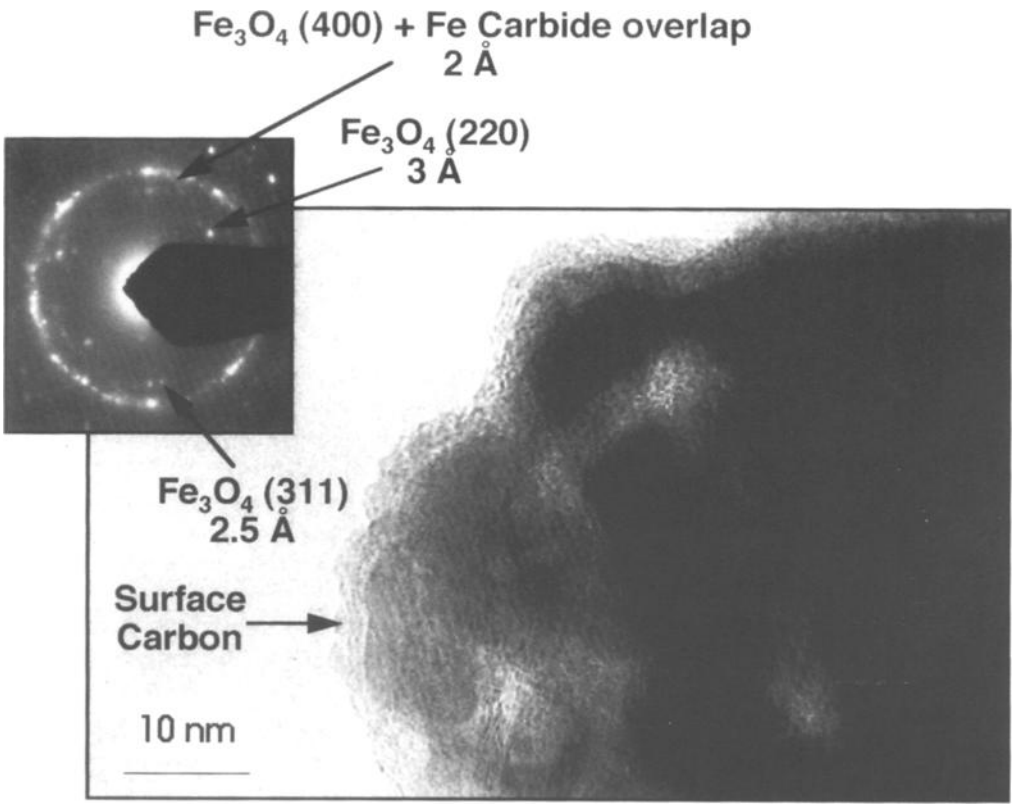

Fig. 1. Transmission electron micrograph of a commercial iron catalyst activated in CO at 543 K for 10 h and examined after careful passivation. The carbide particles are surrounded by a film of carbon. The inset diffraction pattern shows a strong ring from iron carbide. Spots corresponding to magnetite, which remained unconverted, are also seen.

