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MORPHOLOGY STUDIES OF IRON-MANGANESE THIN FILMS

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Abstract

Fe-based catalysts are known to be effective for Fischer-Tropsch synthesis from coal but are sensitive to sulfur poisoning. Addition of manganese to these catalysts has been proposed in an effort to combat this catalyst deactivation. To investigate the fundamental physical aspects of Mn incorporation into Fe, different compositions of model thin films of Fe-Mn, ranging from 100% Fe to 100% Mn were studied for the very first time, using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and scanning electron microscopy. Our preliminary results indicate that the grain size of iron varied from 50 nm to 150 nm using the AFM image, in general agreement with others. Also the mixture with small amounts of manganese had large oxidic area. The surface was modified by the addition of manganese. The STM images of the samples showed similarities between pure iron and 75% Fe-25% Mn, while the 25% Fe-75% Mn looked very similar to 100% Mn. The mixture of 50% Fe-50% Mn seemed to contain two distinct surface features. This leads us to believe that STM and AFM can be useful tools to further investigate the model iron-manganese thin films and hence give insight into the un-known atomic scale interactions and also to study the catalytic properties better.

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Introduction

Iron-based Fischer-Tropsch (FT) catalysts have been examined for their activity and selectivity in converting CO and H_2 to hydrocarbons and oxygenates of high fuel value, and for use in petro-chemical industries, for over 60 years (Fischer, 1935; Fischer and Tropsch, 1926; Fischer and Dilthey, 1930). Generally, structural and/or electronic promoters are incorporated in FT catalysts in an effort to enhance their performance and lifetime. One of the most interesting promoters for which there are uncertain data is Fe-Mn catalysts. While no reports have been published to study surface properties of iron-manganese catalysts, we developed some model thin films of iron and manganese, and investigated their topography.

Under low-ratio H_2/CO synthesis gas reaction, it has been shown that the olefin-to-paraffin ratios were enhanced during the use of Fe-Mn catalysts as compared to other Fe-based catalysts (Maiti et al., 1985; Lochner et al., 1986), and especially in the case when potassium was added as a promoter to Fe-Mn, olefin-to-paraffin ratios could be dramatically enhanced (Pennline et al., 1986). Any further insight into this problem can have a big impact in controlling the production cost of the hydrocarbon products, and hence our interest in developing the model iron-manganese thin films for atomic scale study. While much work has been done on "bulk" properties, no reports using atomic force microscope (AFM) or scanning tunneling microscopey (STM) have been published. This is where we plan to make our contribution.

After catalyst preparation and use in FT synthesis reactions, the Mn phase is expected to be oxidic in nature. There are reports that probably MnO on the surface is responsible for the catalytic activity (in the presence of H_2S) of iron by preserving the active iron in its pure state (Chaffee et al., 1989), because of the absence of sulphur beyond the first few layers. The surface oxide reacts with H_2S to form MnOS. Other studies have suggested the association of occluded Fe^{3+}/Fe^{2+} islands with MnO and/or the creation of $MnFe_2O_4$ (Stencel et al., 1987; Jensen and Massoth, 1985). The possibility of OH surface groups associated with the Mn

phase has also been surmised to be important during synthesis gas testing (Stencel *et al.*, 1987). Probably, MnO forms a surface layer on top of the iron (Stencel *et al.*, 1987; Jensen and Massoth, 1985; Venter *et al.*, 1989). This MnO may be in the form of thin sheets on top of iron with small occluded iron particles. Other investigations have shown that MnO migrates during catalyst activation and use (Stencel *et al.*, 1987; Benecke *et al.*, 1984).

To have a better understanding of the role of Mn as a promoter of the Fe catalyst in the FT process, it is meaningful to study the thin films themselves in the hope of getting some new insight on how the adsorption of CO (Lohrengel and Baerns, 1983) and H_2 is affected by sulfur atoms on the iron-manganese, of different compositions, during FTS process. Before we started hydrogenation of CO, it was important to see what if any, were the changes in the surface topography. In this paper, we report synthesis of model Fe-Mn thin film catalysts for these studies, and their surface morphology by different microscopic techniques to get a better understanding prior to any gas adsorption.

