ANALYSIS OF COBALT AND IRON FISCHER-TROPSCH CATALYSTS USING TRANSMISSION ELECTRON MICROSCOPY

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ABSTRACT

ANALYSIS OF COBALT AND IRON FISCHER-TROPSCH CATALYSTS USING TRANSMISSION ELECTRON MICROSCOPY

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Using Transmission Electron Microscopy we have investigated the structure of two Fischer-Tropsch catalysts, looking specifically for the formation of discrete metal nanoparticles approximately 10 nm in diameter to form on the gamma aluminum oxide support. Using Scanning Transmission Electron Microscopy and Energy Dispersive X-ray analysis we have studied the two samples. The data shows that in the case of the cobalt sample that the cobalt has been secured to the alumina support, but exists as cobalt oxide, not elemental cobalt. Large cobalt oxide crystals were also found unattached to the alumina support. The iron catalyst showed similar oxidized iron particles on the alumina support, but without any unattached iron oxide particles. The iron sample also showed the presence some elemental iron particles on the alumina support. A brief description of Transmission Electron Microscopy theory and techniques, as well as a short explanation of Fischer-Tropsch catalysis is included.

ACKNOWLEDGEMENTS

I would like to acknowledge Dr. Richard Vanfleet for his help, perseverance and patience in dealing with perhaps his most challenging assignment, me. I would like to also thank Dr. Jeffery Farrer and the TEM Research Group for their unending willingness to teach me the same things over and over again. I am forever grateful to my wife for her support and love in convincing me that I really could (and would) get this done. Finally, I would like to thank the electrons that have made it all possible.

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Chapter 1

Transmission Electron Microscopy

1.1 TEM Basics

Light microscopes have long been used to study small particles but have an inherent limitation. Because light microscopes require visible light to work, there is a limit to how much magnification they can provide. Visible light has wavelengths that range from about 400 to 700 nanometers (nm) and cannot be used to see features smaller than that wavelength. Without light (or something else) with a smaller wavelength microscopes would have been unable to provide magnification greater than about 1000x.

This problem was solved with the invention of the electron microscope. DeBroglie first showed that all particles have wave-like properties and have a wavelength that is dependent on their momentum:

$$\lambda = \frac{h}{mv} = \frac{h}{p}. \qquad (1.1)$$

The wavelength of a particle (such as an electron) is inversely proportional to its momentum; the faster it is moving, the smaller the wavelength. Electrons accelerated through potentials of several hundred thousand volts achieve very high velocities and have wavelengths that are only fractions of nanometers long; typical accelerating voltages of 100 to 300 kV produce electrons with wavelengths of 0.0037 to 0.0019 nm. Electron microscopes can provide far greater magnification than ordinary light microscopes.

Transmission electron microscopes work by sending a beam of electrons through a thin specimen. The electrons interact with crystalline materials according to Braggs law,

$$2\,d\,\sin\theta = n\lambda\,, \qquad (1.2)$$

where d is the distance between planes of atoms, θ is the scattering angle, λ is the wavelength of the electron and n is a positive integer greater than zero. Electrons scattered to a certain location will constructively interfere if their path lengths differ by an integer number of wavelengths and destructively interfere otherwise.

The beam interacts with the electrons in the sample which deflects some of the electrons while others pass through unaffected. Images and other information can then be retrieved from the beam in a variety of different ways.

1.2 TEM Techniques

Various different imaging and analytic techniques can be used with TEMs. A few of these that have been used in this research are presented briefly here.

1.2.1 Bright Field Imagery

One common TEM technique is that of bright field imaging. The electron beam is extracted from the source and accelerated through a large potential. Electro-magnetic lenses then collimate the beam before it hits the thin specimen. If the sample is sufficiently thin, a large percentage of the electrons pass right through the sample unaffected while a few are scattered out. The beam is then passed through more lenses and focused to a spot. Each diffracted beam is also focused to a spot that is spatially separated from the main beam and the other diffracted spots. An aperture is places at this location and the main (unscattered electrons) beam is allowed to pass through the aperture. The aperture blocks all diffracted electrons. The beam that passed through the aperture is then passed through more lenses to reproduce an image on a fluorescent screen (fig. 1.1). In a Bright Field image, most areas are bright and darker areas show regions where electrons have been removed from the beam (blocked by the aperture) because of stronger scattering at that location. This can be caused either by crystal orientation (better or more efficient diffraction), a thicker part of the sample (more diffraction due to more specimen), or by an element with a higher atomic number (more scattering). The image can be captured on either photographic plates, or by a CCD camera.

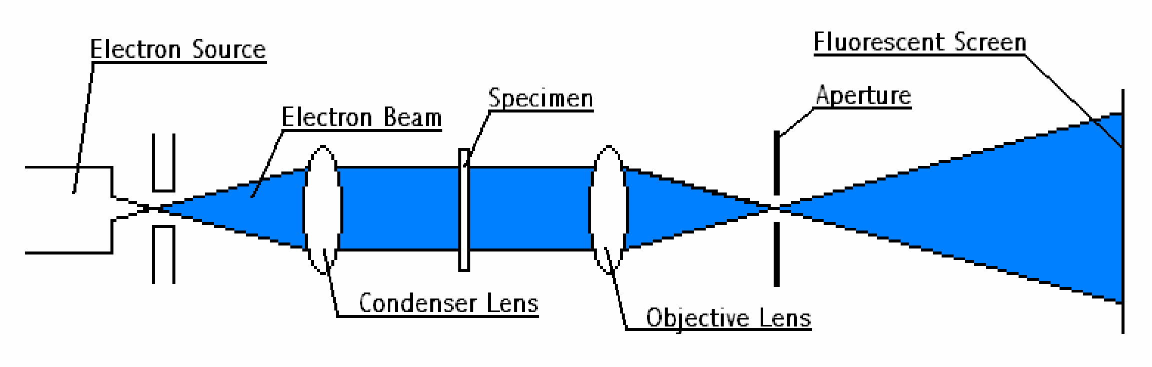

Figure 1.1 This diagram shows a simplified view of how a TEM works. The electrons originate at the source at the left and move to the right. The beam first passes through a condenser lens and then through the sample before being focused by the objective lens onto a fluorescent screen.

