TITLE: Particle size Distribution of Catalysts determined by X-Ray Diffraction and Magnetometry

AUTHORS: M. M. Ibrahim and M. S. Seehra

INSTITUTION: Physics Department, West Virginia University, Morgantown, WV 26506

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OBJECTIVES:

The primary objective of this work is to develop methodology for determining the particle size distribution of catalysts used in coal liquefaction (since the efficiency of a catalyst depends on the particle size). We show that for particles in the range of 10Å to about 500Å, line broadening of the Bragg peaks in x-ray diffraction (XRD) provides an accurate determination of the particle size. For catalysts which exhibit superparamagnetic behavior (such as those based on Fe, Co and Ni), a determination of the particle size distribution using magnetometry is possible. Comparison of the results obtained on an Fe_2O_3-based catalyst using x-ray diffraction, magnetometry and Mössbauer spectroscopy are presented.

EXPERIMENTAL DETAILS:

The sample of α-Fe_2O_3 based catalyst employed in this work (Sample I) was provided by Dr. G. P. Huffman on which some Mössbauer and XAFS studies [1] and catalytic studies [2] have been reported recently. This sample is partially sulfated to α-Fe_2O_3/SO_4 (up to 6%). For XRD studies, a Rigaku D-max diffractometer available in our laboratory was employed. For magnetic measurements, a SQUID magnetometer (Quantum Design Model MPMS) was used, employing about 10 mg of sample, temperature range of 5 K - 400 K and magnetic fields up to 55 kOe. For comparison purposes, measurements on a bulk sample of α-Fe_2O_3 obtained by powdering a single crystal, are also reported.

ACCOMPLISHMENTS:

Details of the theory used for determining the particle size distribution from the XRD and magnetometry data have been given in a recent publication [3]. Here we report only some major results and conclusions.

In Fig. 1, we show the x-ray diffractograms of the powdered α-Fe_2O_3 sample and the α-Fe_2O_3/SO_4 catalyst (before and after the liquefaction experiment). It is obvious that the Bragg lines are broader for the α-Fe_2O_3/SO_4 sample as compared to the powdered Fe_2O_3 sample. This broadening is due to smaller particle size. Using the Scherrer equation for line broadening of Bragg peaks in XRD, particle radii varying between 75Å and 110Å using different peaks are obtained. After liquefaction, XRD data shows that the sample has converted primarily to pyrrhotite (Fig. 1).

Determination of the particle size from magnetic measurements is more complicated and involved although in favorable cases, this technique allows determination of not only the average particle size but also a particle size distribution (for details see Ref. 3). In Fig. 2, we show four sets of graphs. In Fig. 2(a) magnetic susceptibility χ for Fe_2O_3/SO_4 is plotted against temperature under the zero-field-cooled (ZFC) and field cooled (FC) conditions. Below about 100 K, the two measurements fork out, suggesting that above this blocking temperature of $\approx$ 100 K, the material is superparamagnetic. The proof of the superparamagnetic behavior is that the reduced magnetization, M/M_∞, should scale as H/T, where H is the applied field. In Fig. 2(b), plots of M/M_∞ vs H/T at several temperatures show that at temperatures of 220 K, 300 K and 350 K, the data coincide confirming the superparamagnetic behavior at these temperatures. This data of M/M_∞ vs H (Fig. 2(c)) can then be used to determine the particle size distribution, assuming a log normal distribution. Details of the procedures are given in Ref. 3, and the obtained distribution is shown in Fig. 2(d). As a consistency check, this obtained distribution is then used to calculate M/M_∞ vs H (dotted curve in Fig. 2(c)). A close agreement with experiment assures self-consistency.

We next compare the above results with the results obtained from XRD and Mössbauer measurements. For XRD, a particle radius of 75 to 110Å was obtained and this is well within the range shown in Fig. 2(d) obtained magnetic measurements. The Mössbauer measurements of Huffman et al [1] yielded the following results: 12% of the particles have < 29Å diameter, 45% have diameters from 29Å - 85Å and the remaining 43% have diameters larger than 85Å. Considering the ±10Å uncertainty in all three techniques, the results presented here are quite consistent.

In comparing the three techniques, XRD provides the most direct and rapid evaluation of the particle size, although the technique works only for crystalline particles and a size distribution is not obtained. Both magnetic and Mössbauer studies involve extensive analysis of the data and the techniques only work for superparamagnetic particles. However, when applicable, they provide more detailed information, in particular the magnetic studies where a particle size distribution can be obtained as shown here.

PLANS:

Future plans include determination of the accuracies, and limitations of the XRD and magnetic techniques for determining the particle size distribution of catalysts. Measurements on catalysts of different shapes and sizes are underway for this purpose.