Experimental Procedure

Deposition of alloy thin films

Preparation of the thin film Fe-Mn alloy sources has been achieved by electro-discharge compaction. This type of preparation has been used in the generation of Ni-Co alloys (Sethuraman *et al.*, 1990), and is a promising method for producing non-stoichiometric film compositions, and physical vapor deposition at a temperature of $\geq 1200\,°C$, on planar CZ Si(111) substrates. After compaction, the composition of bulk alloy (Figure 1) was determined to make sure that the bulk alloy was of the same composition as that of the starting mixture. The deposition of the alloy thin films was performed in a Veeco VE-7700 metal evaporator equipped with a diffusion pump backed by a mechanical pump and a liquid nitrogen trap. Thickness of the deposited films can be monitored and controlled with the aid of a thickness monitor (Model GM-311 of KRONOS, Inc.) within about 0.1-0.5 nm. The rate of evaporation was kept greater than 1-2 Å/sec. Before the deposition of the thin film, the silicon substrate was treated with 10% dilute hydrofluoric acid to dissolve any impurities. Silicon was chosen as the substrate because it does not form an alloy with Fe or Mn.

At a predetermined stoichiometry, the powdered alloy (200-mesh) is loaded into a pyrex glass tube and subjected to a high voltage and high current density electric discharge having approximately a 100 microsecond pulse to reduce the oxygen content to the minimum. This energy release causes the powder mixture to compact without incorporation of contaminants that are external to the mixture. This compacted alloy is then evaporated onto a substrate, to a predetermined thickness of about 300 nm. Samples were placed over the cone of the evaporation boat at different distances and

angles and the most uniform film selected. The temperature of the substrate could be anywhere from 200°C and up due to their different positions inside the chamber. A shutter was placed above the evaporation cone, so that the substrate does not have any low melting point impurity. Only when the thickness monitor started to register an increase in thickness, was the shutter opened.

STM and AFM analysis

Scanning tunneling microscope (STM, Binnig *et al.*, 1982) analysis of the thin films were carried out using a STM constructed based on a tube scanner design. The piezoelectric tube was calibrated using interferometry, and voltages on electrodes were balanced by a potentiometer to achieve highest orthogonality. The tube was made longer than usual to enhance the dynamic scan range. Electronic feedback was applied to the STM which was operated in constant current mode during analysis of the Fe-Mn thin films. The STM could be locked in the tunnelling position by a provision built into the system. The Pt-Ir tips were electrolytically etched before each measurement to ensure a very pointed tip. The STM was mounted on a double stage vibration isolation platform to minimize vibrational noise in the scan. All STM scans (Fig. 3) have been acquired on an area of 300 nm × 300 nm.

The Atomic force microscope (AFM, Binnig *et al.*, 1986) scans (Fig. 4) were performed using a Nanoscope III AFM (Digital Instruments) on 500 nm × 500 nm surface area. Constant force mode was used for sample analysis with a silicon nitride cantilever of force constant 0.03 N/m. The force was maintained at about 10^{-9} N. Because of the interaction of the surface with the cantilever, the deflection that we can calculate from these quantities, will only be approximate.

SEM images (Figure 2) were obtained using an ETEC OMNISCAN SEM that was equipped with a PGT IMIX-II ultrathin window detector capable of detecting elements from boron upwards. All samples were studied at 20 kV at a magnification of about 125X.

Results and Discussion

The bulk chemical composition of the as prepared alloy sources were analyzed using energy-dispersive X-ray microanalysis (Figure 1), and the results indicated that the alloy source composition was identical to that of the starting material. Small elemental peaks, associated with iron and manganese, were present even for the 100% metal samples. This residual is a consequence of using the same electrodes for preparing all the samples.

The scanning electron micrographs of the compact are shown in Figure 2. If 100% Fe, 100% Mn, and 50% Fe-50% Mn (by weight) were compared, the micrographs of 50% Fe-50% Mn contained features representative of 100% iron and 100% manganese. Thin films prepared from these compacts are extremely flat and smooth.