1.2.2 Dark Field Imagery

Dark Field imaging is similar to bright field imaging, but instead of viewing the main beam (letting it pass through the aperture), one or more diffracted beams are viewed (let pass through the aperture). By blocking the main beam and allowing only a diffracted beam to pass, the image is reversed like a negative with most areas being dark and strongly scattering areas being bright. Bright areas in the image are a result of many electrons in the diffracted beam; in dark field imagery well oriented parts of the sample, thicker parts of the sample, or elements with higher atomic numbers appear brighter. Dark Field images are often beneficial because different diffracted beams contain electrons that were diffracted by different angles and can highlight different features in the image.

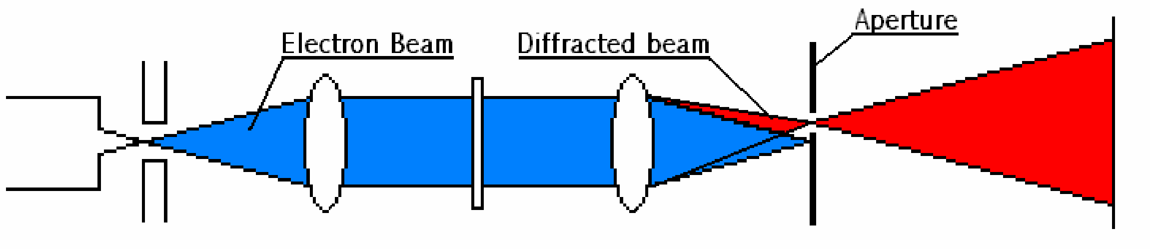

Figure 1.2 Dark field images are created by moving an aperture to block the main electron beam (blue) and allowing one or more diffracted beams (red) to pass through.

1.2.3 Scanning Transmission Electron Microscopy

Scanning Transmission Electron Microscopy (STEM) is another technique which was used extensively in this research. In STEM, the beam is condensed down to a very small spot, only a nanometer or so across. The small spot is then scanned over an area of interest and the image is built pixel by pixel during the scan. Electrons that interact strongly with the sample are deflected and then detected by a High Angle Annular Dark

Field (HAADF) detector. The electrons that hit the HAADF detector are used to create a picture similar to a dark field image in which thicker regions or regions with elements with higher atomic number appear brighter. It is relatively insensitive to sample orientation (unlike Bright Field and Dark Field imaging) because it collects electrons scattered to larger angles that contain less orientational information. STEM can be very useful because the very small beam can be used to probe specific areas with other analytical techniques, such as Energy Dispersive X-Ray spectroscopy (EDX).

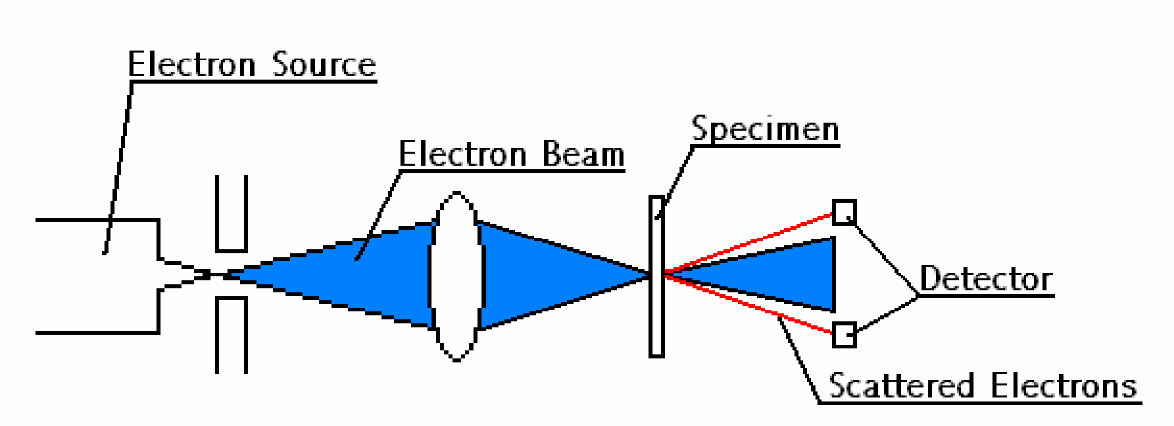

Figure 1.3 A simplified diagram of a TEM in STEM mode. The scattered electrons are detected by a circular HAADF detector and then used to create an image.