REFERENCES:

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3. M. M. Ibrahim, J. Zhao and M. S. Seehra, J. Mater. Res. (submitted).

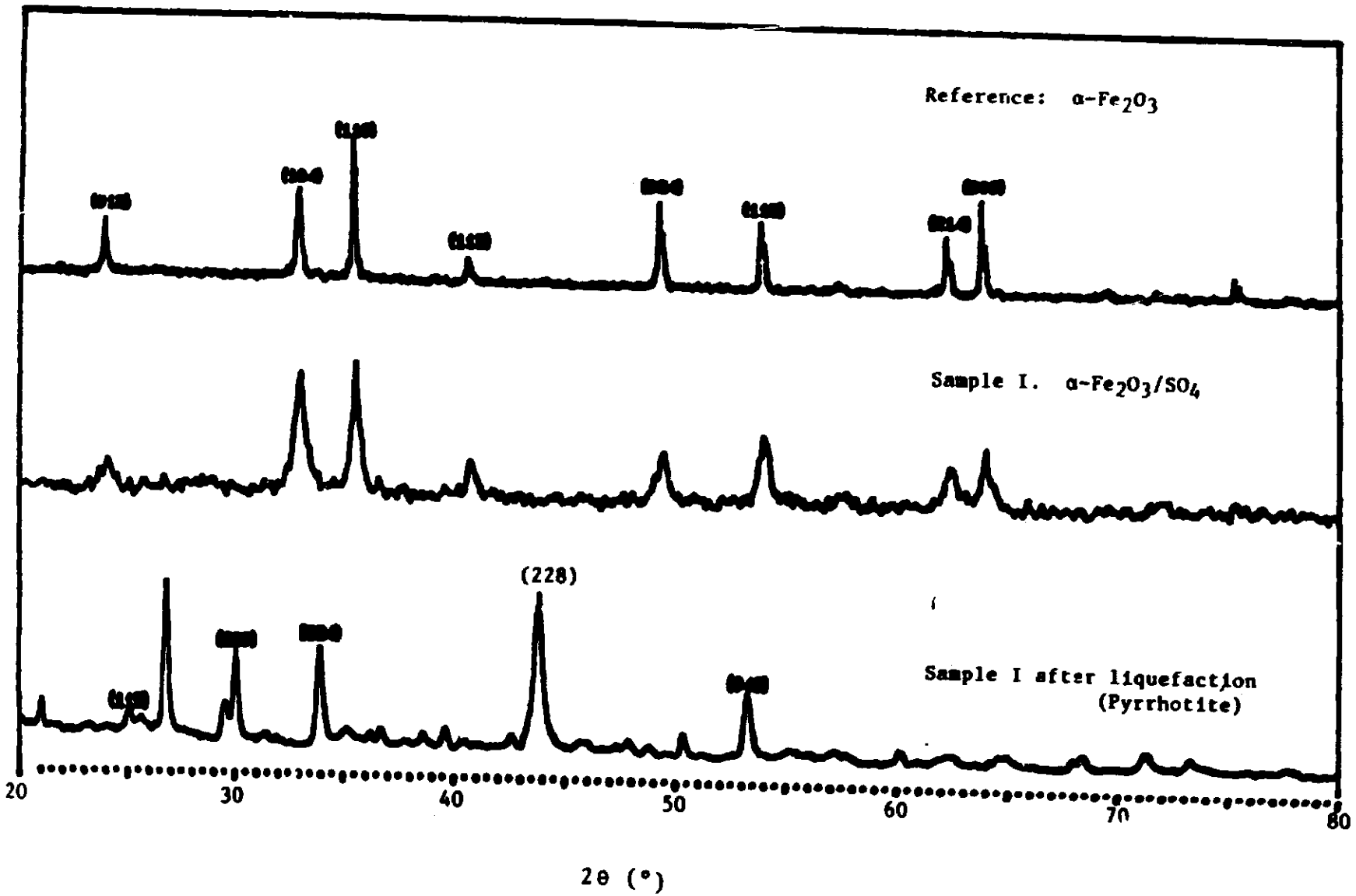
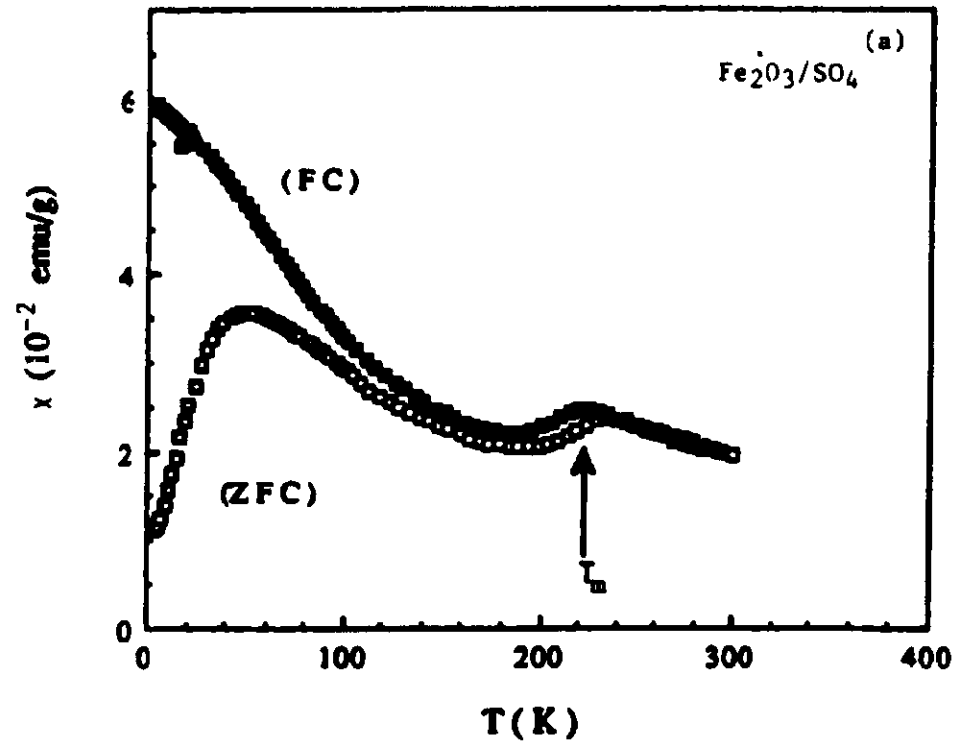
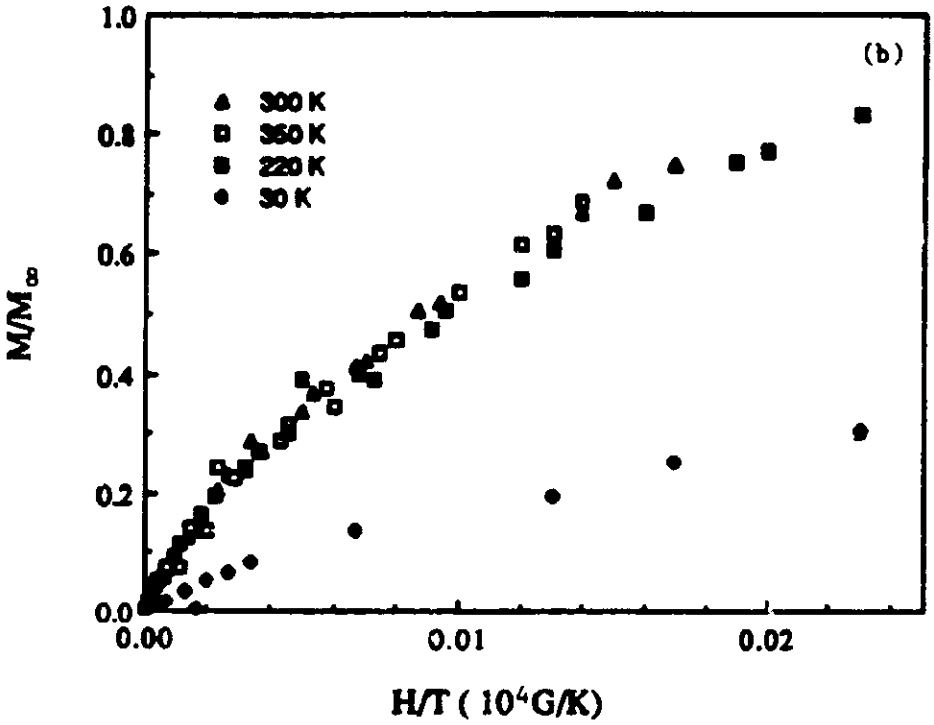
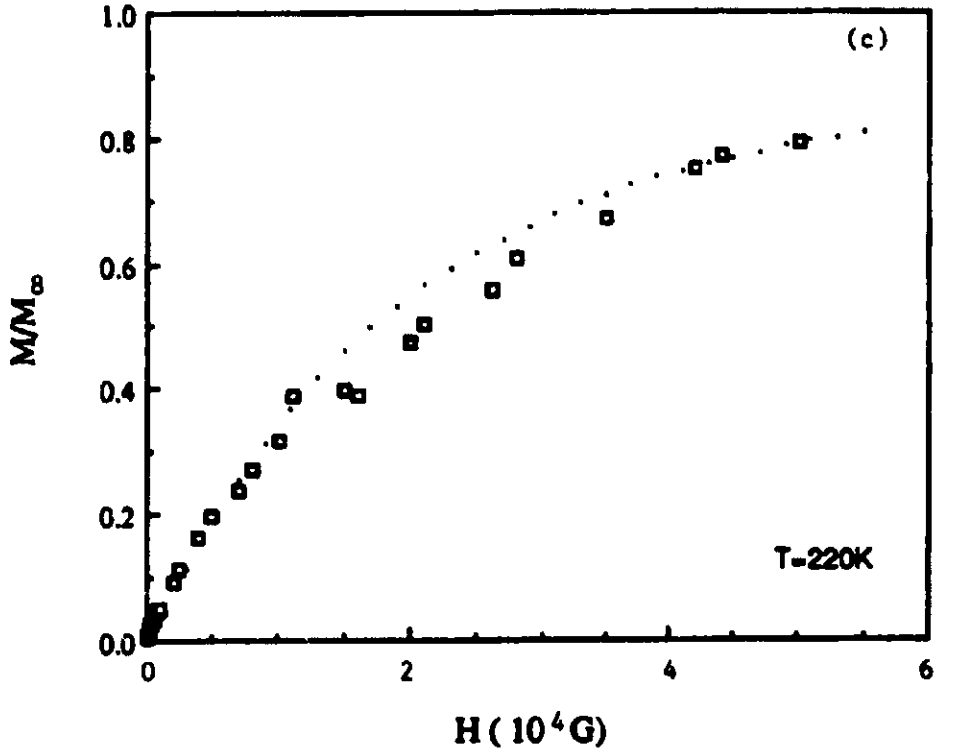


