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Synchrotron X-Ray Microprobe and Computed Microtomography for Characterization of Nanocatalysts

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Abstract

Gas-to-liquids (GTL) is a viable pathway for synthesis of clean fuels from natural gas. One of the attractive synthesis options is the Fischer-Tropsch (F-T) method using an iron catalyst to yield a broad range of hydrocarbons. We collected catalyst samples during three separate F-T runs that utilized nanophase (mean particle diameter (MPD): 3 nm and 20-80 nm) and micrometer-sized (32.5 ? m) Fe_2O_3 that served as catalyst precursors. The collected samples were characterized with micro x-ray fluorescence and computed Microtomography at the National Synchrotron Light Source **(NSLS).** Results found with two different measurement techniques indicated that there was heterogeneity on a spatial scale corresponding to volumes of roughly 10^3 μm^3.

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Introduction

Gas-to-liquid fuel conversion (GTL) refers to processes in which natural gas is catalytically converted, in sequential steps, to clean fuels. Employment of natural gas or biogas starting materials can reduce reliance on petroleum fuels that are in short supply. When burned, clean fuels produce lower concentrations of aromatic compounds, particulate matter, SO_x, and NO, than conventional gasoline or diesel fuels and are thus more environmentally acceptable. They also have higher cetane numbers than petroleum derived diesel fuels and can therefore improve the performance of diesel engines.

Since the GTL pathway yields environmentally fiiendly fuels, it is likely that large-scale clean fuels production plants will be built in the near future. One such production method is based on the well known Fischer-Tropsch (F-T), a catalyzed conversion of natural gas derived synthesis gas (primarily a mixture of carbon monoxide and hydrogen) to yield a mixture of hydrocarbon fuels (gasoline, diesel, waxes, etc.). The F-T catalyst can be selected from metals such as iron, cobalt, and ruthenium depending very much on the nature of the desired product and the process economics. The present commercial F-T technology falls short of the ultimate atom economy that is needed and therefore, enhancing catalyst performance is of great importance. One possible avenue to explore is the effect of nanosizing the F-T catalyst

(commercial catalyst is micrometer sized). Nanosized catalysts are appealing since they can provide higher surface area, amorphous surfaces, and more active reaction sites per unit area than larger particles of the same material.

The objectives of the present experiment were to establish the activity/catalyst-size relationship and to use the synchrotron x-ray technique to complement other spectroscopic techniques that have been previously employed to determine time resolved changes in catalyst composition, morphology, and state that accompany the F-T reaction. The synchrotron x-ray beams were used to determine if the catalysts are uniformly distributed in the product material or whether they form agglomerates, possibly as a result of their colloidal nature, that could effectively diminish the relative differences in surface area expected from the sizes of the catalyst particles. Other investigations on this topic have been reported by Jones et al.[1] and Mahajan et al.[2,3]

Experimertal Approach

We were interested in measuring the distribution of the catalysts in a waxy medium (by taking samples directly out of the F-T reactor) using x-ray fluorescence techniques. The applicability of the method for examination of nanosized catalysts is dependent on the mass to be measured compared to the spatial resolution of the x-ray microprobe and the escape depth of the x-rays measured. The mass of individual particles catalyst particles was calculated assuming a spherical shape and a density of 5.25 g/cm for Fe_2O_3. The values for the particle volume and the corresponding mass of Fe as a function of the particle diameter are shown in Figure 1. Detection limits for Fe on the X26A beam line at the NSLS are about 1 fg with a beam diameter of about

10 ym under normal conditions at the NSLS. Thus, single particles with a diameter of around 70 nm will be detectable.

The amount of material analyzed depends on the analytical method employed. The simplest approach is to employ x-rays with energy just above the Fe K-x ray absorption edge to scan across a thick sample of the product material. The volume of material analyzed then is fixed by the size of the beam and the absorption of the incident **x** rays and the emerging Fe K x-rays. The relative number of detected fluorescent **x** rays for a wax with a CH_2 composition, density of 0.95 g/cm^3, and negligible amounts of Fe CH2 is given in Figure 2 as a function of the depth in the sample at which the x rays are produced. Summing these values shows that 90% of the observed x-rays are produced in a volume of 1.7×10^5 μm^3. Addition of Fe at the percent level will increase the absorption of x rays in the sample and reduce the volume probed.

Samples for the study were prepared in a slurry reactor, operated in continuous mode, at a temperature of 513 °K and a pressure of 2.77 MPa. The total run time was 120 h during which hydrocarbon were continuously produced by catalytic reduction of carbon monoxide (CO) by H_2. The initial catalyst-precursor loading was 15.7 grams of Fe_2O_3, 300 ml ethylflopolyolefm-164 solvent (a C_{30} hydrocarbon oil), and CO and H_2 in a stoichiometric proportion of 1/2. The yield of solids from the reactor including catalyst particles, solvent, and high molecular-weight waxes (a lion-volatile product that stays in the reactor) was 356 grams with an iron content of 3.1% by weight. Runs were made with catalyst precursors as follows: unsupported catalysts with MPD of 3 and 20-80 nm and a run with a SiO_2-supported catalyst of MPD 32,500 nm. The surface areas of the catalyst were 255, 16-20, and 232 m^2/g respectively.

