

Characterization of Iron Fischer-Tropsch Catalysts

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Abstract

Iron Fischer-Tropsch catalysts developed for slurry reactor processes were characterized using x-ray diffraction. As we show in this paper, iron catalysts are very reactive and can undergo oxidation during sample removal from the slurry reactor, as well as during sample processing, before analysis. This complicates considerably the determination of the phase composition of a working catalyst. Our results show that soxhlet extraction, a technique commonly used for preparation of Fe catalysts, may be unsuitable, since it appears to cause extensive oxidation of the catalyst. A second conclusion is that when the hot wax is removed from the slurry reactor, one should take care to prevent exposure of the hot wax to the ambient atmosphere, since this may cause transformations in the catalytically active constituents. When catalyst samples in the F-T wax were studied by x-ray diffraction, we observed the presence of an α -Fe peak, even in catalysts that were pretreated entirely in CO before syngas reaction.

Introduction

Fe Fischer-Tropsch catalysts are of considerable interest in the conversion of coal-derived syngas to liquid fuels ⁽¹⁾. These catalysts start off as the hematite (Fe_2O_3) phase which transforms to a mixture of iron oxide and iron carbide phases during reaction ⁽²⁾. However, there is still some debate about the nature of the catalytically active phase. While it is recognized that iron carbides are formed during activation in CO and during reaction, the presence of iron carbides is not sufficient to ensure high activity, and as shown in this study, catalysts that contain almost all carbide can also deactivate rapidly on stream. Hence, we felt it was important to perform a study of the phase composition of Fe Fischer-Tropsch catalysts. Besides helping to determine the nature of the catalytically active phase, this work could help shed light on the origins of catalyst deactivation.

The need for careful passivation of iron F-T catalysts has been reported by us previously ⁽³⁾. If the catalysts are not handled carefully, considerable oxidation occurs making it impossible to accurately determine the relative amounts of the reduced and oxidic iron species. In the previous study ⁽³⁾, we developed suitable passivation procedures for fixed bed, unsupported catalysts that resulted in a surface oxide film only a few nm thick. If the passivation was not done carefully, significant transformation to magnetite, Fe_3O_4 , occurred.

When working with catalysts in a slurry reactor, an additional complication is that the catalyst is suspended in a hydrocarbon (HC) oil (MW ~28 to ~40), which is replaced by the waxy liquid products of FT synthesis, as the reaction proceeds. The first step in the analysis procedure requires removal of the catalyst in the hot wax while the reactor is operating. Subsequent steps in the analysis are shown schematically in figure 1. In this work, we have studied the consequences of various catalyst removal and processing steps on the microstructure of the Fe catalysts using x-ray diffraction. Catalyst handling steps that cause major changes in microstructure are indicated on this

Methods of Sample Removal and Analysis: Results

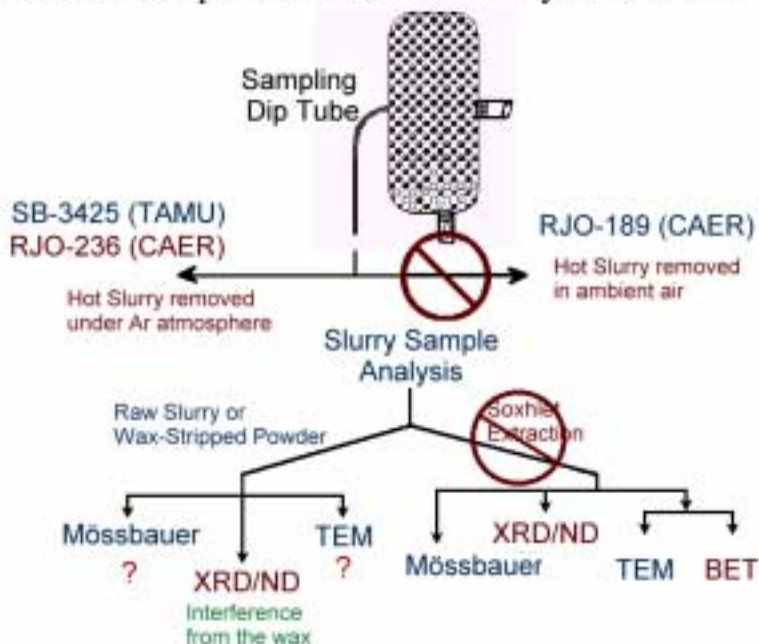


Figure 1 Schematic of various characterization methods

figure and the work that led to this conclusion in described in more detail in this report. For the purposes of this study, we examined catalysts removed as a function of time on stream from reactor runs performed at the Center for Applied Energy Research (CAER) as well as at Texas A&M

