

CHARACTERIZATION OF SULFIDED IRON CATALYSTS

Ram Srinivasan, Robert A. Keogh, and
Burtron H. Davis

Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511

ABSTRACT

An ultrafine iron oxide and a FeOOH sample were sulfided using a H₂S/N₂ mixture at room temperature. The sulfided samples obtained at room temperature were also run in a microautoclave reactor using a temperature of 200°C for 30 min. using a H₂S/H₂ atmosphere and tetralin as a solvent. The sulfided iron catalysts were characterized by TEM and EDAX.

INTRODUCTION

Coal liquefaction can be accomplished by thermolysis; however, it was quickly realized that improved yields could be obtained through the use of catalyst (1). One of the first catalysts studied was an iron oxide in one of several forms (1-3) and is still widely used today (4).

Initial coal liquefaction products may have very high molecular weights. These initial dissolution products are so large that they will not be able to diffuse into the smaller pores of most heterogeneous catalysts. It is therefore desirable that catalysts, especially those used in the reactor which involve the initial dissolution reactions, have the active component on the geometric surface of the catalyst particle. It is also desirable that these catalysts have a high surface area in order to obtain a high rate of conversion. These two factors indicate that the desirable catalyst will be one which is comprised of colloidal or smaller nonporous individual particles.

Although a large volume of work has been carried out to determine product yield, reaction conditions, etc., very limited work has been available in terms of microscopic characterization of catalyst powders. The results presented in this work used an ultrafine γ -Fe₂O₃ (S.A. = 270 m²/g) and an γ -FeOOH precursor which have been sulfided at room temperature and at higher temperatures. The characterization of these catalysts are presented.

EXPERIMENTAL

The γ -Fe₂O₃ and γ -FeOOH were hydrated in a chamber saturated with H₂O prior to sulfidation. Both catalyst precursors showed approximately a 28 wt.% gain in 48 hours. The dry samples could not be sulfided at room temperature. The catalyst precursors were sulfided using 5 mole % H₂S in nitrogen. Approximately 2g of the hydrated precursors were placed in a flask containing ca. 20g of tetralin and the H₂S/N₂ mixture was bubbled through the catalyst/tetralin slurry. The resulting sulfided samples were stored in the flask under the H₂S/N₂ atmosphere prior to running at 200°C in the batch autoclave and

analysis. Aliquots of the sulfided catalysts/tetralin slurry were transferred to a 25cc microautoclave reactor. The reactor was pressurized to 800 psig (ambient) with a 10% H₂S in H₂ and placed in a fluidized sand bath. The reaction was run at 200°C for 30 min.

The samples for electron transmission microscopy (TEM) analysis were prepared in the glovebox in flowing nitrogen. A few drops of the sample were transferred to a 100 cc beaker and washed with ethanol twice, and then ultrasonically agitated in ethanol. A drop of this suspension was placed on a carbon coated 200 mesh copper grids. Ethanol evaporated leaving a thin film of particles on the grids. These TEM grids were then transferred to a vacuum desiccator until they were inserted into the microscope. While transferring the samples into the microscope the samples were exposed to the atmosphere less than a minute.

For TEM analysis, a Hitachi H800 NA scanning microscope was used at 200 kV. Microdiffraction and energy-dispersive X-ray (EDX) analyses were carried out in a nanoprobe mode (5 nm). This implies that the microdiffraction and EDX data obtained were from a 5 nm regions of the sample. This microscope is equipped with a silicon-lithium diode detector (Link) and a multi-channel analyzer (Tracor 500). The X-rays emitted by the specimen were collected in the range 0-20 KeV for 60 seconds.

RESULTS AND DISCUSSION

Room Temperature Sulfidation of γ -FeOOH

Many agglomerated large "blobs" were seen for this sample. Microdiffraction patterns could not be obtained from these blobs. A typical electron micrograph is presented in Figure 1. EDX from these blobs yielded very strong FeK α and SK α lines. These large blobs easily disintegrated under the beam giving rise to a good dispersion of small hexagonal particles. A representative micrograph from such a dispersed area of the sample is presented in Figure 2. EDX from these particles showed only FeK α , and these individual particles yielded microdiffraction patterns.

γ -FeOOH Sulfidation at 200°C

Contrary to the results of the above sample at room temperature, this sample contains large, thin hexagonal iron sulfide crystals. A typical micrograph of this sample is presented in Figure 3. EDX analysis of the large hexagonal crystals yielded strong signals for both FeK α and SK α lines. A typical electron microdiffraction pattern obtained from one such crystal is presented in Figure 4. This microdiffraction patterns indicates that the crystal is Fe₇S₈ in [001]_{hcp} orientation. Microdiffraction patterns and EDX data from several hexagonal particles consistently proved that these large hexagonal crystals are Fe₇S₈.