1.2.4 Energy Dispersive X-Ray Spectroscopy

Electron microscopy techniques extend beyond just creating images. Energy Dispersive X-Ray spectroscopy (EDX) extracts information about the elements that make up a sample. High energy electrons in the main beam can knock inner orbital electrons away from atoms in the sample. Other electrons can then fall into these holes and the energy lost as they fall into these potential wells is carried away by an X-ray. The energy of the X-rays corresponds to the size of the potential well that the electron has fallen into and is characteristic of individual elements. Each element has different energy levels and the X-rays can be used to identify elements present in the sample. A detector in the microscope can sense the energy of each X-ray that is incident upon it, and create a graph of the results, like in the figure below. The computer can then label the peaks according to the energy of the X-rays. A higher the number of counts indicates a greater the presence of a particular element. Multiple peaks per species are a result of electrons being knocked out of different orbitals or the initial orbital being refilled by electrons from different higher energy orbitals. When the microscope is in STEM mode, X-ray spectra can be obtained for specified areas of the image; while the X-ray detector is gathering data, the computer restricts the beam to the selected area.

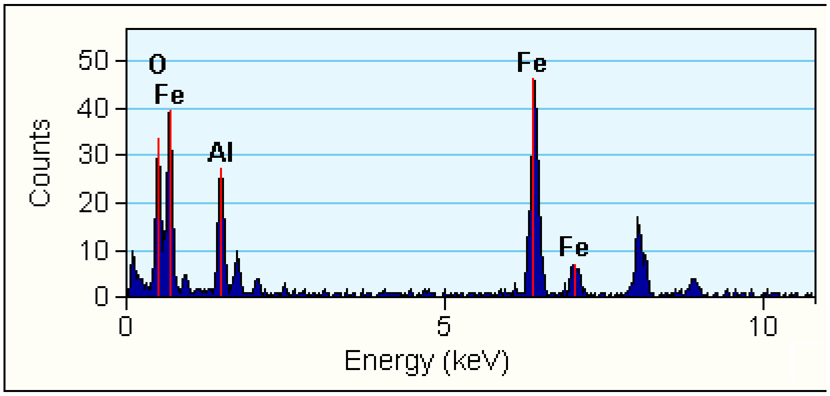

Figure 1.4 A typical EDX spectrum, showing labeled peaks for Oxygen, Iron and Aluminum.

1.2.5 Line Scans

STEM and EDX can also be used to create line scans which create an elemental cross section of the sample along a user designated line. The beam is controlled to stop at a given number of points along the line for a short amount of time. Figure 1.5 below shows a sample that has been marked where the beam has stopped, giving a good view of how the beam probes many sites along its path. Typically 10-20 points are measured for 15 to 30 seconds. (The more points and time that are used, the better the data that is collected. In this respect line scans are only limited by the user's patience, specimen damage, or specimen drift.) The data from each point can be collected and analyzed to graph the amount of a certain element at each point across the scan. This process shows how the amount of different elements may be changing as the beam moves from one area of the same to another.

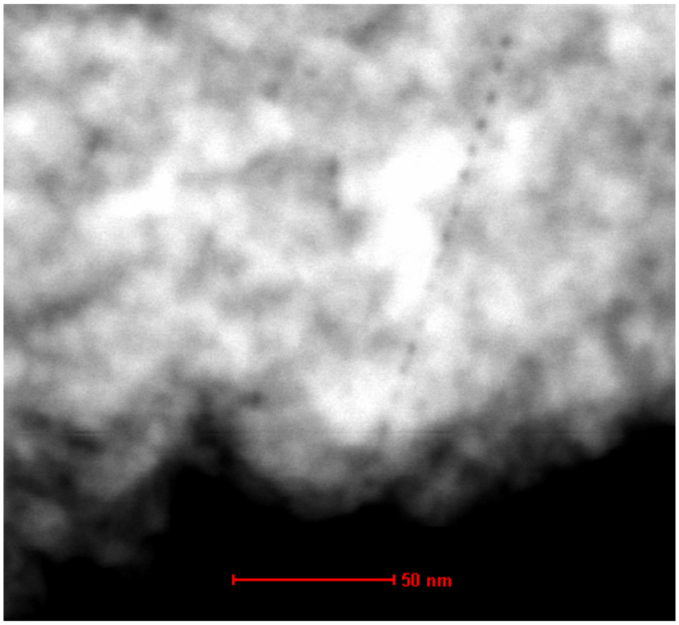

Figure 1.5 STEM image showing beam damage from a line scan. The 15 marks on the sample along a line about 100 nm long indicate where the beam stopped to gather data.

1.3 Specifications

A 200 kV field emission TECNAI-F20 TEM was used in the research for this paper. The TEM is located in U183 of the Underground Lab in the Eyring Science Center of Brigham Young University.

Chapter 2

Fischer-Tropsch Catalysis

2.1 Fischer-Tropsch Catalysis

In 1925 Franz Fischer and Hans Tropsch first catalyzed the reaction of small hydrocarbons to form paraffins of measurable amounts [1]. This type of catalysis eventually came to bear their names and is known as Fischer-Tropsch Catalysis. Fischer-Tropsch (FT) Catalysis provides a mechanism to create large hydrocarbons out of smaller molecules. Carbon monoxide (CO) and hydrogen gas (H_2) are often produced industrially as waste gases in oil mining, but can be combined to produce valuable hydrocarbons such as diesel fuels [2].

The role of a catalyst in a reaction is to provide a way for the reaction to occur under more favorable conditions. In order for chemical reactions to occur, the atoms and electrons in the reacting compounds must rearrange themselves. Some amount of energy is required to break off an atom from a molecule before it can react with another molecule. Many reactions occur spontaneously, as the kinetic energy of room temperature is more than sufficient to start a reaction. Other reactions require high temperatures and/or pressures to make the reaction happen, or to increase the rates of reaction. Catalysts provide a different chemical mechanism for a reaction to proceed that requires less energy, allowing the reaction to take place at lower temperatures or pressures. These lower temperatures and pressures make running these reactions both cheaper and safer in many instances.