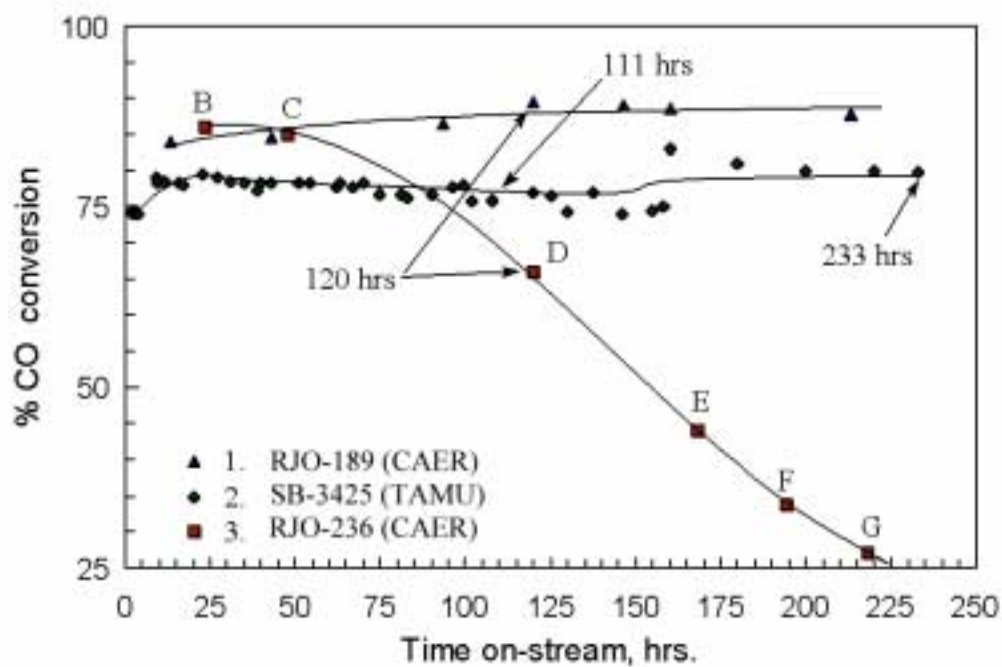


Figure 2 Activity profiles for various FTS runs (slurry bubble column reactor)

university (TAMU).

Figure 2 shows the reactivity in terms of %CO conversion vs. time on-stream for the three runs which we analyzed. One of the runs, RJO-189, was continued well beyond the time shown in this plot, while the other two were shorter in duration. The catalyst compositions and pretreatment for each were as follows:

- RJO-189: 100 Fe/2.6 Cu/1.0 K/4.4 Si; pretreated in H₂ at 1.39 MPa and 220°C, overnight (CAER),
- SB-3425: 100 Fe/3.0 Cu/4.0 K/16.0 Si; pretreated in H₂ at 1.48 MPa and 250°C, 4 hours (TAMU), and
- RJO-236: 100 Fe/0.0 Cu/.71 K/0.0 Si, pretreated in CO, 270°C, ~13.1 MPa, overnight (CAER).

It can be seen that despite differing activation conditions, all three of the runs show similar activities initially, but the two runs involving catalysts reduced in H₂ show greater long-term stability. It should also be pointed out that the third catalyst, which deactivated rather rapidly, did not contain any Si while the other runs contained varying amounts. Figures 3, 4, and 5 illustrate the XRD patterns for samples removed during the course of runs RJO-189 (CAER), SB-3425 (TAMU), and RJO-236 (CAER). Despite similar activity behavior at short times on stream, the