The samples, taken at 120 hours for analysis, were mounted as blobs of wax on the end of 0.100 mm glass rods for x-ray micro probe mapping or inside a glass capillary for computed

microtomography measurements. The X26A beam line uses NSLS bending magnet radiation. The x-ray beam passes through a monochromator and is then focused with Kirkpatrick-Baez mirrors to a size of about 10 pin x 10 µm at the sample position. Fluorescent x rays are observed with a 9-element intrinsic Ge x-ray detector. Mapping measurements are made by rastering the beam across the sample in steps of the spot size and collecting data at each point that could then be displayed as a map of the sample surface. Non-destructive computed microtomography (CMT)) measurements were made to obtain information on a single section through the sample. Data were collected in a translate-rotate mode. CMT gives results for concentrations of Fe in well defined voxels that were about 15 pm x 15 pm x 15 pm in size. The volume of the voxel, 3400 μm^3 is, very roughly, ten times smaller than the volumes analyzed in the simpler mapping measurements. The amount of Fe in the volume, assuming a uniform distribution and a 1% amount by weight in a density 1 material is then $3.4 \times 10^{-11} g/cm^3$. This is far above the detection limit so that sensitive determinations can be made of the homogeneity of the catalyst distributions.

Results and Discussion

Mapping measurements made on the materials produced using the three catalysts with the x-ray microprobe at the NSLS X26A beam line are shown in Figure 3. All three materials show variations in the Fe concentrations with the largest found for the 32500 nm supported catalyst. The CMT results obtained for 2 sections through the sample (Figure 4) show the same type of results with high-intensity regions combined with void space (dark color). TEM measurements showed that the final catalyst sizes were very similar indicating that there was agglomeration of

the smallest sized catalyst, fragmentation of the largest, and essentially no change for the intermediate size.[3]

The F-T process produces a mixture of hydrocarbons as products. **As** the F-T process proceeds, the concentration of non-volatile heavier hydrocarbons (waxes) increases in the reactor and affects the catalyst activity (for example, the catalyst may get coated with waxes) and contributes to the observed decreased catalyst activity. The extension of the present work to samples taken at earlier stages of the F-T process should be an excellent method for viewing the way the catalysts interact with the feed materials and with themselves during the reactor operation. This could help in optimizing the hydrocarbon synthesis via F-T, an important reaction with commercial potential.

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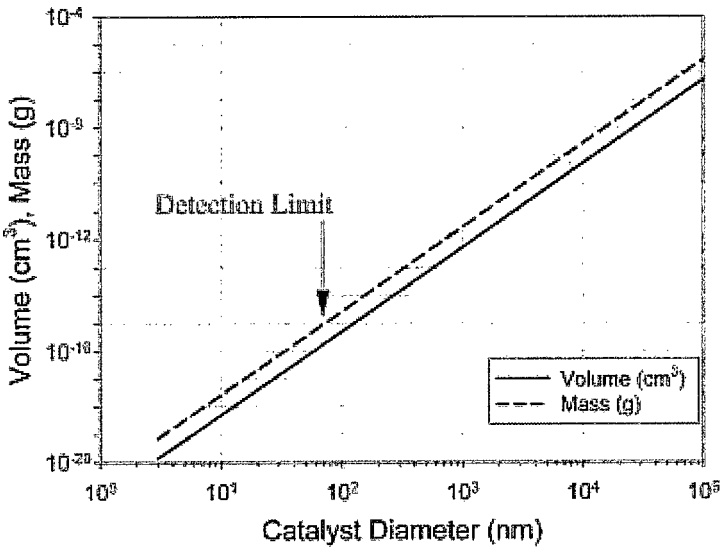

Figure 1. The mass of the Fe content of a catalyst particle of Fe_2O_3 and its volume are shown as a function of the particle diameter. The arrow gives the single particle detection limit. Particles with a smaller diameter are not detected.

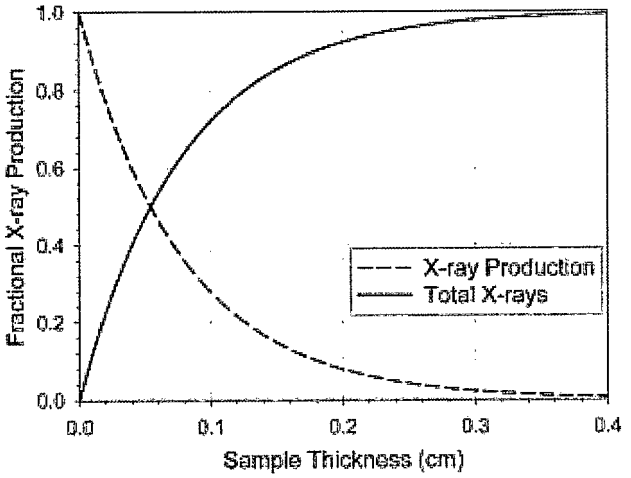

Figure 2. The relative number of detected x rays is plotted as a function of the depth in the sample at which they are produced.