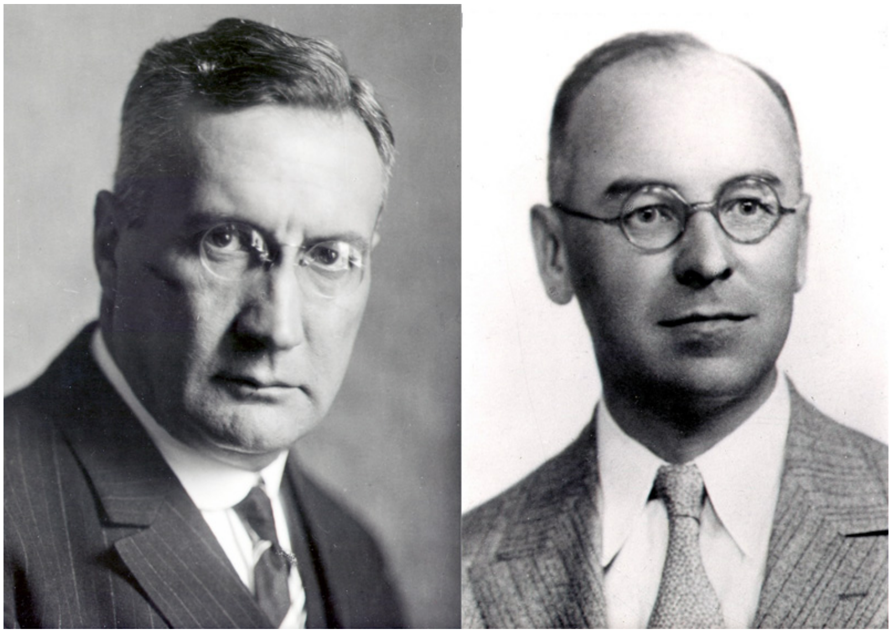

Figure 2.1 Franz Fischer (left) and Hans Tropsch (right) [3].

The production of hydrocarbons was reported in 1913 at 120 atm of pressure and 300-400 °C. These numbers contrast greatly with the 1 atm and 220-250 °C achieved by Fischer and Tropsch 12 years later [1]. FT catalysts can help by decreasing reaction pressure, decreasing reaction temperature, increasing reaction rates and increasing selectivity of products [4].

2.2 Cobalt and Iron FT Catalyst Samples

Catalysts must be able to participate in reactions in order to be of any use. A large bowling ball sized lump of catalyst would be an ineffective use of catalyst material, because reactions can only be catalyzed on the surface, and all of the internal material would be wasted. To increase the effectiveness of the catalyst, surface area should be maximized to allow as many possible sites for catalysis as possible. However, care must often be taken to ensure that the catalyst is not affected by the reaction. In the case of cobalt and iron FT catalysts, the reaction environment can cause the catalysts to oxidize. Once the catalyst has been oxidized, its chemical properties change and it will no longer catalyze the reaction; this process is called deactivation. Small catalyst particles are more easily oxidized than large particles, and so large catalyst particles are more likely to be unaffected by the reaction and can be used for longer periods of time before deactivating.

The metal catalyst particles were originally attached to the alumina support as a metal oxide, which was then reduced to leave only the metal particles. If the particles were not fully reduced, they could remain as oxides, which would not effectively catalyze the reactions.

It has been determined that the optimal size for the catalyst particles is about 10 nm in diameter to maximize the catalyst efficiency and lifespan. The catalyst particles must not only be the correct size, but they must be held on some sort of support structure to keep them from sticking together. For this reason, the catalyst is supported on gamma phase aluminum oxide (Al_2O_3). The metal particles should be anchored securely to the alumina support to provide an even dispersion allowing for the maximum number of catalyzing sites [5].

In this research, we studied 2 different FT catalysts created by the Catalysis Lab at Brigham Young University lead by Dr. Calvin Bartholomew. The cobalt sample is 30% cobalt and 0.3% ruthenium by weight. The iron sample is 40% iron by weight. Both catalyst samples are supported on gamma phase aluminum oxide.

Chapter 3

Experimental Methods

3.1 TEM Sample Preparation

Sample preparation is very important to transmission electron microscopy. The sample must be very thin, about 100 nm thick or less, in order for the electrons to pass through. Sample preparation is often a delicate process in order to make the sample thin enough without destroying the delicate features to be studied. In this study, both the samples that were analyzed were fine powders with many particles that were already sufficiently small for TEM work.

Lacy carbon grids were chosen as an ideal method to support the small catalyst particles. The lacy carbon grids consist of a small round copper disk (3 mm diameter) with a copper grid in the middle. Carbon lace then spans the gaps in between the copper grid looking quite like a spider web. Small particles then stick to the carbon lace. The particles that stick to the lace often hang over the edge of the lace allowing for viewing of the particle with no background support. Figure 3.1 shows the grid under increasingly greater magnification showing its various features.

The cobalt sample was a very fine powder which could be placed directly on the lacy carbon grid. This was done in one of two ways: a small amount of the sample was sprinkled on to the grid, or the grid was dropped into a small glass vial of the sample and shaken.

The iron sample was slightly coarser so the sample was first ground up between two ordinary glass slides to break up any larger particles. The ground powder was then sprinkled onto the grid.