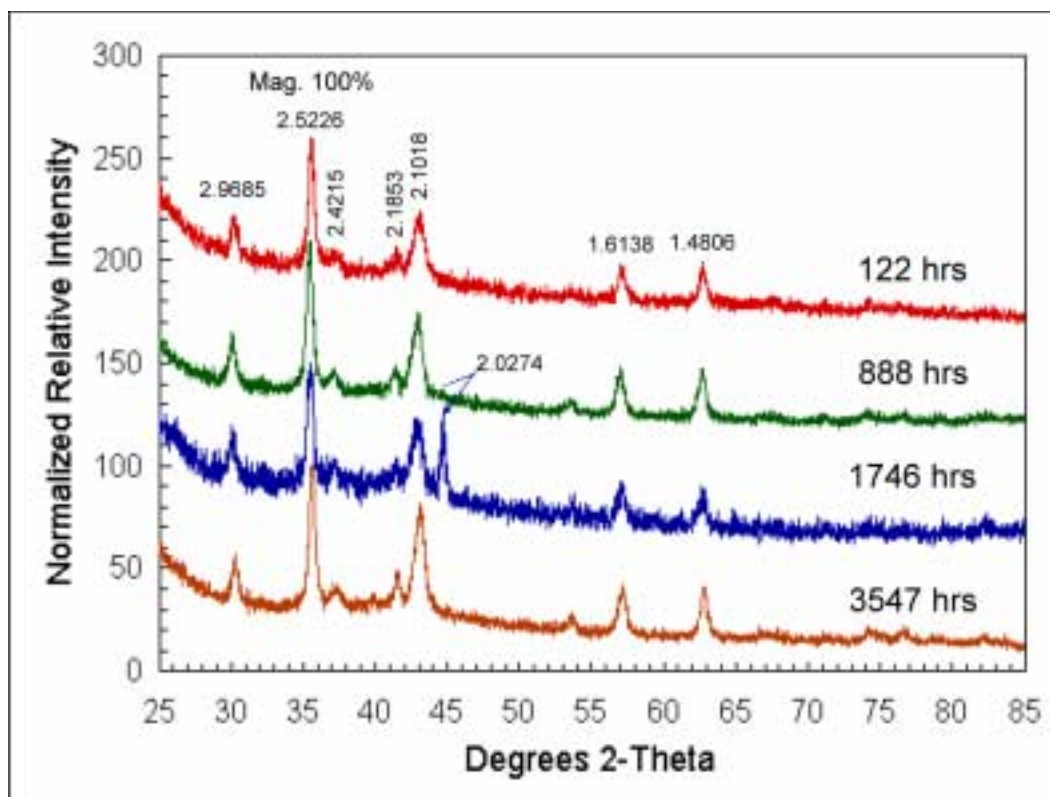


Figure 3 XRD patterns for catalysts (in wax) from CAER run RJO-189 (including end-of-run)

catalyst XRD patterns are remarkably different.

The samples which comprise CAER run RJO-189 (figure 3), were discharged from the working reactor under ambient atmosphere. The XRD profiles show significant amounts of magnetite, Fe_3O_4 (at 30° , 35.42° , 43.42° 2θ), and what is known as the χ -carbide, Fe_5C_2 or $\text{Fe}_{2.5}\text{C}$ (present as very small peaks between 38° and 43.3°). This is in contrast with the TAMU run, SB-3425, and CAER run RJO-236 (figures 4 and 5, respectively), which were discharged under inert, blanketing atmosphere and show no discernable magnetite. Both runs show the presence of significant amounts of α -Fe and iron carbide.

It should be noted that in figure 6, we show XRD patterns for catalyst slurry samples removed from these three runs at a time on-stream where the overall conversion was similar. The reduction temperature for run RJO-189 was lower than that for run SB-3425, and hence some of the magnetite present may represent unreduced material from the Fe catalyst precursor. Or, differences in the activation treatment for runs RJO-189 and RJO-236 may have resulted in the significant amount of crystalline magnetite, with relatively large particle size, observed in RJO-189. However, it is evident that in cases where the catalyst is discharged under inert (SB-3425 and RJO-236), there is clearly some α -Fe present, as represented by the 100% α -Fe peak at 44.8° , and, that under working conditions, FT slurry reactor catalysts do not contain any magnetite that is visible by XRD. We therefore conclude that removal of hot slurry, consisting of catalyst and wax product, under an inert blanketing atmosphere is essential to preservation of the catalyst microstructure.