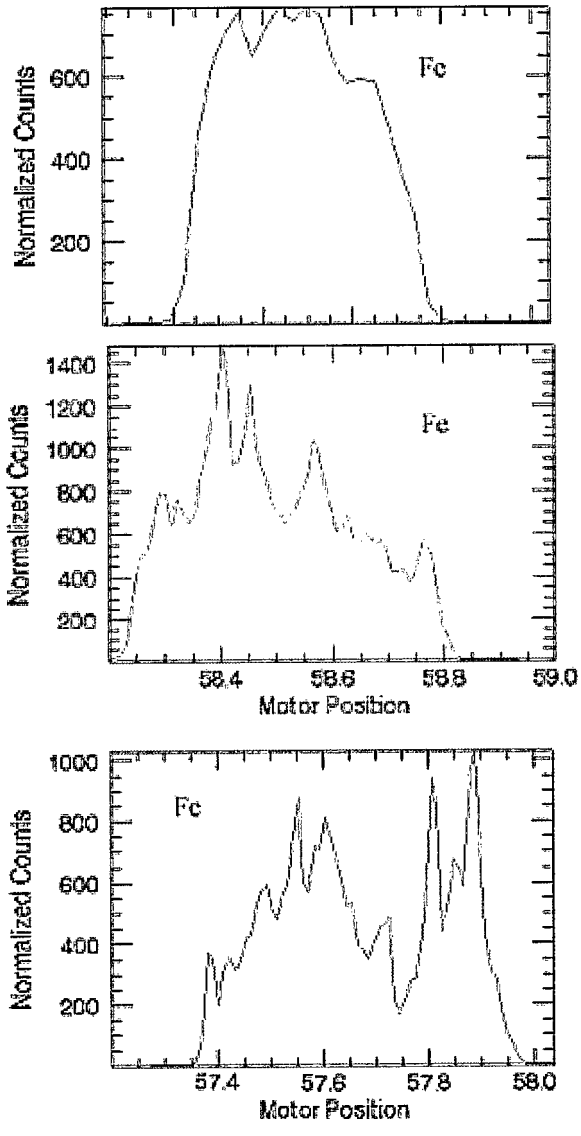

Figure 3. Concentrations of Fe measured with the x-ray microprobe in line scans across samples produced with the three different size catalysts show clear evidence for heterogeneity in the Fe concentrations.

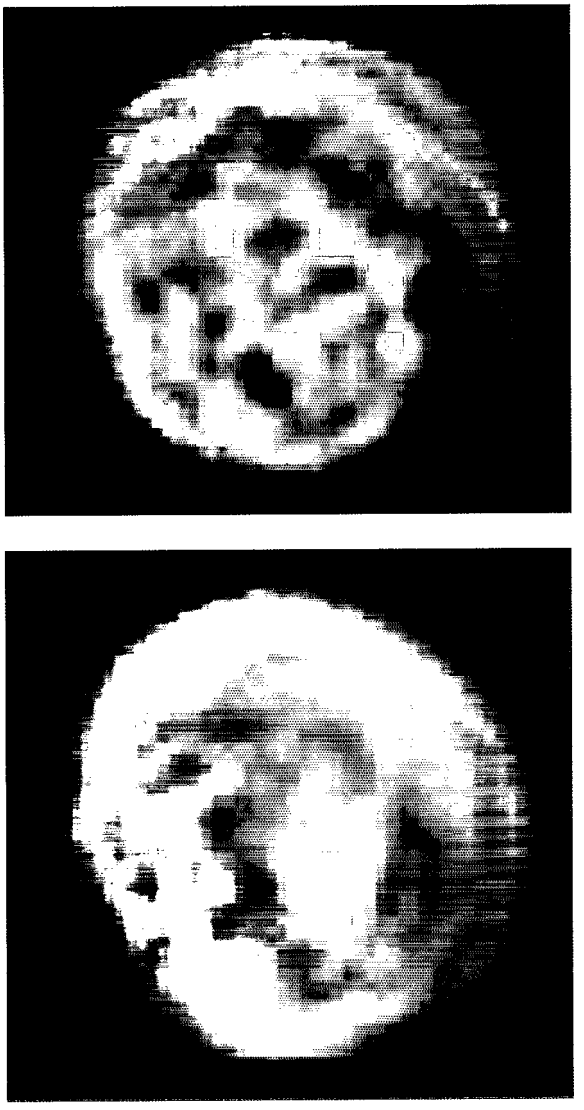

Figure 4. The Fe concentrations measured using x-ray fluorescence tomography are shown for two sections through a wax sample contained in a glass capillary. The initial catalyst MPD was 3 nm.