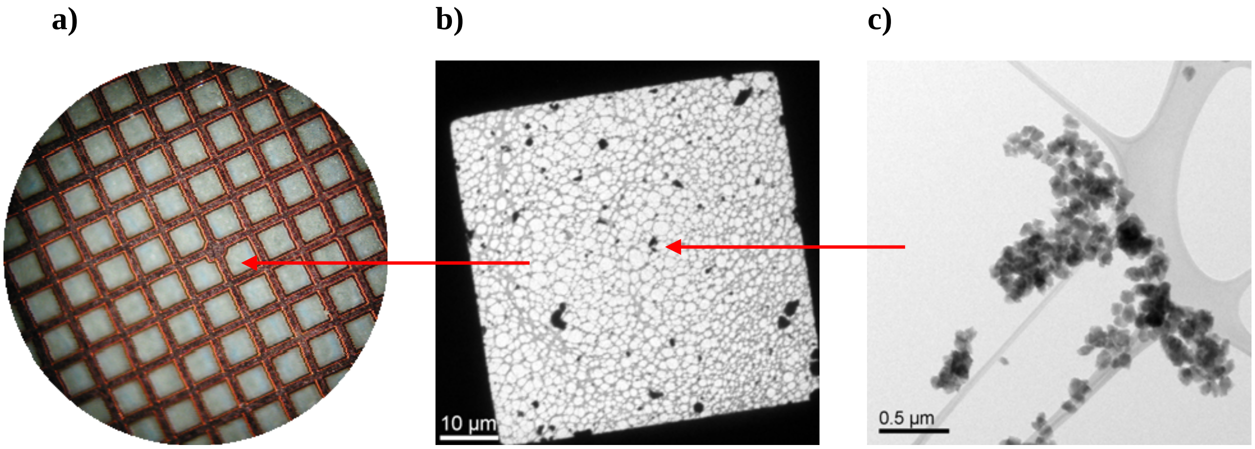

Figure 3.1 **a)** Lacy carbon grid magnified 55 times to show the small copper grid and carbon lace in between. **b)** TEM image of one square of the grid. Catalyst particles a few microns in size are visible. **c)** TEM image of a few small particles caught on a piece of the carbon lace.

Chapter 4

Results

Transmission Electron Microscopy has been employed to study directly the catalyst that has been created. Though direct examination, the structure of the catalyst and chemical makeup and arrangement of the catalyzing metals can be studied in order to determine if the process used to make the catalyst worked as it was intended.

4.1 EDX Calibration

The details of the X-ray spectra used for much of the analysis of the samples are highly dependent on the X-ray detector. The spectra can be analyzed by the computer to determine atomic ratios of elements present in a sample, which can point towards the chemical structure of the sample. The X-ray detector is not equally sensitive to all X-ray energies; a lower percentage of low energy X-rays are detected. The detector automatically adjusts the data when calculating the atomic ratios to account for the undetected X-rays.

This calibration was tested using gamma phase aluminum oxide (Al_2O_3), the same alumina used as a support for the catalyst particles being studied. More than a dozen X-ray spectra were collected different small particles of the alumina. All of the spectra showed were in very close agreement that the sample was 36-37% aluminum and 62-63% oxygen. (Percentages may add up to just under 100% because of round off errors.) The aluminum/oxygen ration ought to be 40:60. The detector slightly over counts the lower energy oxygen X-rays (or under counts the higher energy aluminum X-rays). This effect is consistent and small and indicates that the detector is fairly well calibrated.

4.2 Cobalt/Ruthenium Catalyst Results

The first images of the sample immediately indicated that very distinct cobalt nanoparticles had not been formed on the alumina support. Two TEM images are shown below. In these images darker parts indicate thicker parts of the sample, or possibly higher atomic number. Cobalt nanoparticles (atomic number 27) would show distinct dark circles against the alumina support (atomic number 13). Distinct metal nanoparticles were not found, eliciting further study to determine how the cobalt had been incorporated into the sample.

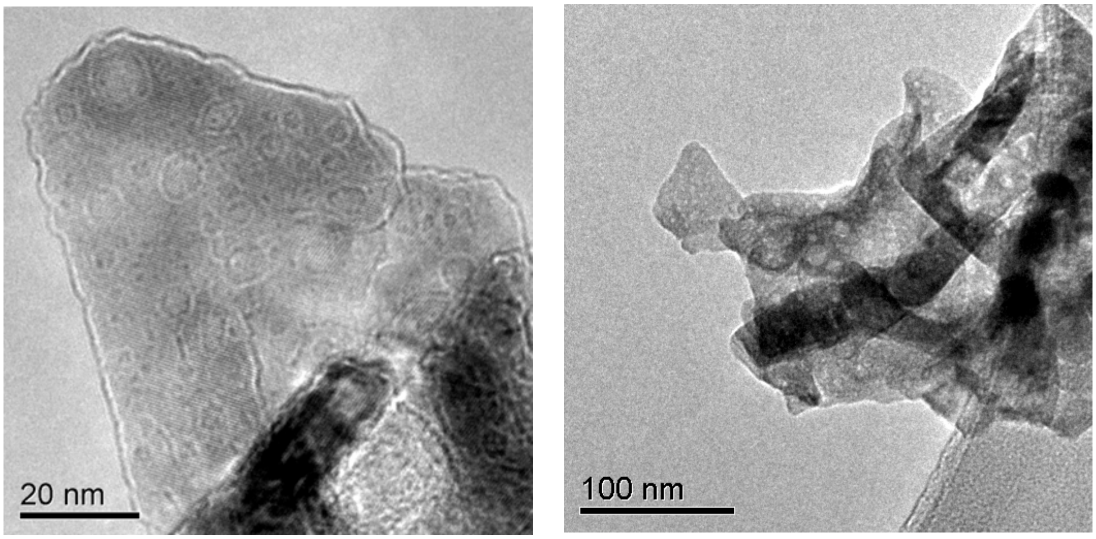

Figure 4.1 Bright field images of cobalt sample. These images do not show any discrete metal particles attached to the alumina support.