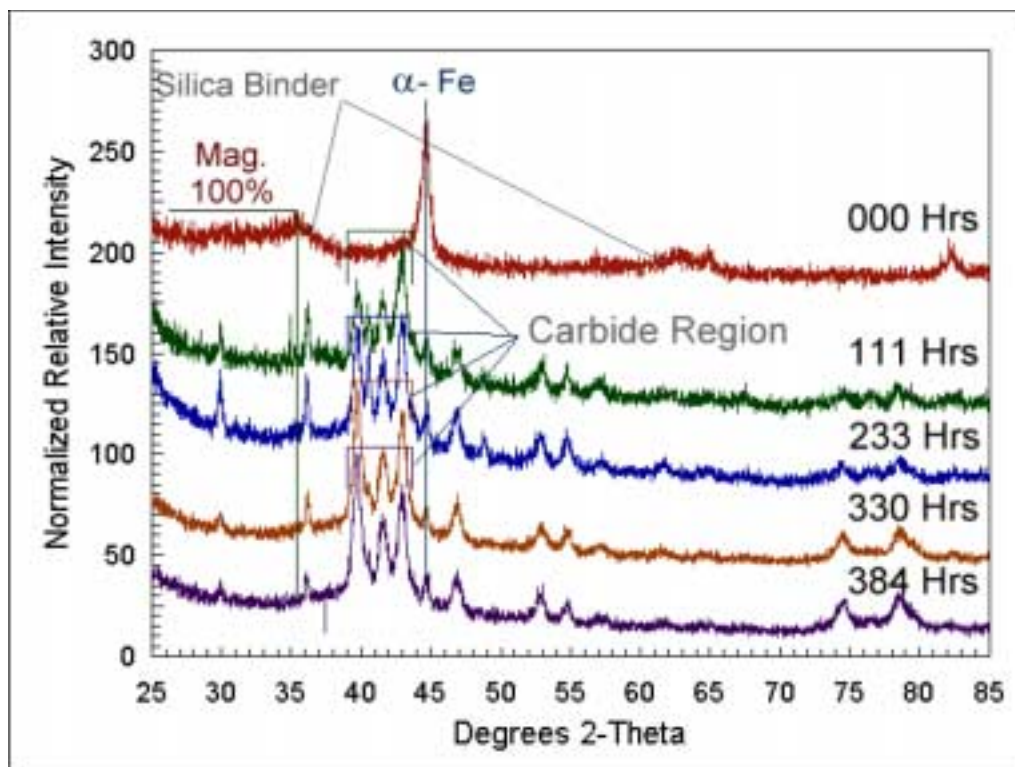


Figure 4 XRD patterns for catalysts (in wax) for TAMU run SB-3425 (including end-of-run)