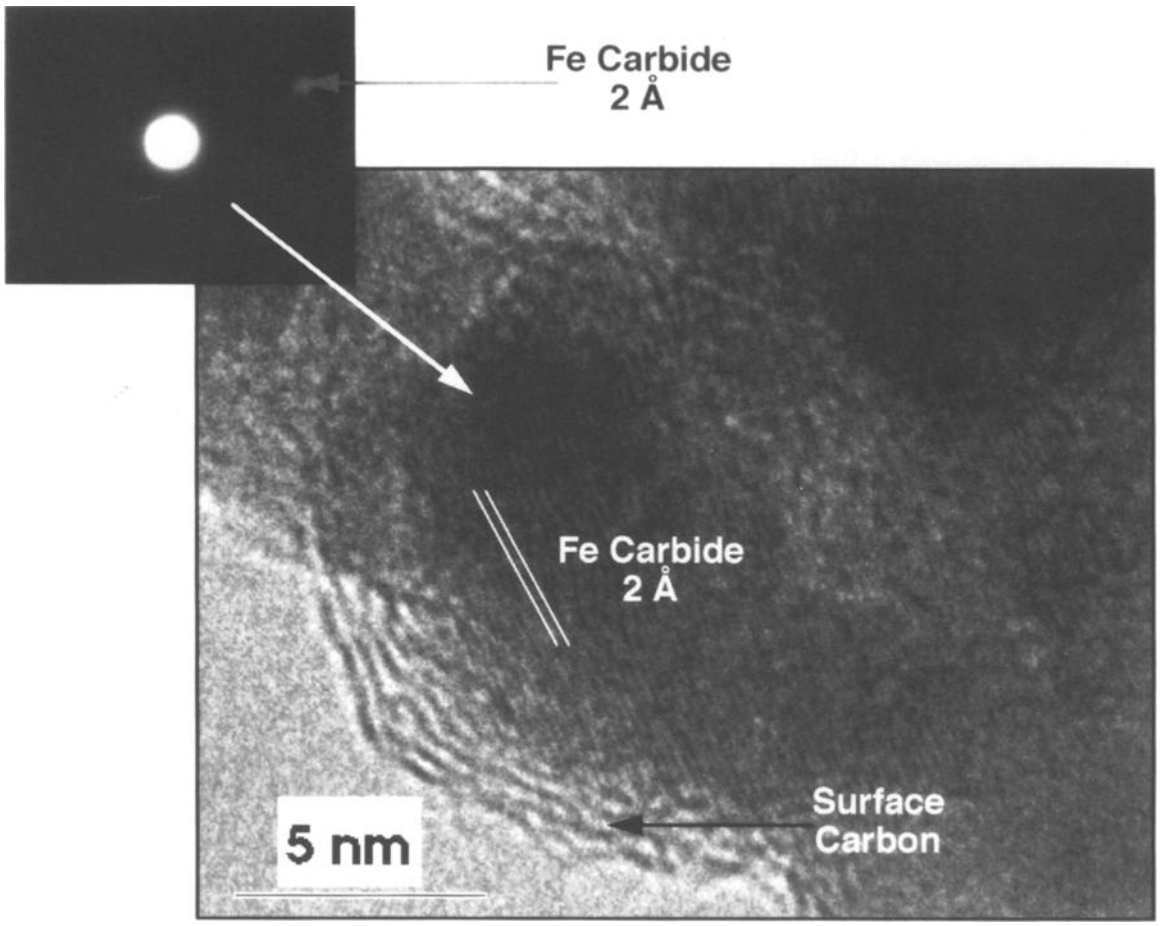

Fig. 2. High resolution transmission electron micrograph of a commercial iron catalyst activated in CO at 543 K for 10 h and examined after careful passivation. Lattice fringes of iron carbide and the accompanying layer of surface carbon are clearly seen. The inset diffraction pattern shows spots corresponding to iron carbide.

responding to iron carbide. This is in contrast to the microstructure of a catalyst sample treated under identical conditions but removed from the reactor without careful passivation. In this case, the sample was cooled to room temperature, flushed in He and then exposed to the ambient atmosphere. Fig. 3 shows that the catalyst surface in this case consists almost entirely of magnetite. Some iron carbide embedded in the core of magnetite particles is visible. Further evidence of this is seen in the high resolution image of fig. 4 showing lattice fringes corresponding to magnetite and carbide. In this case, the surface magnetite is clearly visible. The inset diffraction patterns in both figs. 3 and 4 show extremely strong spots corresponding to magnetite and a very weak ring of polycrystalline iron carbide. This suggests that oxidation of iron carbide to magnetite has occurred as a result of atmospheric exposure.

As a further test of the efficacy of our passivation procedure, we reduced a catalyst sample to metallic Fe using flowing H_2 (space velocity 4000 h^{-1}) at 723 K for 15 h. In this case, after transferring the sample to the microscope in air, we can see a thin skin of magnetite on the surface of the α-Fe particles (fig. 5). The inset high resolution image shows lattice fringes corresponding to magnetite. This microstructure was stable over time suggesting that further oxidation of the α-Fe was slow. In contrast, if we were to flush the reactor with He and expose this catalyst to ambient air, the sample would be pyrophoric.

