Synthesis of Iron Cobalt Nanocrystals

A Major Qualifying Project Report

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Advisor

Professor Weiyong Yu

Author

Jordan Lackner

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Abstract

The objective of this project was to synthesize iron cobalt nanocrystals of specific sizes ranging from 5nm to 25nm in diameter. Starting materials of iron chloride and cobalt chloride were first reacted with sodium hydroxide to produce iron and cobalt oxides. These oxides were mixed in varying ratios with oleic acid in ODE solvent and reacted for 40 to 90 minutes by pyrolysis at 320°C to 335°C, with each variable intended to alter the size of the resulting nanocrystals. After purification, the products of favorable reactions were analyzed using TEM. Despite eight months of procedural adjustments, the experiment yielded poor results. No clear iron cobalt nanocrystals were produced, although one experiment resulted in magnetically reactive crystals that were visible to the naked eye.

Reaction

To prepare the reactants for the pyrolysis experiment, hydroxides of cobalt and iron needed to be synthesized from their respective chlorides. The reactions took place as follows:

$FeCl_3 + 3*NaOH \rightarrow Fe(OH)_3$

$CoCl_2 + 2*NaOH \rightarrow Co(OH)_2$

The pictures show iron chloride and cobalt chloride (on right).

The synthesis of the $CoFe_2O_4$ nanocrystals required a pyrolysis reaction at 325°C with oleic acid (OA). The metal hydroxides were heated past their decomposition temperature allowing the removal of water, while the oleic acid formed a complex with the metals to allow them to form a nanocrystal structure. The reaction is as follows:

$Co(OH)_2 + 2*Fe(OH)_3 + n*OA \rightarrow (325°C) \rightarrow Fe(OA)_3 + Co(OA)_2 + \mathbf{CoFe_2O_4}$

Above, n is the number of moles of OA, which varied in each experiment.

Procedure

The following steps represent the procedure carried out in the final experiment that was run.

Preparation of starting materials:

A clean 250mL flask with a magnetic stir bar was zeroed on an electronic balance. To it was added 6.25g $FeCl_2$ (2.67 moles) as well as 3.13g $CoCl_2$ (1.32 moles). About 100mL of water was added to dissolve the chlorides in solution. A solution of NaOH was prepared using 5.60g NaOH and 100mL of water. This solution was added drop-wise to the stirring chlorides, creating a thick brown precipitate. After all of the sodium hydroxide was added, the solution was centrifuged at 4000 RPM for 10 minutes. The liquid waste decanted off, and the solution was rinsed with dH2O and centrifuged three more times, before a final rinse with acetone. After the acetone was decanted off, the pellet was spread on a watch glass to dry. After drying, the metal hydroxides were ground to a fine mesh and sealed.

Starting materials (ground to a fine mesh prior to use)

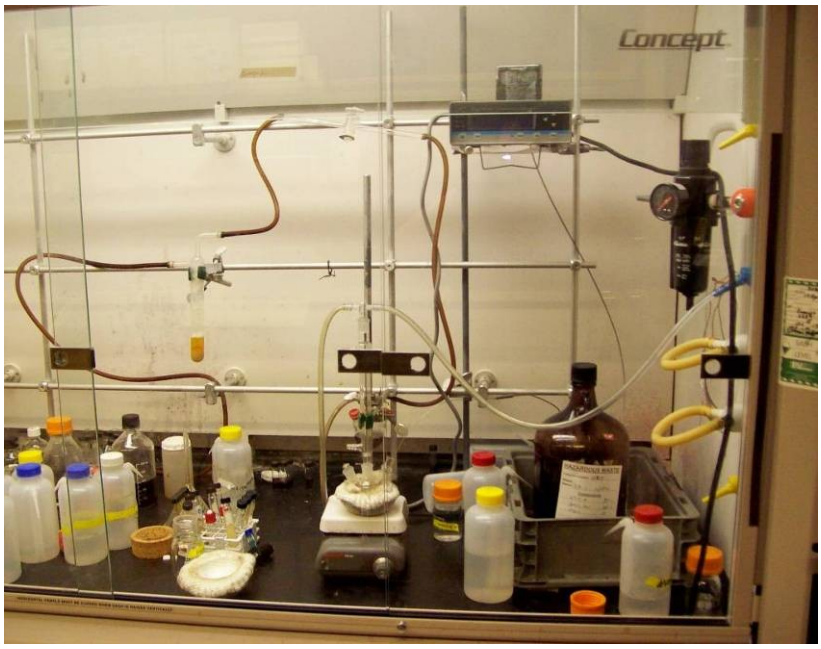
Pyrolysis of iron and cobalt hydroxides:

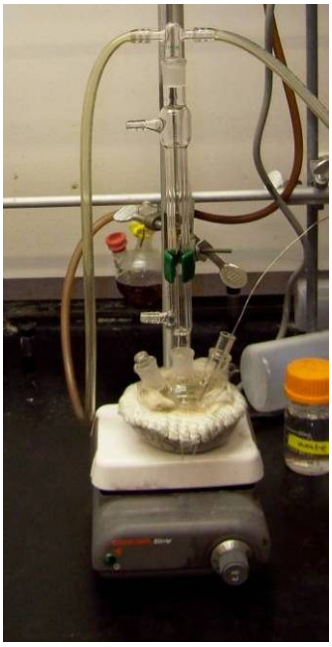
A 25mL three-neck flask was zeroed on a balance. The iron cobalt hydroxide powder was added first in the quantity of 0.10g. Then 5.16g of ODE was pipetted into the flask. After

swirling the flask briefly to mix, 5.80g of oleic acid was added to the solution. The flask was placed on a heating mantle with a stir bar, thermocouple, ground glass stopper, and jacketed condenser (similar setup to Figure A). The system was cleared with nitrogen gas, which continued to flow for the duration of the experiment. The stir bar was set to its maximum speed, while the thermocouple was run at 325°C. After reaching 325°C, the solution was held at that temperature for 60 minutes, before the thermocouple was reset to room temperature. The solution was allowed to cool slowly to 100°, before being removed from the heating mantle and cooled to room temperature.

25mL three-neck flask

Oleic acid, Fe/Co hydroxide, and Octadecene



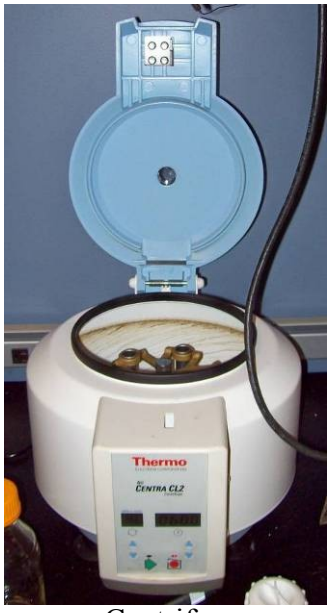


The pictures above show the pyrolysis reaction setup.

Purification and isolation of nanocrystals:

The liquid from the reaction flask was transferred to four sealable test tubes in equal quantities. Acetone was mixed into each tube, until they were full and mixed. The tubes were then centrifuged for 4 minutes at 4000 RPM, and the supernatant was decanted. About 2mL of chloroform was used to resuspend the pellet, before refilling each tube with acetone and centrifuging again. This process was repeated three more times, allowing the oil to be removed from the nanocrystals. If the four minute centrifugation failed to produce a clear supernatant, a portion of the supernatant was mixed in a new tube with methanol to determine whether black nanocrystals precipitated out.

Methanol, ethyl alcohol, acetone, and chloroform



Centrifuge

Analysis and Results

The best instrument for analyzing nanocrystals is the TEM (Transmission Electron Microscope). The experimental product needed to be completely cleaned of oil to allow the individual particles to be clearly resolved. After the purification and isolation step of the procedure, the product should have been a fine black powder suspended in solvent. The pyrolysis and purification steps were conducted on twelve separate occasions, but only two products appeared good enough to analyze by TEM. Neither product was visible on the display, indicating that nanocrystals were not formed. One of the products had visible magnetically reactive particles, indicating that the particle size was too large. The experimental objective of synthesizing nanocrystals was not achieved.