Another feature common in the cobalt catalyst sample were large crystals. The image in figure 4.2 shows one such crystal. The lower portion of the image particularly shows square, straight-edged crystals. EDX spectra show that these crystals are approximately 65% oxygen and 35% cobalt, with only small traces of aluminum being detected, possibly as accidental data collected from other parts of the sample. These crystals are almost exclusively cobalt oxides, not elemental cobalt.

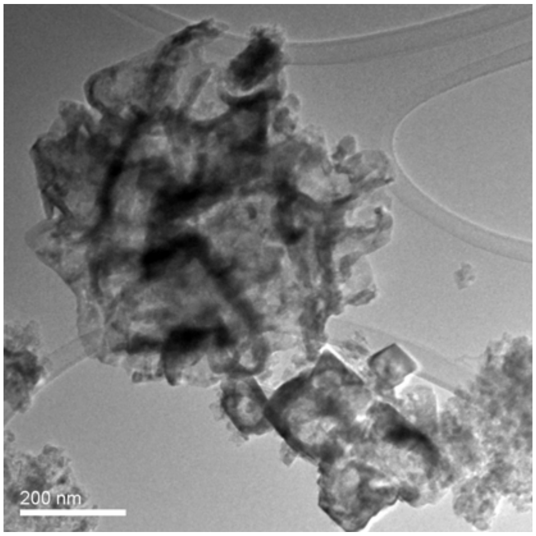

Figure 4.2 Large, square crystals of cobalt oxide.

Line scans were also used to study the cobalt catalyst with similar results. The image on the left below shows a STEM image of one catalyst chunk. The contrast in the STEM images is reversed; holes are dark, whereas thicker and denser matter is lighter. The sample shows a few bright spots up to 10 or 15 nm which are areas of increased cobalt concentration. A line scan was run across the sample along the red line from left to right; 15 points were sampled along the 50 nm path. The number of X-rays detected corresponding to each element have been counted for each point along the line scan and used to produce a graph. It is important to remember that the total number of counts can not be compared between species because of the X-ray detector sensitivity; 1500 counts of oxygen does not indicate the same number of oxygen atoms as does 1500 counts from cobalt. However, 3000 counts from oxygen do indicate twice the number of oxygen atoms as do 1500 counts.

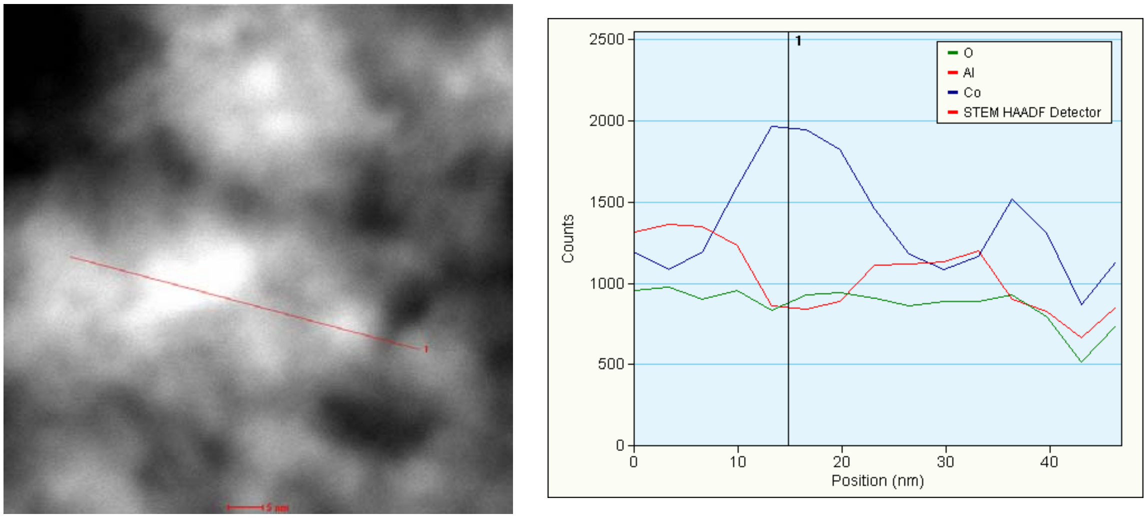

Figure 4.3 STEM image of cobalt sample at 2.3 Mx magnification (5 nm scale bar), left, with graph of oxygen, aluminum and cobalt EDX counts, right. Results show the bright areas the red line in the image passes through are areas of higher cobalt.

The graph of the results clearly shows that the two brighter spots the line passes through have higher amounts of cobalt atoms. The existence of aluminum along the entire path is not necessarily an indication that the cobalt and aluminum have mixed. The beam is transmitting completely through the sample which is only a few tens of nanometers thick and data is collected equally from the top, middle and bottom of the sample.