We have used the passivation procedure described here to investigate the effect of activation and reaction conditions on the precipitated iron catalyst. These observations [6,7] help explain some of the controversies over the origin of the active phase discussed earlier in this paper. For example, since the carbide phase is invariably covered by carbonaceous films while the magnetite is not, it is clear why XPS of the working catalyst detects only the magnetite phase. Only after Ar etching is the carbide phase detected, in agreement with the observations of Kuivila et al. [4]. In our work [6,7], we also found that if one starts with large crystals of Fe_2O_3 ($\sim$0.1–1.0 μm) that transform into Fe_3O_4, the carbide particles that form upon activation are much smaller in diameter (typically 0.02–0.03 μm). The XRD peaks from the carbide particles suffer from particle size induced line broadening, making them difficult to detect amidst the

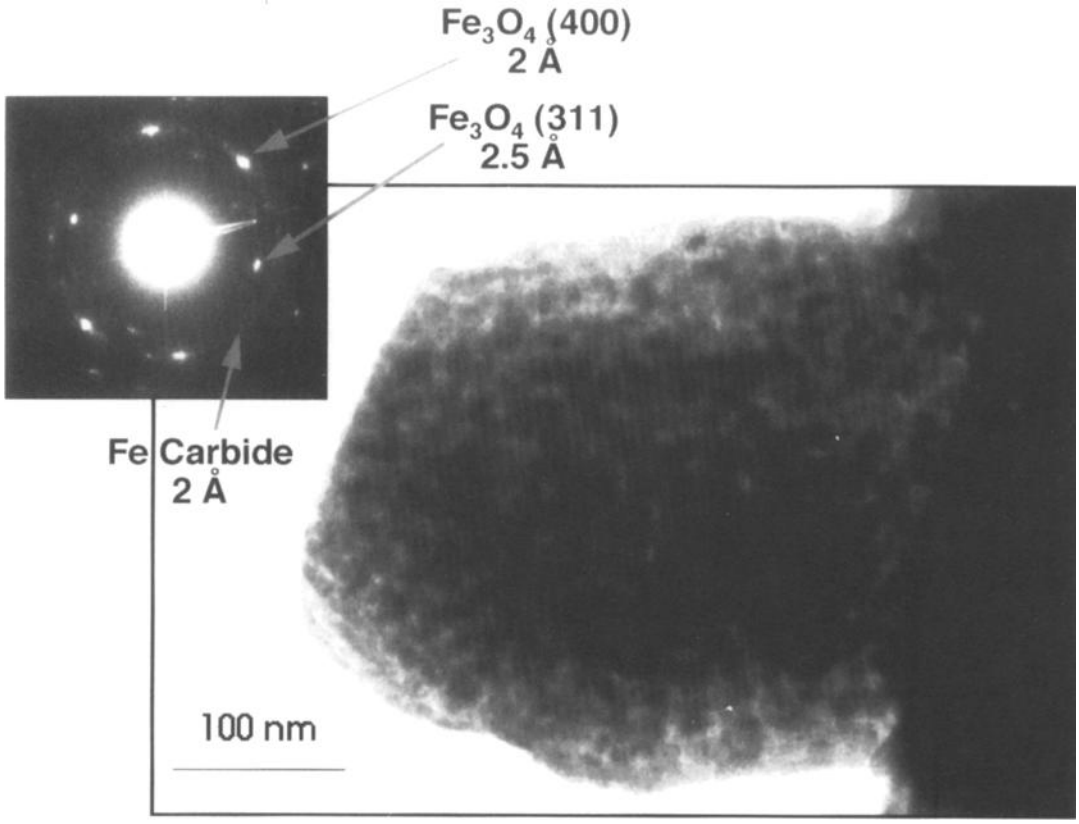

Fig. 3. Transmission electron micrograph of a commercial iron catalyst activated in CO at 543 K for 10 h and examined without proper passivation. The surface is almost entirely magnetite. Some bulk carbide is also seen. The inset diffraction pattern shows strong spots corresponding to magnetite and a very faint ring of iron carbide.

