Appendix C

PHASE TRANSFORMATIONS IN IRON FISCHER-TROPSCH SYNTHESIS (FTS) CATALYSTS

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Iron Fischer-Tropsch synthesis (FTS) catalysts are in the form of Fe_2O_3 as prepared. After activation in H_2 or CO and introduction into the FTS reactor, the catalyst is known to consist of a mixture of iron oxide, reduced iron and carbide phases (**1**). Previous work has relied on Mössbauer spectroscopy and X-ray diffraction to characterize the phase composition of iron FTS catalysts. These techniques provide information averaged over the sample, and both techniques have difficulty analyzing highly dispersed iron phases having particles less than 5 nm in size (**2,3**). This has made it difficult to establish the relationship between specific iron phases and overall FTS reactivity (**1-4**). The active phase(s) responsible for the FTS activity of iron FTS catalysts is still unknown and remains a subject of intense debate and discussion.

Transmission electron microscopy (TEM) allows a study of the spatial distribution and morphology of the various iron phases present in the working catalyst. The difficulty in applying TEM arises because the FTS catalyst is present at a loading of only 5 wt% in a hydrocarbon wax

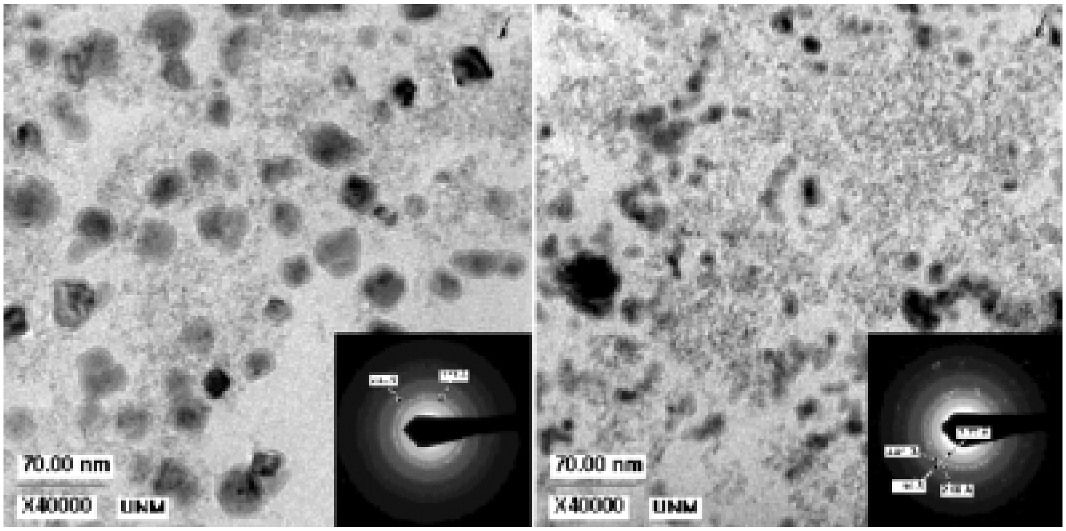

Figure 1 TEM pictures of SA0706 show phase transformations in the iron carbides in the reaction environment. A) After CO activation the catalyst contains particles of χ-carbide [$(CO+H_2)$ conversion = 36.1%]. b) After use for 113 hours for F-T-S at a H_2/CO ratio of 0.67 and a pressure of 100 psig, the χ-carbide has transformed into smaller particles of the ϵ'-carbide with a dramatic increase in activity [$(CO+H_2)$ conversion = 77.9%].

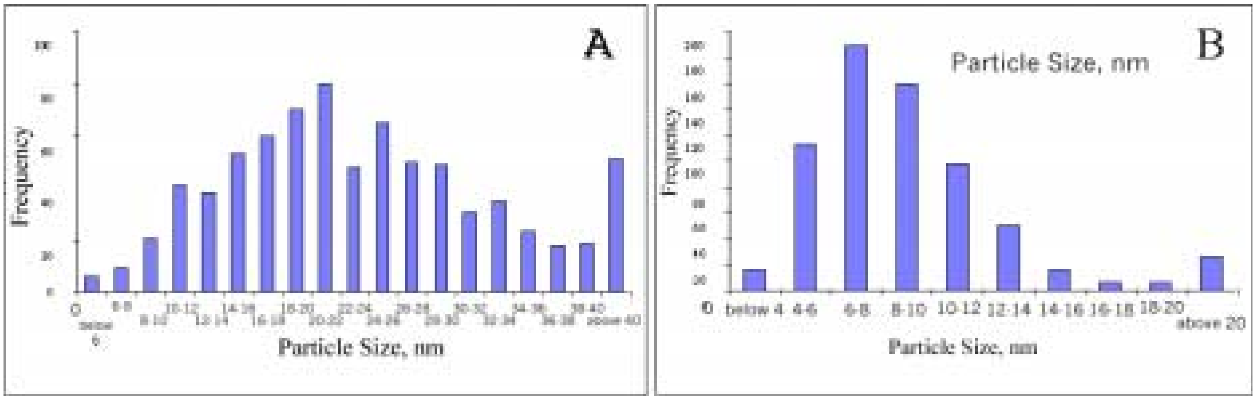

Figure 2 The particle size distribution of the iron carbides seen A) after initial activation TOS= 0 hour and B) after reaction for TOS=113 hours. The χ-carbide particles have broken up into smaller ϵ'-carbide particles, causing an increase in reactivity for FTS.

of high molecular weight. The wax must first be removed by a process called Soxhlet extraction. We have recently (**5**) shown that removal of the wax can lead to catalyst oxidation, either during the hot extraction process or during subsequent air exposure. To analyze the catalyst while it is still embedded in the wax, we have used ultramicrotomy to prepare thin sections of the catalyst. In this paper, we describe the nature of phase transformations that occur during activation and as the catalyst is used for F-T synthesis. The samples analyzed here were prepared at Texas A&M University (**6**) and were used for F-T synthesis in a medium pressure stirred tank reactor. At various times on stream, a sample of the catalyst was removed under a protective inert blanket. The phase composition of these catalysts was studied by Quantitative Rietveld Structure Refinement (**5**).

Figures 1 shows a cross-section TEM image of the catalyst from run SA-0706 at time on stream TOS = 0 hour, and after use in the F-T synthesis reaction (TOS = 113 hours). After activation for 8 hours at 280 ºC in CO, the catalyst has transformed into well defined particles of χ-carbide which is dispersed over a matrix that contains amorphous silica and unreduced iron oxides. During reaction, the χ-carbide transforms into ϵ'-carbide with a break up into smaller particles (see particle size distribution in Fig. 2) and a change in phase. The smaller particles in Fig. 1B can be indexed to the ϵ'-carbide phase based on their lattice fringes of 2.0 Å and from the diffraction pattern (see inset). These phase transformations are key to understanding the remarkable increase in catalyst activity seen on this catalyst over this period.

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6. We thank Prof. Dragomir Bukur of Texas A&M University for providing these samples, which were prepared as a part of a larger program devoted to synthesis of Fe F-T catalysts.
7. Financial support for this work was provided by the US DOE grant DE-FG22-95PC95210