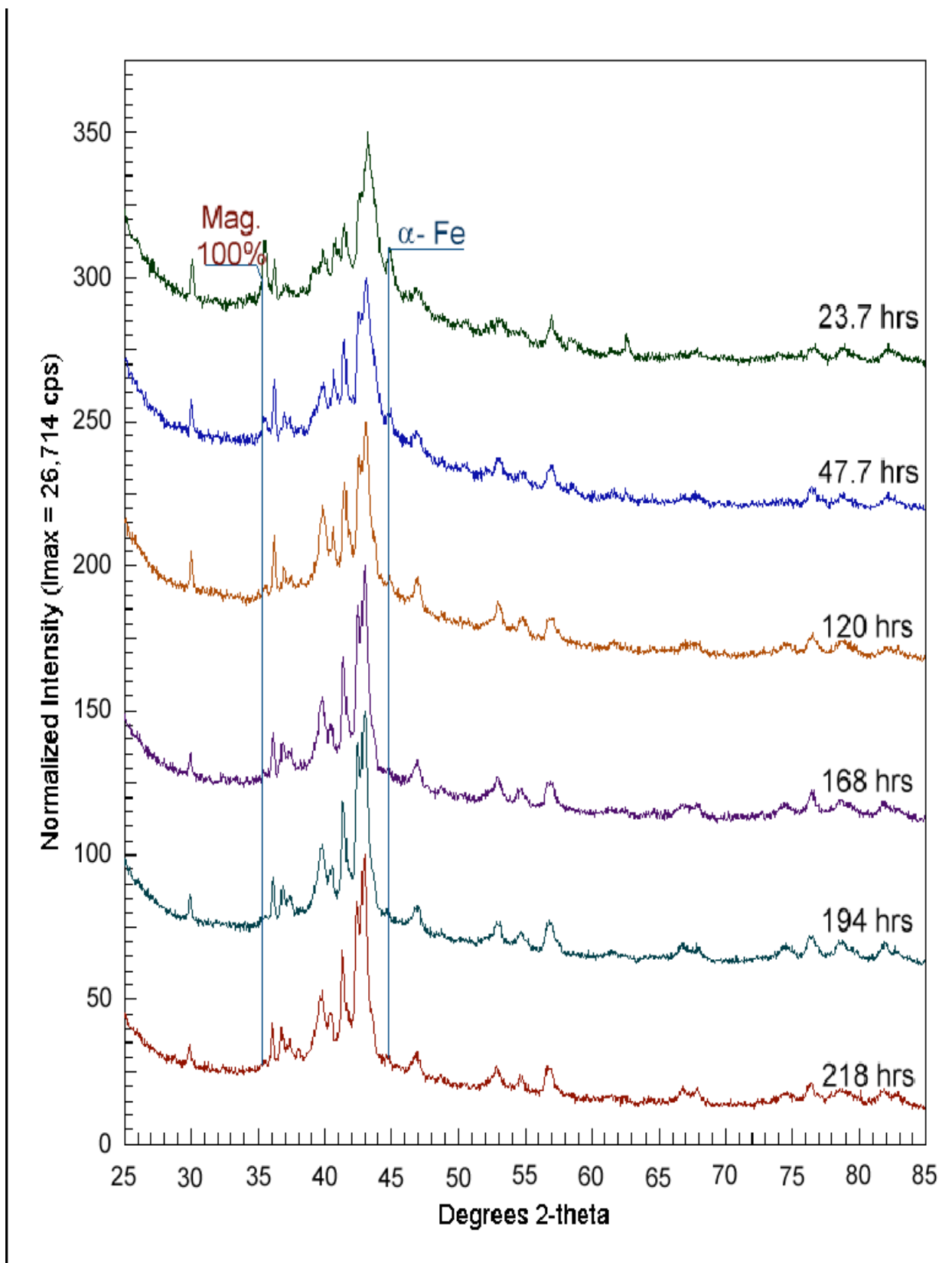


Figure 5 XRD patterns for catalysts (in the wax) for CAER run RJO-236 (including end-of-run)

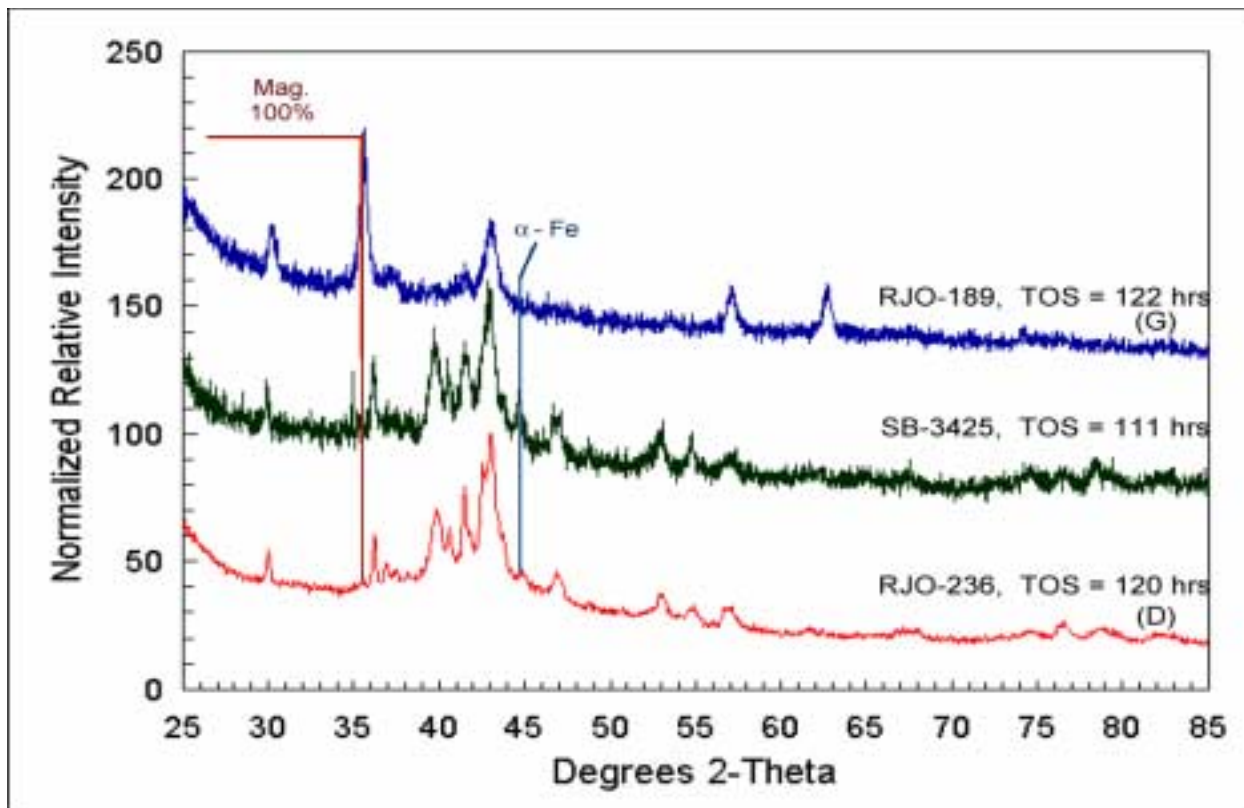


Figure 6 XRD patterns of slurry samples from 3 runs, at comparable time on-stream