For comparison, the AFM images of the thin films are shown in Figures 4a through 4d. The size of
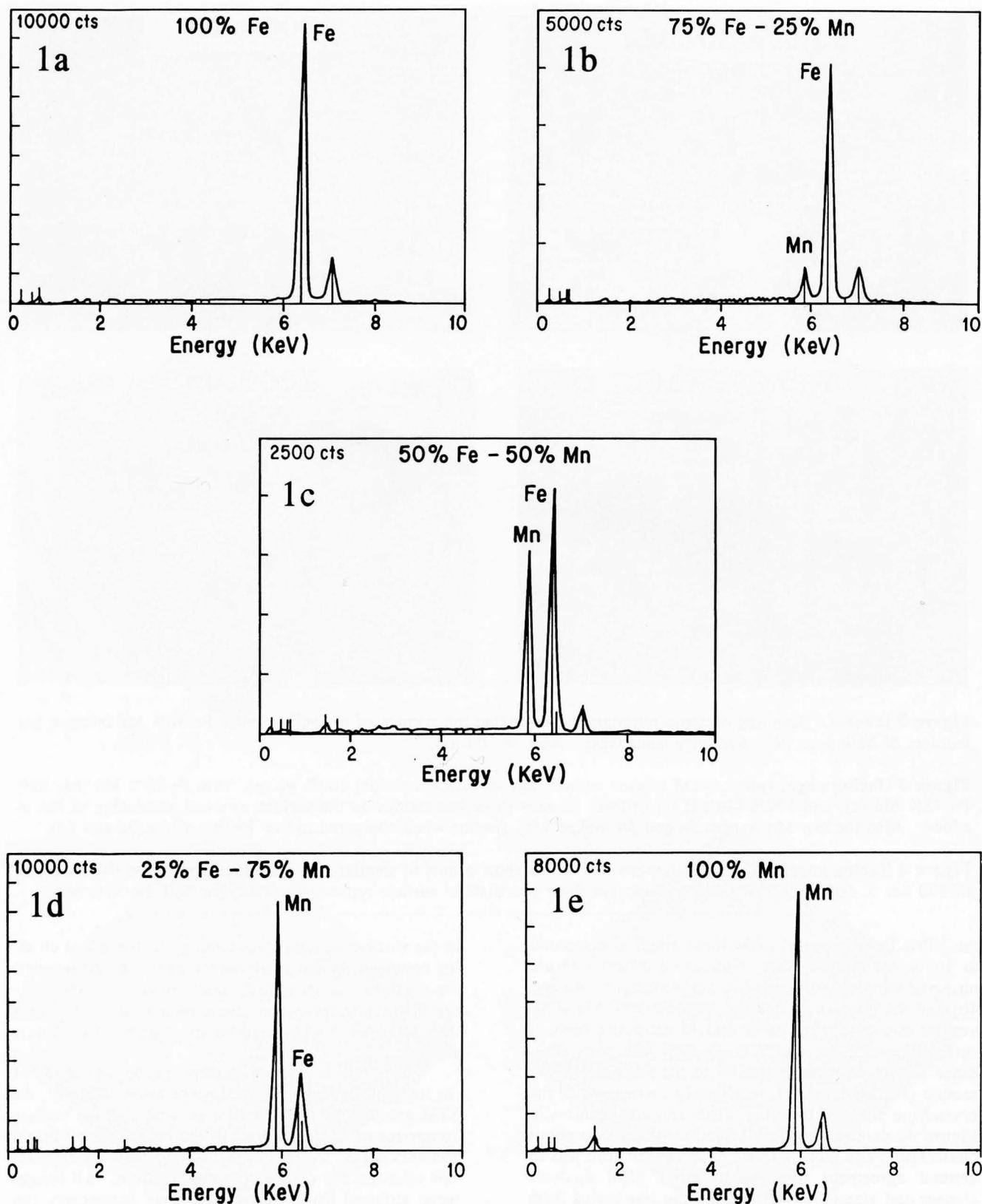
Figure 1: The composition of the bulk alloy prepared by electro-discharge compaction for various composition is shown: **a:** 100% Fe; **b:** 