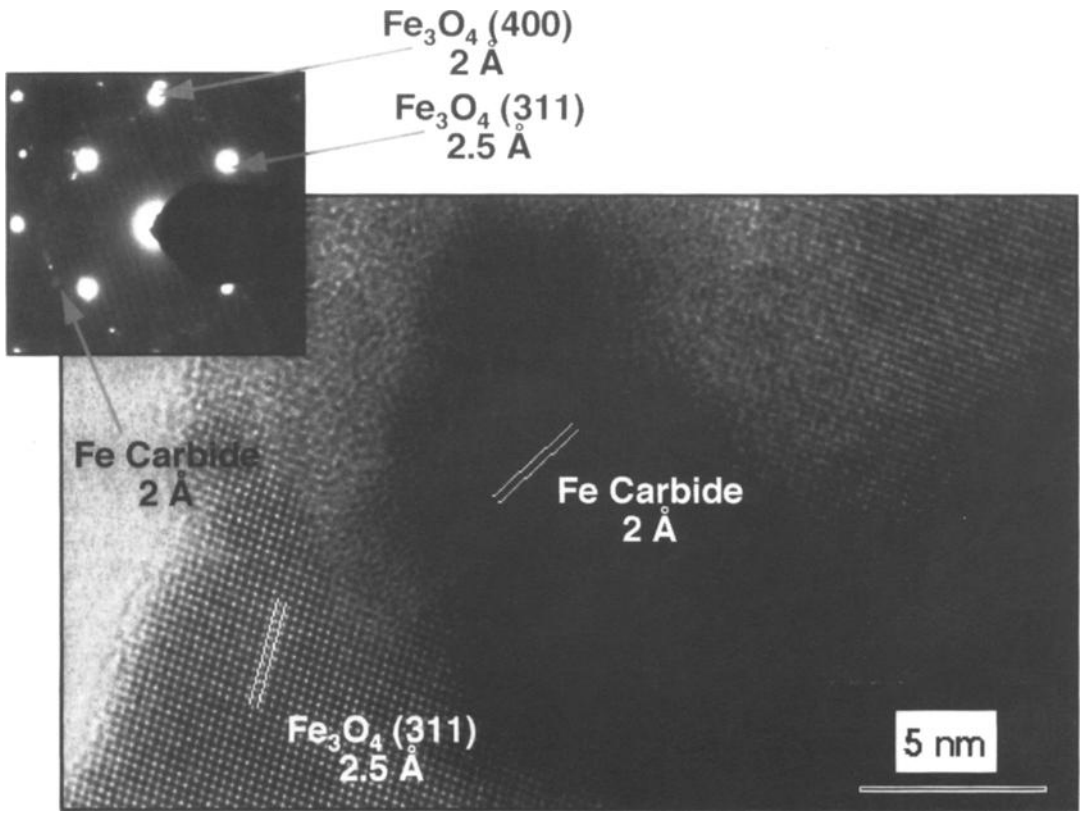

Fig. 4. High resolution transmission electron micrograph of a commercial iron catalyst activated in CO at 543 K for 10 h and examined without proper passivation. Magnetite fringes are clearly seen on the surface. Some bulk carbide is also seen. The inset diffraction pattern shows strong spots corresponding to magnetite and a very faint ring of iron carbide.