Room Temperature Sulfidation of γ -Fe₂O₃

This sample contains regions of free sulfur and needle-shaped α -Fe₂O₃. A region containing long needles of α -Fe₂O₃ is shown in Figure 5. Electron microdiffraction pattern obtained from these particles indicated that these sticks are α -Fe₂O₃. EDX data from these needles showed only FeK α . A typical region containing free sulfur in the form of flowers is shown in Figure 6. EDX from this region showed only sulfur. Also, regions containing hexagonal dense sulfur particles were evident as shown in Figure 7. No evidence for iron sulfide particles was obtained. Consequently, it appears that the α -Fe₂O₃ converts H₂S to

S plus H₂, more likely, that the sulfide formed is oxidized during the brief exposure to air during sample transfer.

γ -Fe₂O₃ Sulfidation at 200°C

This sample contained regions of both long, rectangular particles and the large hexagonal particles. As before, the large, thin hexagonal particles were found to be Fe₇S₈ crystals both by electron microdiffraction and EDX analyses. A bright field electron micrograph (Figure 8) shows the presence of both these two kinds of particles. A typical electron microdiffraction pattern obtained from one of the large hexagonal crystals is presented in Figure 9, which is [001]_{hcp} orientation. No free sulfur could be identified as was the case for the sample sulfided at room temperature.

ACKNOWLEDGMENT

This work was supported by the Commonwealth of Kentucky and DOE Contract No. DE-FC22-88PC8806 as part of the Consortium for Fossil Fuel Liquefaction Science (administered by the University of Kentucky).

REFERENCES

1. Bergius, F., "Chemical Reaction Under High Pressure", Nobel Lecture, May 21, 1932.
2. Stranges, A. N., *Fuel Proc. Tech.*, **1987**, 16, 205.
3. Wu, W. R. K.; Storch, H. H., "Hydrogenation of Coal and Tar", Bulletin 683, Bureau of Mines, U.S. Department of Interior, Washington, DC, 1968.
4. Lee, J. M.; Cantrell, C. E.; Gollakota, S. V.; Davies, O. L.; Corser, M. M.; Vimalchand, P., *ACS Div. Fuel Chem. Preprints*, **1991**, 36, 1915.

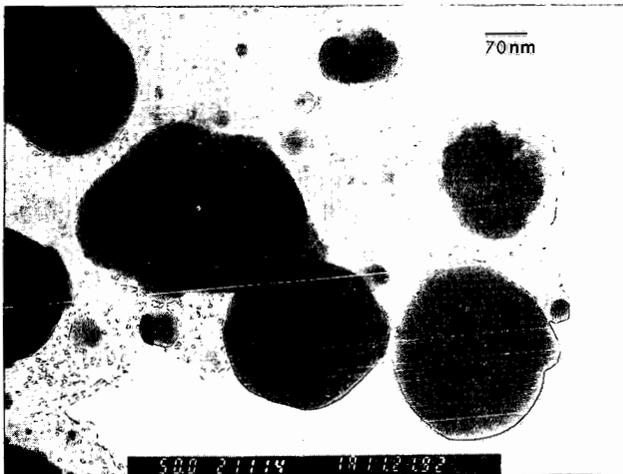


Figure 1. Typical micrograph of the "blobs" from the room temperature sulfidation of γ -FeOOH.

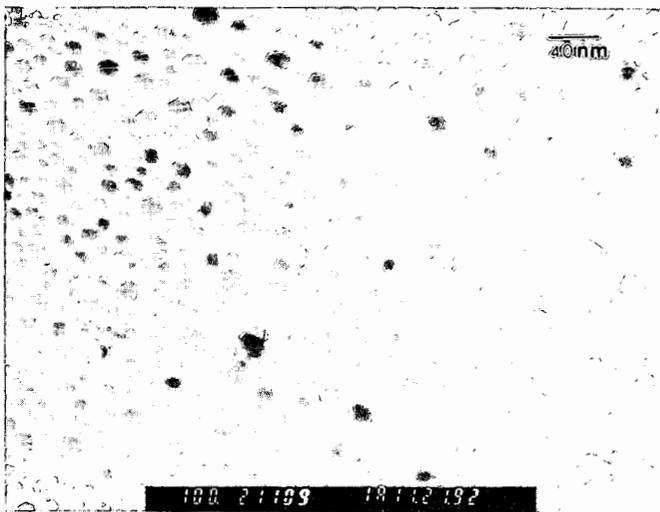


Figure 2. Micrograph of the disintegrated "blobs" using the electron beam.