75% Fe-25% Mn; **c:** 50% Fe-50% Mn; **d:** 25% Fe-75% Mn; and **e:** 100% Mn.
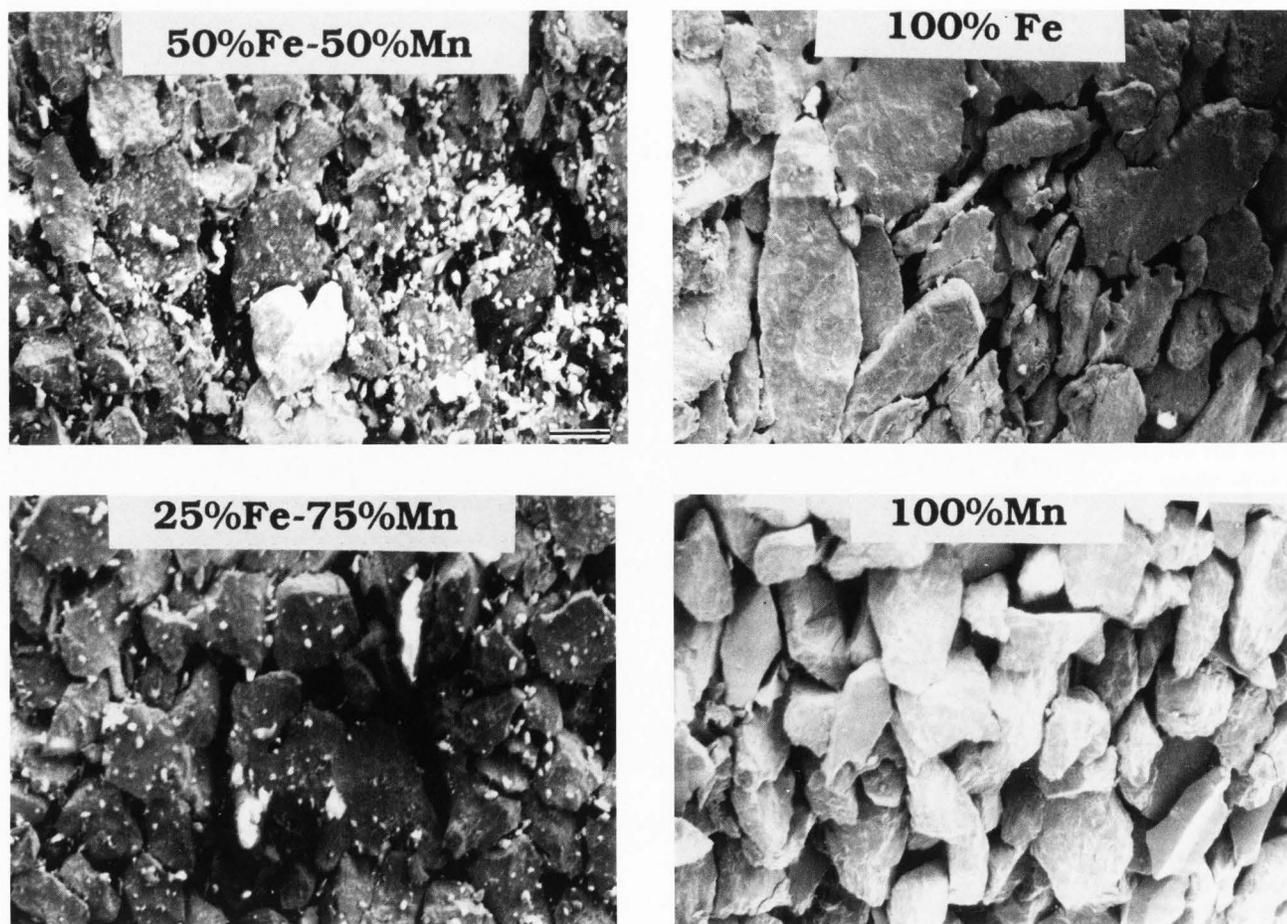
Figure 2 (above). Scanning electron micrographs show that the surface of the bulk of 50% Fe-50% Mn mixture has features of both pure iron, and pure manganese. Bars = 100 μm.