The most telling piece of data is the amount of oxygen found in the sample. In the center of the large cobalt particle (at about 15 nm where the vertical line in the graph is) the aluminum counts have dropped while the cobalt counts have peaked. The oxygen, however, remains fairly constant throughout the scan. At all 15 points in the scan the oxygen percentage is between 60% and 65%. The Al and Co values move up and down, but always combine to account for the remaining 35-40%.

The ration of 40:60 ratio between Al/Co and O indicate that the cobalt is not elemental, but instead has been oxidized. The aluminum oxide base has a chemical formula of Al_2O_3. Subtracting the appropriate number of oxygen atoms to account for the aluminum atoms still leaves a Co:O ratio of 40:60. If the cobalt were elemental metal, the aluminum would account for all of the oxygen atoms leaving no oxygen atoms to be associated with the cobalt.

Another image below shows a cobalt oxide particle attached to the edge of an alumina particle. The particle does not appear brighter because it is not see on top of the larger chunk, but in profile jutting off the side. The line scan run through the middle of the particle shows very low amounts of aluminum atoms present but clearly shows a peak of both cobalt and oxygen atoms across the particle. Again, the ratios show 3 oxygen atoms for every 2 cobalt atoms, indicating the presence of cobalt oxide, not elemental cobalt.

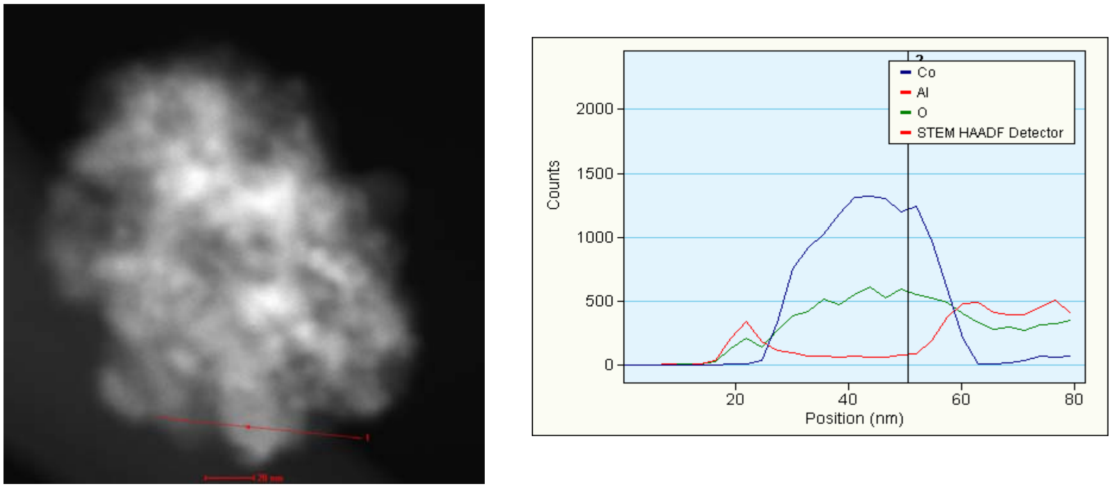

Figure 4.4 STEM image of cobalt sample (20 nm scale bar), left, with graph of oxygen, aluminum and cobalt EDX counts, right. Results show the portion of the sample the red line passes through is almost entirely cobalt oxide with very little aluminum present.

4.3 Iron Catalyst Results

The iron catalyst sample was very similar to the cobalt sample in many respects. One difference that was initially very confusing was the presence of odd looking shards in the sample. (see fig. 4.5) However, these pieces were quickly determined to be silicon dioxide (or glass) that was likely introduced to the sample during preparation. The powder was ground between two glass slides which had broken edges. Either the grinding action scraped off microscopic pieces of the slides, or they fell off the broken edge of the slide into the sample.

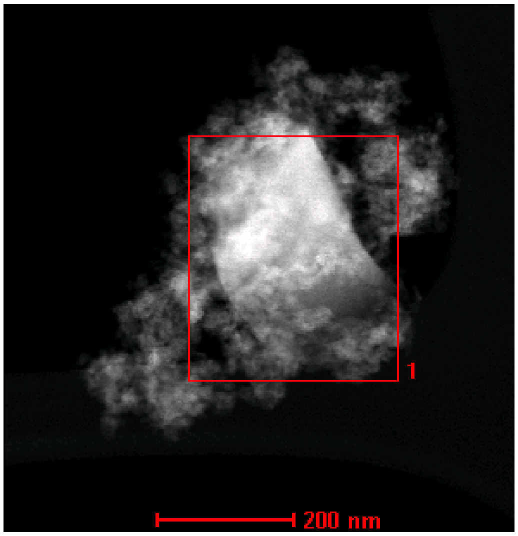

Figure 4.5 STEM image of iron catalyst sample and large glass shard.

Many of the iron catalyst samples were virtually indistinguishable from the cobalt samples. The bright field TEM images did not show any discrete iron particles (atomic number 26) which would show up clearly against the alumina support. STEM and EDX analysis showed many cases of less distinct iron oxide particles just like the cobalt oxide particles.

The iron catalyst did show some isolated elemental iron particles, however. One of these is shown in figure 4.6. The graph of the EDX spectra shows that the line passes though a part of the sample that is almost entirely elemental iron, with only a small presence of alumina support. The iron particle is not sharply defined, but is unoxidized.