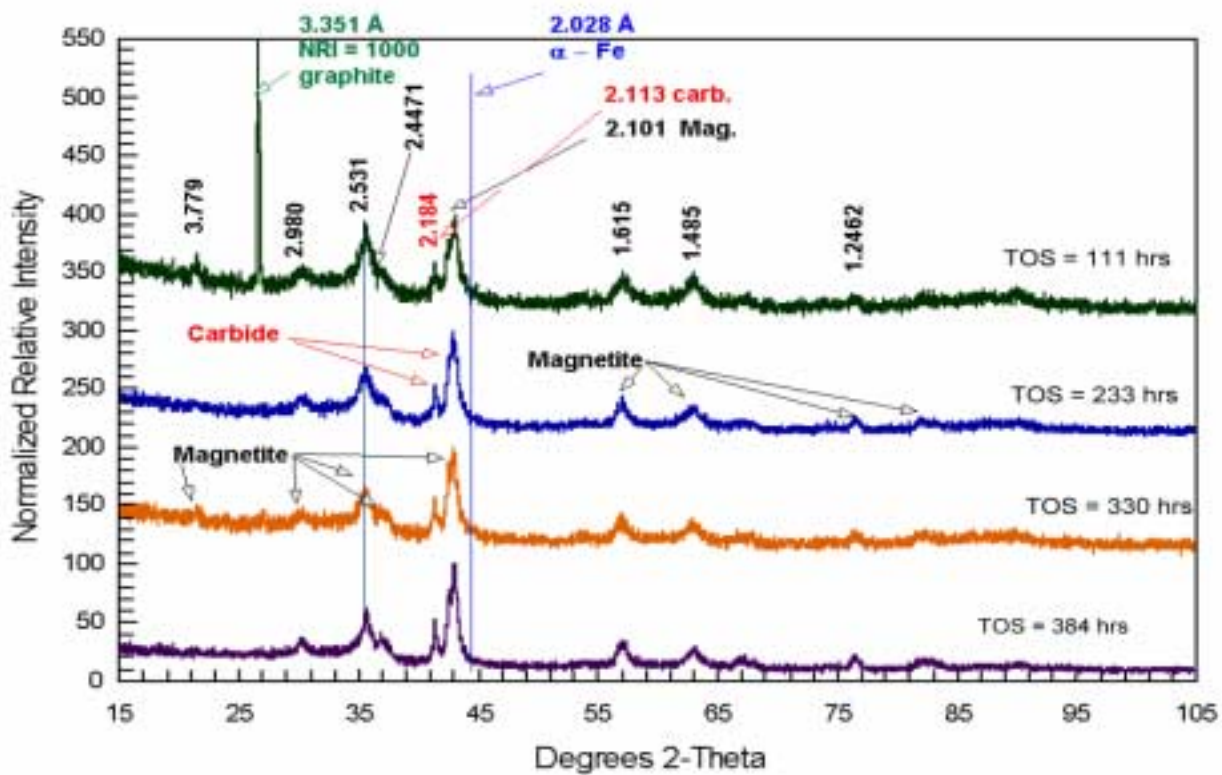


Figure 7 Soxhlet-extracted samples from TAMU series SB-3425 (including end-of-run)

Further examination of figures 3, 4, and 5 will lead one to conclude that there is no conversion from reduced iron species into magnetite during the course of the run, at least as seen by XRD. However, these catalysts are being analyzed in the wax product matrix, which is of high molecular weight, and could be highly crystalline. That raises a new question - could the wax exhibit a diffraction pattern that interferes with the overall diffraction profile of the catalyst slurry? In order to answer that question, it would be necessary to analyze the wax product, free of the catalyst. The most common procedure used for removal of the wax is soxhlet extraction of the slurry, using a suitable solvent.

Figure 7 shows the same catalyst samples as shown in figure 4, but after soxhlet extraction. Four samples, taken at times on-stream of 111, 233, 330, and 384 (end-of run) hours, are shown. All four samples show significant amounts of Fe_3O_4 and $\chi\text{-Fe}_{2.5}\text{C}$. It would appear that the extraction process somehow induces oxidation of the iron phases.

Comparison of an extracted TAMU sample at 111 hours to a comparable sample from run RJO-189, in wax, at time on-stream of 122 hours (figure 8), shows that the samples are remarkably similar in phase composition, the major differences being the particle size. The magnetite from SB-3425 appear to be of smaller particle size (or poorly crystallized) than the magnetite in RJO-189. Note that SB-3425 in unprocessed slurry shows no magnetite at all. This provides support for the conclusion that oxidation of catalyst in the hot slurry can occur, when it is removed under an oxygen-containing atmosphere.