Figure 3 (facing page, top). STM images without any modification from 100% Fe (a), 75% Fe-25% Mn (b), 25% Fe-75% Mn (c), and 100% Mn (d) thin films. Images show less oxides on the surface as more percentage of Mn is added. Also the low Mn images 3a and 3b looked very similar when compared to low Fe thin-films (3c and 3d).

Figure 4 (facing page). The AFM images of iron (a) show grains of smaller size than pure manganese (b) for scans of 500 nm × 500 nm. The AFM images also show two distinct surface types (4c and 4d) for 50% Fe-50% Mn.

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the 100% Fe (Figure 4a) grain looks small as compared to 100% Mn (Figure 4b). Noticeable differences are observed between pure metallic sample (Figures 4a and 4b) and the mixture containing 50% Fe-50% Mn (Figures 4c and 4d). Figures 4c and 4d show two distinct surface features on the 50% Fe-50% Mn thin film. Since Figure 4d appears similar to the surface of pure sample (Figure 4a or 4b), this should correspond to the crystalline phase of the alloy. The irregular features in Figure 4c demonstrate the formation of an amorphous phase also. The grain size we observed for iron was in general agreement with results from TEM analysis (Jensen and Massoth, 1985). Our grain size varied from 50 to 150 nm, whereas others reported grain sizes varying from 50 to 200 nm. It may be said that the change
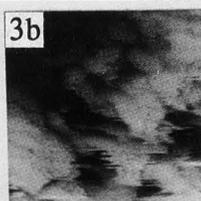
in the surface structure/morphology is dependent on alloy composition and synthesis temperature. At present, the crystal structure is not known for our mixtures. X-ray diffraction technique should be able to readily give that information. This will be investigated in the future studies.

The thin film samples were loaded into the STM for imaging immediately after preparation. Clearly, the STM analysis of the thin film showed that the surface comprises of 'hills and valleys' as evidenced by bright and dark areas. Figures 3a through 3d show the relevant raw micrographs without any modification. All images were acquired using exactly the same parameters and conditions. Figures 3a (100% Fe) and 3b (75% Fe-25% Mn) indicate that the tip was frequently scratching the
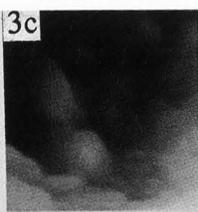
3a
100% Fe

3b
75% Fe – 25% Mn

3c
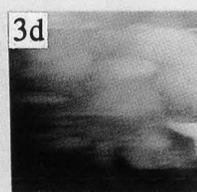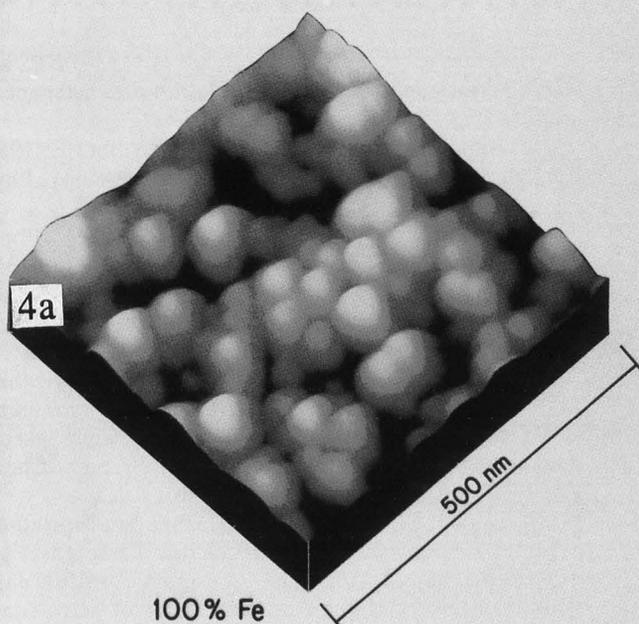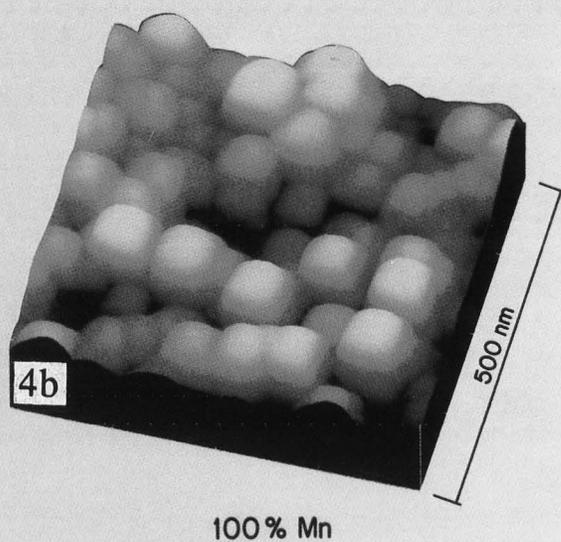25% Fe – 75% Mn