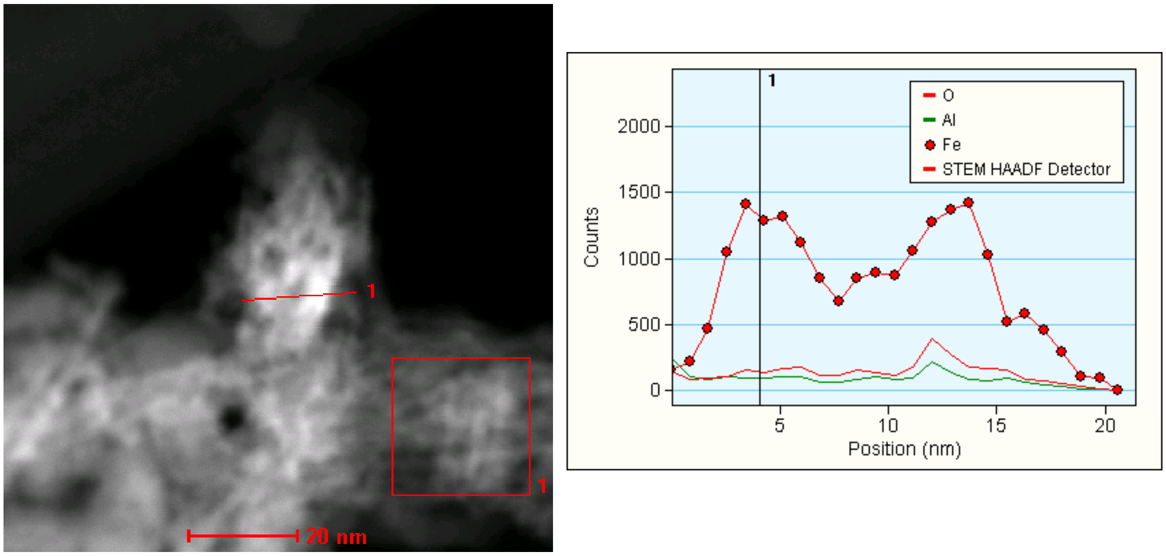

Figure 4.6 STEM image of iron catalyst at 810 kx magnification, left, with graph of EDX spectra showing oxygen, aluminum and iron counts. Data shows that the particle is almost entirely iron.

Another image (figure 4.7 on next page) shows further evidence of iron metal particles in the sample. The results are not as easily visible because this metal particle sits on top of the alumina base. For the most part, the red oxygen line tracks well with the green aluminum line; they both peak at about 4 nm and 20 nm and the oxygen counts rise only very slightly with the large iron peak with extends from about 5 to 15 nm.

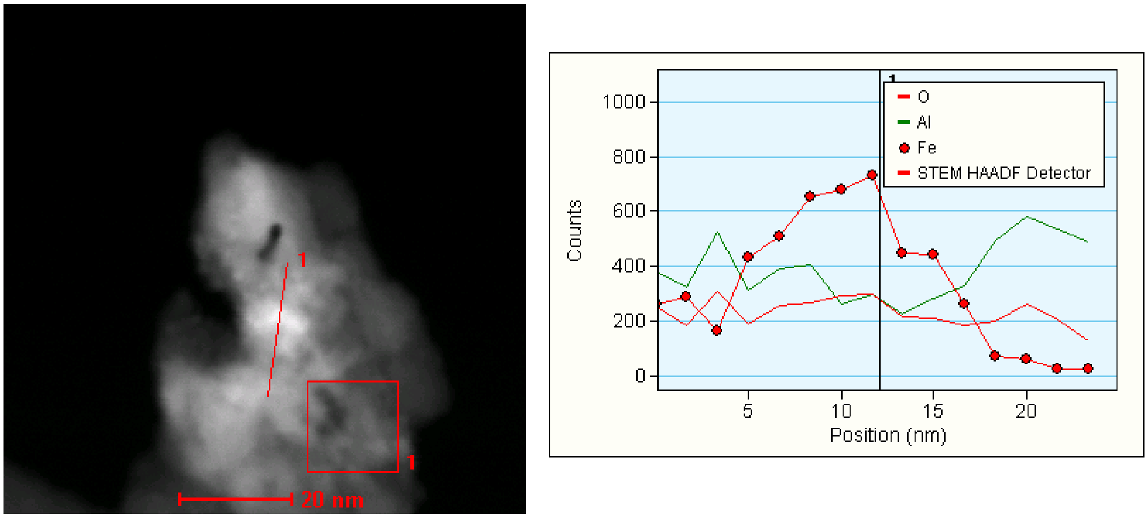

Figure 4.7 STEM image (left) of iron catalyst sample and line scan data (right) showing oxygen, aluminum and iron counts from EDX. The bright area the red line in the image passes through is an iron particle.

Chapter 5

Conclusions

The goal of creating a catalyst with many discrete metal nanoparticles evenly dispersed over the alumina support structure has not been achieved. Although nanoparticles were formed on the alumina support, they were not distinct, but rather diffuse, as though the metal had been smeared across the alumina.

The cobalt catalyst showed many large (200 nm or larger) cobalt oxide crystals where the cobalt metal had not been attached to the alumina support. Cobalt particles that did form on the support were shown to be cobalt oxide particles, not elemental cobalt, with a cobalt:oxygen ratio of 2:3.

The iron catalyst sample was somewhat more successful than the cobalt sample. In many cases the iron sample was similar to the cobalt sample, showing diffuse areas of iron oxide on the alumina support, again with an iron:oxygen ration of 2:3. However, some areas of the iron sample did show strong iron presence with very little oxygen. These iron nanoparticles had been attached to the alumina support and had not been oxidized. Also, the iron sample showed no unincorporated iron particles that were free of the alumina support.

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