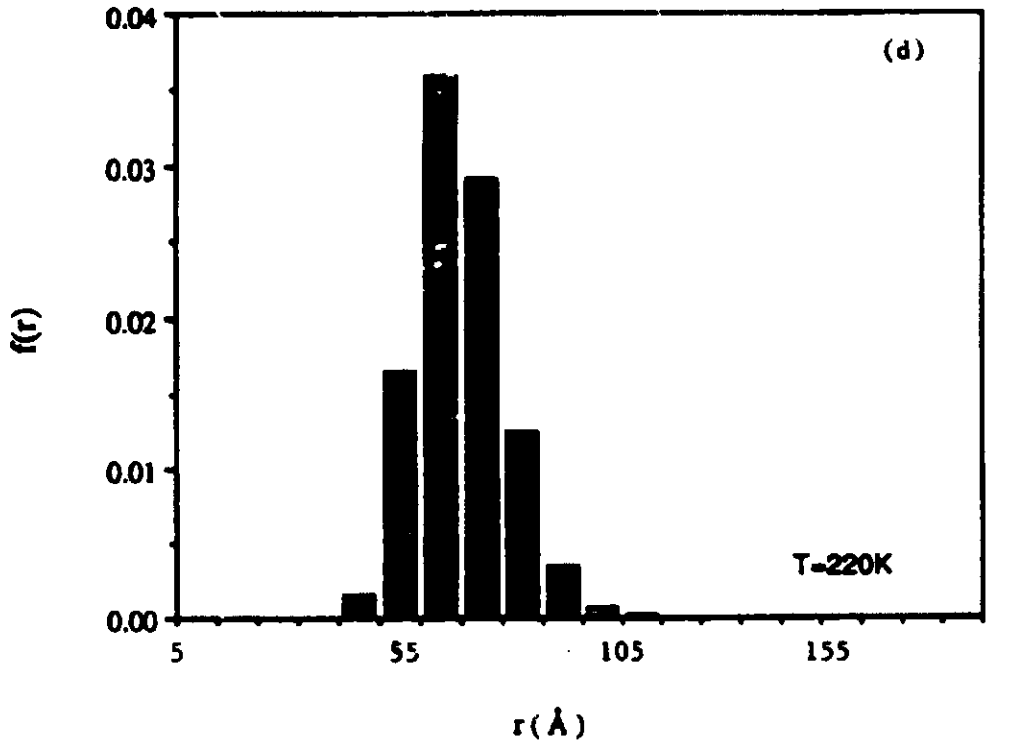
Fig. 1. X-ray diffractograms of coarse Fe_2O_3 particles, Fe_2O_3/SO_4^{2-} catalyst before liquefaction and after liquefaction.





Figs. 2a and 2b. See text for details.





Figs. 2c and 2d. See text for details.