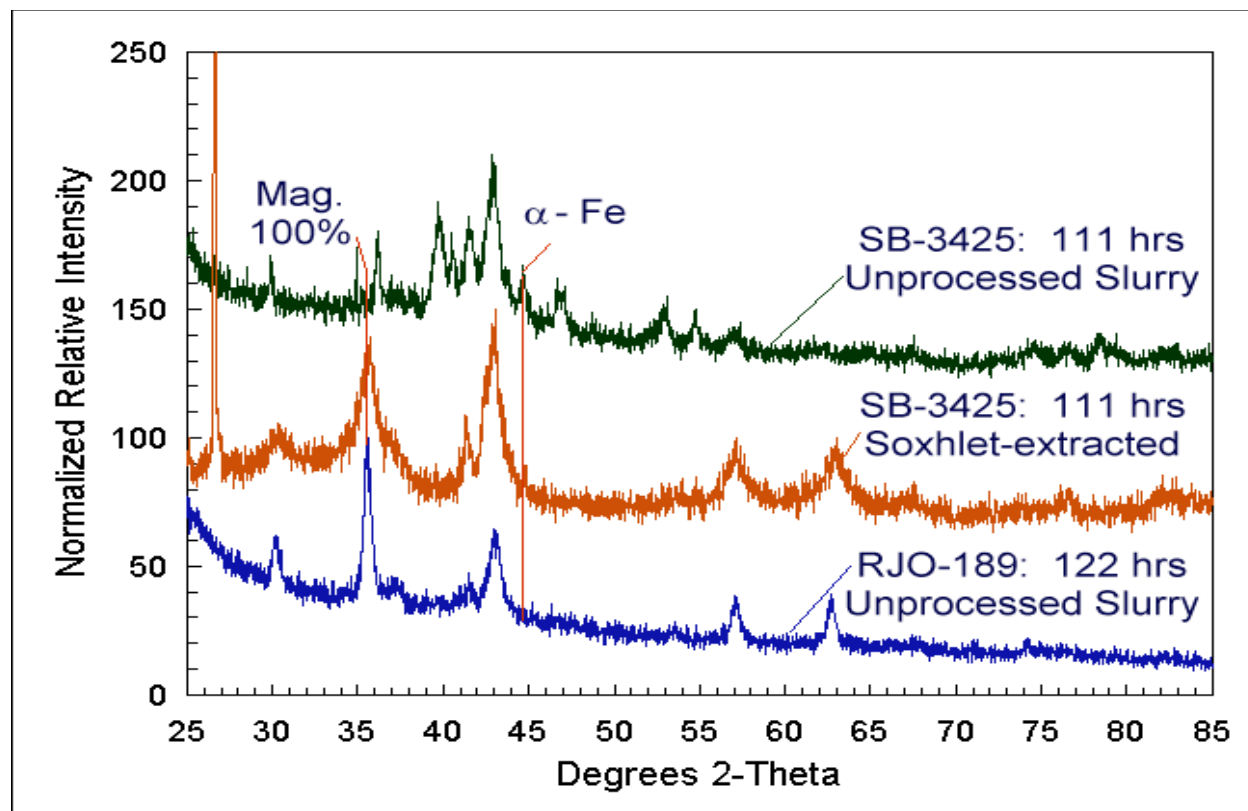


Figure 8 Comparison of TAMU Soxhlet-extracted sample to TAMU slurry removed under Argon and to CAER slurry removed in air