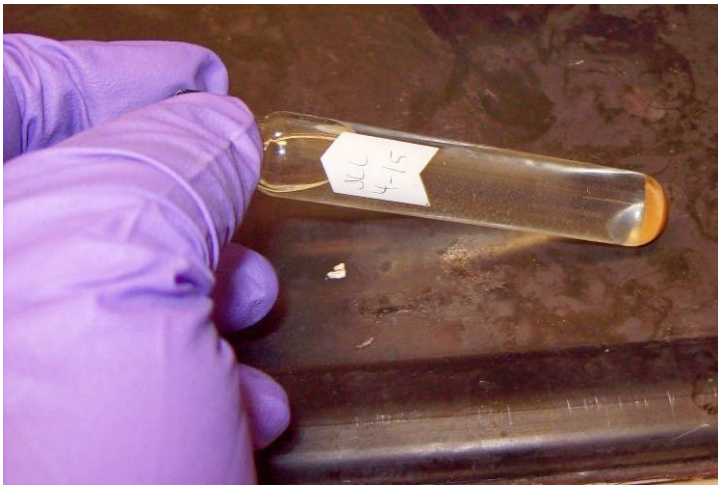
There are several possible reasons the experiments didn't work. At first, a ratio of 6 moles of oleic acid per mole of metal hydroxides was used. This ratio did not allow the formation of crystals, because there was not enough oleic acid for the metals to be stable in the solvent without water. The ratio was increased to 20:1 for a few experiments, but that was still not enough. In one experiment with an oleic acid to metal ratio of 40:1, magnetically active iron cobalt particles were formed, but they were too large to be nanocrystals. Despite more attempts with this ratio, nanocrystals would not form. Another variable that was changed repeatedly was the pyrolysis run time. The runs varied from 40 to 90 minutes, but most were from 55 to 65 minutes. The longer run times, with all other variables kept the same, tended to produce blacker, thicker products than the shorter run times. The heating time needed to be kept short enough that the particles created were not too large, but long enough that the hydroxides completely decomposed. A time of about 65 minutes seemed to work the best. If future experiments are

conducted using this method, a 30-40 to one ratio of oleic acid and 65 to 70 minute run time should be tested first.

The most thought intensive part of the project was the purification and isolation steps in preparation for the TEM. Even if nanocrystals were created in any of the experiments, they needed to be treated appropriately to be seen. Acetone was the primary chemical used in the procedure, because it was able to bind with the ODE and OA, removing them from the metal products. After centrifuging and decanting the clear acetone and oil mixture from the product, a small amount of chloroform was added to remove oil from the particles more harshly, before acetone was added to help dissolve the waste products. This process required careful monitoring to ensure the product was centrifuged long enough to not be lost in the decanting step. When the solution would not turn clear, a portion of the liquid was transferred to another tube containing methanol. Out of twelve reactions, only two were purified to a decent looking product, neither of which actually contained nanocrystals. It is difficult to say whether improvement was needed in this area without knowing whether nanocrystals were formed in any experiment.

In the last five experiments, a different procedure was used to make the hydroxide starting materials (represented in the "Preparation of Starting Materials" section of the procedure). Previously, separate iron and cobalt hydroxides were made in their own flasks, but for the new batch, they were made together. These experiments produced a dark solid that centrifuged to the bottom of each tube, as well as a small amount of tan solid at the top of each pellet. The purification of each of these resulted in completely tan particles, which often were suspended in the chloroform/acetone mixture even after centrifugation. Even when only the dark particles were extracted from the bottom of the pellets by pipette, a black crystal could not be procured. Since each of the five experiments with vastly different variables ended with very

similar results, the starting materials are likely to blame. Producing the iron and cobalt hydroxides separately seems preferable to synthesizing them in the same reaction vessel.



The most recent product after centrifugation in acetone.

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