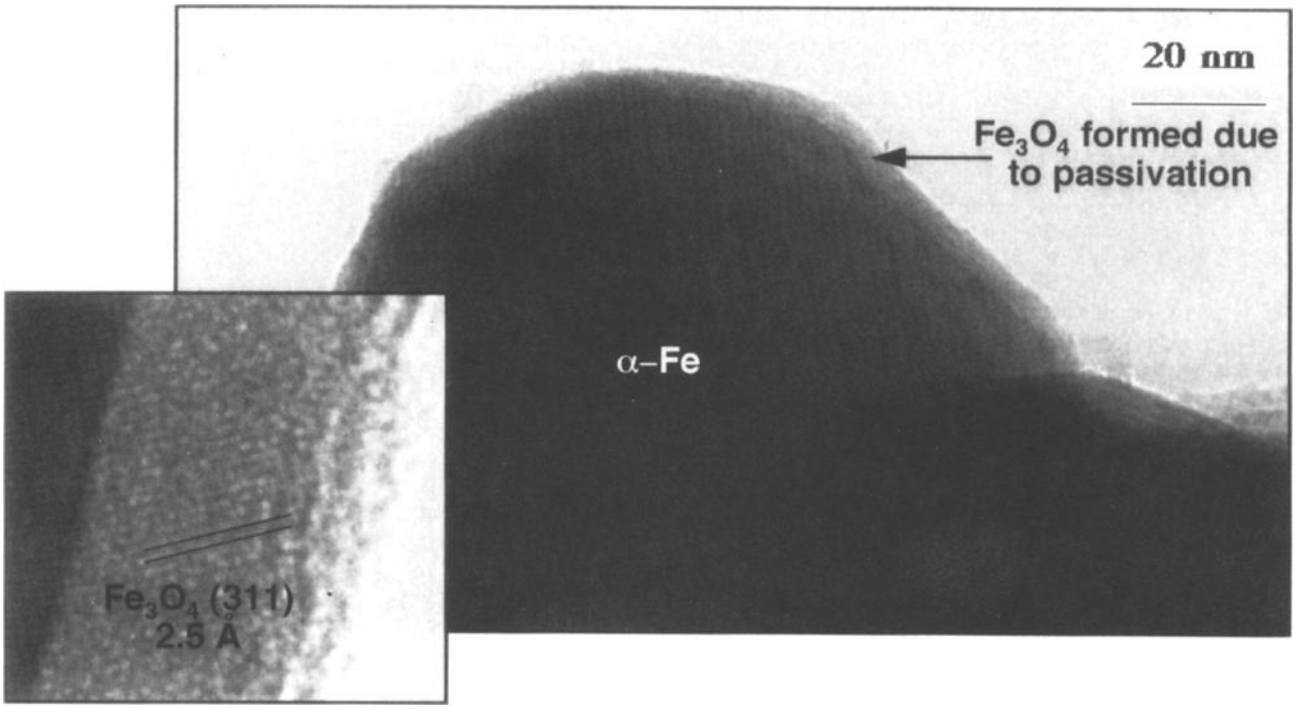

Fig. 5. Transmission electron micrograph of a commercial iron catalyst activated in H_2 at 723 K for 15 h and examined after careful passivation. The bulk is metallic iron with a thin skin of surface magnetite formed as a result of highly controlled passivation. The inset high resolution image shows magnetite lattice fringes in the surface layer.

larger and more crystalline magnetite particles. This may explain the observation of Huang et al. [5] who found that magnetite was the only crystalline phase detected on the active catalyst. Of course, as shown in this paper, it is important to perform careful passivation to be able to determine the amounts of magnetite and other phases in a working catalyst. Furthermore, when the catalyst is operated at high conversions, the high partial pressures of H_2O and/or CO_2 may transform the iron carbide back into magnetite. The importance of such a transformation on the activity and selectivity of precipitated iron catalysts is being studied in our laboratory at present.

While we have proposed a reliable method of passivation in this work, there have been other methods proposed in literature. These include the use of a CO_2/Ar mixture for passivation [8,9] and the use of a Parlodoin film to embed iron particles in order to passivate them [10]. The latter method, while effective, may be unsuitable for high resolution TEM imaging since it would degrade the resolution and make it impossible to observe the surfaces of the metal particles.

In summary, we have shown that proper passivation is essential in order to obtain a true measure of the relative amounts of magnetite and carbide in a working FT catalyst. When properly passivated, FT catalysts transform into carbide particles that are covered by amorphous carbonaceous layers. The presence of these carbonaceous overlayers on the carbide particles may affect the results of surface characterization techniques like XPS for quantifying the amount of the carbide phase. The different sizes of the magnetite crystals and the carbide crystallites that form from them can further complicate the interpretation of X-ray diffraction spectra obtained from these catalysts. These factors may have been responsible for some of the controversy surrounding the microstructural transformations in the catalyst during Fischer–Tropsch synthesis and the nature of the active phase.

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