3d
100% Mn

4a
100% Fe

4b
100% Mn

500 nm
500 nm

4c
50% Fe – 50% Mn
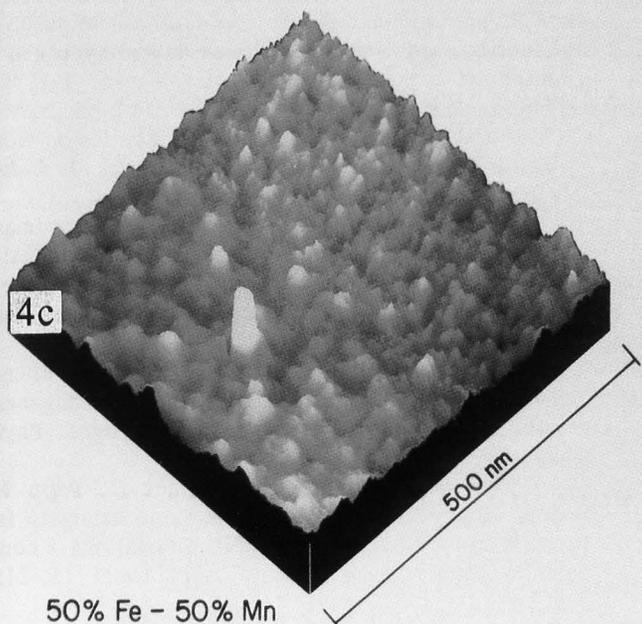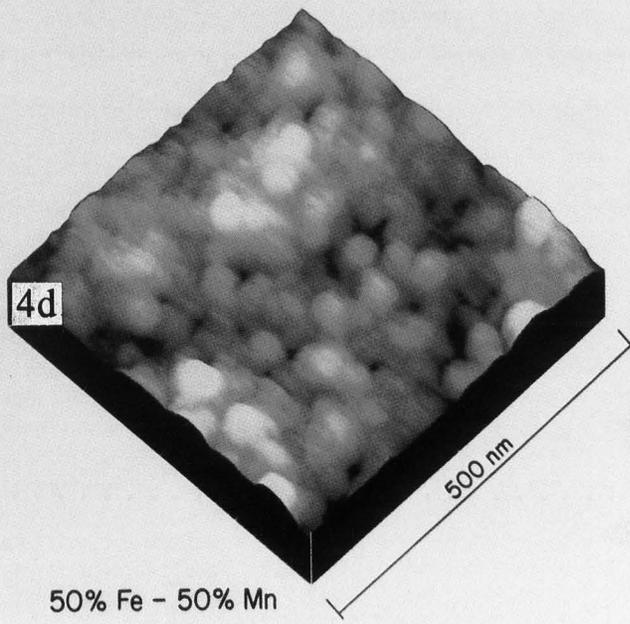500 nm

4d
50% Fe – 50% Mn
500 nm

sample surface. We attribute this to the presence of oxidic layers. Interestingly, further addition of manganese diminishes the oxidation of the surface. The oxides of Mn play a major role in catalysis. Chaffee *et al.* (1989) claims that the manganese oxide formed on the surface preserves the iron in its pure state at the core. Therefore, it can be inferred that addition of Mn to the alloy modifies the bulk structure. There are several reasons for such an observation such as mobility of individual atoms, possible surface tension effects from the substrate, and melting point differences (the melting point of iron is 1535°C and that of manganese is 1244°C). The role of melting point differences was minimized by suddenly increasing the temperature of the ceramic boat, and so its dependence on the structure should be significantly low. Mobility of Fe and Mn could play a role, however, in the absence of further information on the diffusion and segregation characteristics of the two atoms, it may be premature to arrive at such a conclusion.