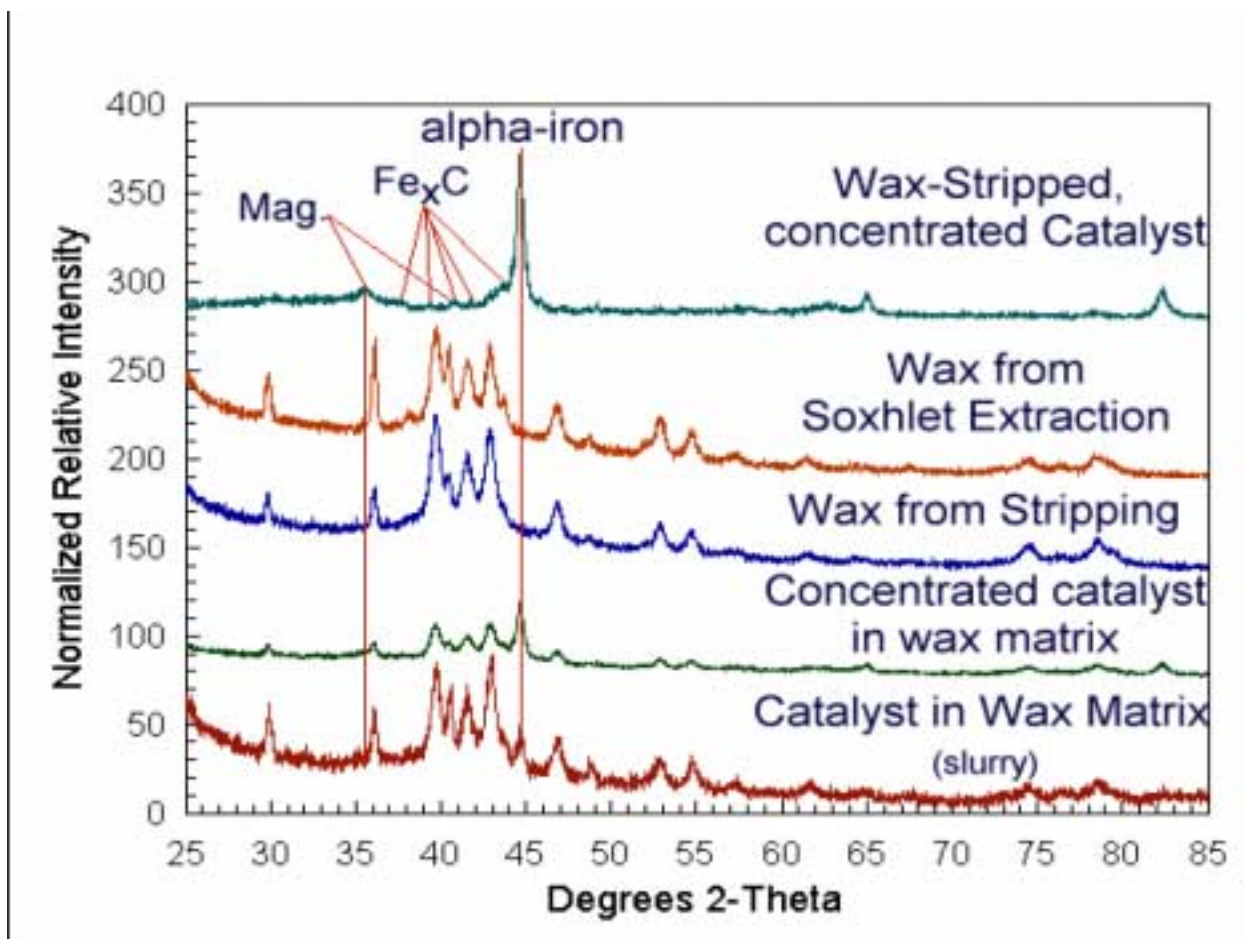


Figure 9 XRD patterns illustrating the effects due to wax interference, and effect of successive concentration of catalyst

When the soxhlet-extracted sample from SB-3425 is compared to the original slurry, at the same TOS (figure 8), it can be seen that, after extraction, there appears to be much more magnetite present than is seen in the wax matrix. This provides support for the conclusion that soxhlet extraction of samples changes the composition of the catalyst contained in the slurry. Therefore we conclude that soxhlet extraction of the slurry (to produce a “clean” powder) leads to oxidation of the catalyst and hence is unsuitable.

We now return to the examination of the slurry samples, and the effect of the wax on the slurry diffraction profile. We also study the powder produced by an alternative method of wax removal, which does not involve hot solvent. A TAMU catalyst sample was stripped of its wax under flowing inert at 260°C. The resulting powder and wax, the original slurry, and a sample, concentrated by warming the same slurry and allowing the catalyst particles to settle, at TOS = 233 hrs., are shown in figure 9. This pattern shows conclusively that the wax and catalyst peaks can overlap in the diffraction pattern, especially when the wax is high molecular weight (lots of long-range order), and that the major difference between the diffraction patterns appears to be the presence of α -Fe, and a small amount of iron carbide. One can infer, also, that the stripping method produces a consistent set of samples, based on the increasing abundance of α -Fe, which is the major phase seen

in this particular case, and on the enhancement of minor peaks between 35° and 47° 2θ , as the amount of wax decreases.

We further conclude that properly passivated catalysts from slurry reactors show negligible amounts of magnetite under working conditions. An α -Fe peak is seen *only* in catalysts that are protected from atmospheric oxidation. In the case of RJO-236, α -Fe is also observed, but in smaller amounts, and appears to vanish in the reaction profile at the same time that the overall activity starts to decline. Magnetite is not seen over the lifetime of a properly sampled, working catalyst. The role of α -Fe in combination with Fe_xC needs further study.

Conclusions

Careful sample removal and passivation is critical to the study of working catalyst morphology and composition. Samples removed under inert atmosphere are less likely to undergo oxidation to magnetite. Stripping of the catalyst from the wax from the catalyst using Soxhlet extraction may cause oxidation of the reactive phase in the catalyst. XRD shows conclusively that an α -Fe peak is observed only in catalysts that are removed from the reactor under an inert blanket. Further study of its morphology and surface area is required to assess the catalytic significance of this phase.

Additional analyses, using X-ray and Neutron diffraction patterns, along with the Rietveld Structure Refinement technique, are in progress. Further study of working catalysts and reference materials prepared from unsupported, as well as doped and supported hematite precursors, using TEM, X-ray diffraction, neutron diffraction, AES, and Mössbauer Spectroscopy is planned.

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