Figure 3. Micrograph of the particles from the sulfidation of γ -FeOOH at 200°C.

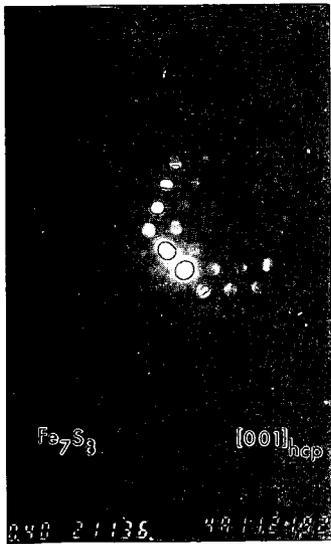


Figure 4. Microdiffraction pattern of the sulfided γ -FeOOH at 200°C.

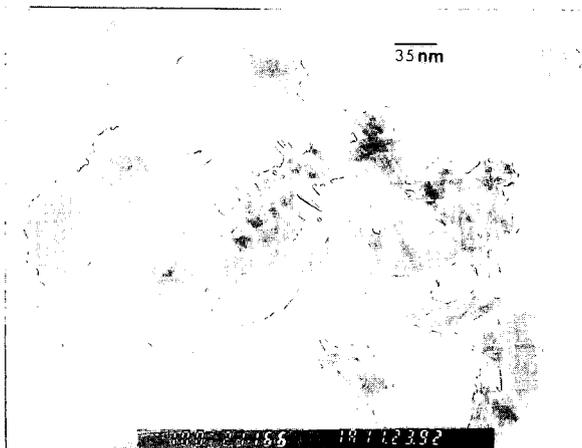


Figure 5. Micrograph of the particles from the room temperature sulfidation of γ - Fe_2O_3 .



Figure 6. Micrograph of the region containing free sulfur from the room temperature sulfidation of γ - Fe_2O_3 .

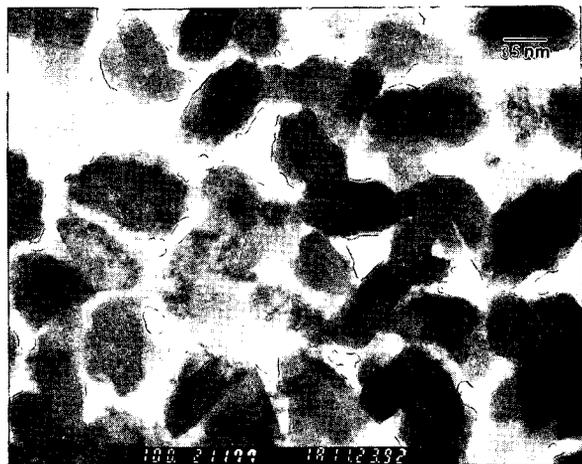


Figure 7. Micrograph of the region containing hexagonal sulfur from the room temperature sulfidation of $\gamma\text{-Fe}_2\text{O}_3$.

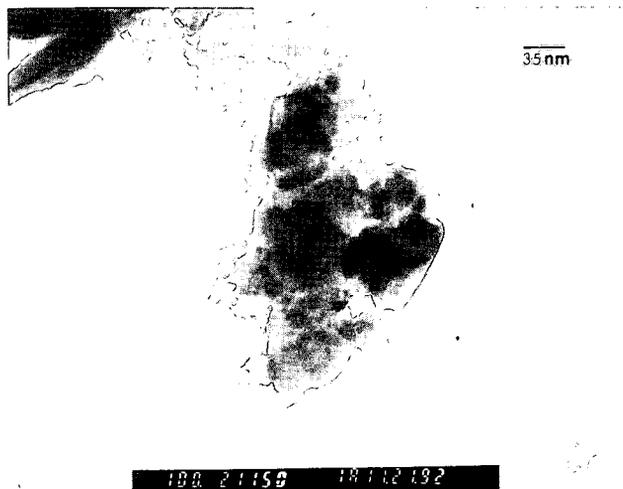


Figure 8. A bright field electron micrograph of the $\gamma\text{-Fe}_2\text{O}_3$ sample sulfided at 200°C.

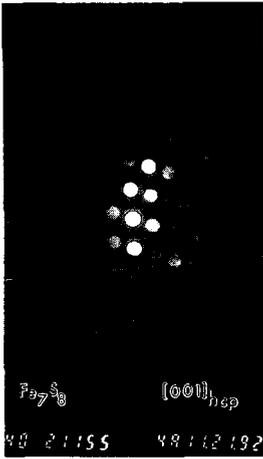


Figure 9. Microdiffraction pattern from the large hexagonal particles ($\gamma\text{-Fe}_2\text{O}_3$) sulfidation at 200°C.