Figures 3b (75% Fe-25% Mn) and 3a (100% Fe) appear very similar to one another. These are the low Mn thin films. Evidently iron seemed to be dominating the surface whenever small amounts of Mn were present. A comparision of the STM images in Figures 3c (25% Fe-75% Mn) and 3d (100% Mn) shows that these images are quite different from those in Figures 3a and 3b. This may be an indication that iron dominates for low Mn thin-films, and Mn dominate for low Fe thin-films, possibly by migration.

The boat was white hot whenever the evaporation took place. Radiation from the hot boat (~1200°C) prevented the crystal of the thickness monitor from giving accurate readings. Also, a potential problem associated with low melting point impurities existed; this was minimized by the use of a shutter which opened only after the evaporation of iron/manganese began. Very good evaporation resulted in a silvery, shiny surface, as expected of a pure metal.

Conclusions

We demonstrated that the iron-manganese alloy thin films can be prepared by evaporation of iron-manganese compacts. These films have been imaged by AFM and STM. Surface morphology varied significantly according to the alloy composition for both the STM and AFM. The STM micrographs showed a real difference between the high Fe thin-films and the high Mn thin-films. The low Mn (less than 50%) Fe-Mn thin-films appeared more like pure iron scans indicating probably a migration of iron particles to the surface. If the idea is to preserve the iron, then the surface should look more like Mn. This suggests to us that the percentage of Mn has to be higher than 50%. Also the low Mn content thin-films appeared to have an oxidic surface as compared to high Mn thin-films of iron and manganese. The AFM micrographs on the other hand, confirmed the modification of the surface by the addition of manganese

to iron. These preliminary results lead us to believe that STM and AFM can be important tools in better understanding the complex catalytic process in FT synthesis.

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Discussion with Reviewers

C.J. Chen: Please discuss the meaning of the STM and AFM observations from the point of view of understanding the problem of catalysis.

Authors: As mentioned in the **Introduction**, for Fe-Mn catalysts, the oxides of Mn play an important role in preserving the core of iron in pure form. The STM micrographs (Figures 3a and 3b) from the low Mn content (less than 50% by weight as compared to pure iron) thin films show many similarities. This suggests to us the possibility that in low Mn mixtures, iron dominates the surface. This may be due to migration of iron particles. On the other hand, Figure 3d (for pure manganese), and Figure 3c (for 25% Fe-75% Mn) look very similar. These are the images for low Fe mixtures. Here Mn seems to be dominating the surface. If we want to preserve the iron in a pure form, surface scans of the thin films should look more like manganese, so that iron is preserved at the core in pure form.

The AFM images (Figure 4a) of pure iron have a smaller grain size when compared to the larger grain size of pure manganese (Figure 4b). Also the grain size was found to vary from about 40-50 nm to about 150 nm in agreement with other researchers.

H. Haefke: Please comment on the conclusion that the "surface morphology varied significantly according to the alloy composition".

Authors: The STM images have not been modified in any way, they present **raw data**. The scratches are an indication of the presence of oxides on the surface. Surface morphology indicates the amount of oxides on the surface in the STM images. The oxides of Mn have been known to play an important role in catalysis. It enhances the activity of iron in FT synthesis.

R.J. Hamers: Please provide more discussion of the results.

D. Dwyer: What is the significance of the results?

Authors: The importance of the STM scans lies in the fact that they are raw data without any modification of any kind. STM was used as a tool for understanding the topography. The study of iron-manganese is a new field of investigation. As mentioned in the earlier paragraphs, the STM gave us a feel for the way the surface looked, and it provided us information on surface morphology when a mixture is varied in composition from 100% iron to 100% Mn, in increments of 25%.

Chaffee *et al*. (1989) claim that the manganese oxide is formed on the surface, and that this manganese oxide may be responsible for the preservation of pure iron at the core. Our images show that the low manganese (less than 50%) Fe-Mn thin films looked more like pure iron scans, indicating probably a migration of iron particles to the surface. If the idea is to preserve the iron, then we want the sample surface to look more like manganese, indicating the preservation of iron in its pure state at the core. Our results then support this theory of Mn protecting the iron in its pure form at the center, possibly by forming the oxide.