AN EVALUATION OF PARTICLE SIZE MEASUREMENT TECHNIQUES FOR DISPERSED IRON CATALYSTS

V.U.S. Rao
Department of Energy
Pittsburgh Energy Technology Center
P.O.Box 10940
Pittsburgh, PA 15236.

Keywords: Highly dispersed catalysts, Direct coal liquefaction

Abstract

Highly dispersed iron-based catalysts are being examined for the initial stage of direct coal liquefaction. Ultrafine (<10 nm) particles are produced by a variety of methods. Mössbauer spectroscopy, magnetometry, XAFS, electron microscopy, XRD line-broadening, and BET surface area measurement are used to estimate the particle size of the catalyst precursor and, in some instances, of the phases found consequent to the reaction process. With Mössbauer and magnetization techniques, data have to be obtained over a range of temperatures, usually from 4 K to 300 K. In addition, obtaining the particle size by Mössbauer spectroscopy requires a knowledge of the magnetic anisotropy energy. For some XRD lines, the broadening is a consequence of the presence of fault planes rather than crystallite size. The utility of the characterization techniques will be evaluated and comparative results that are available will be presented.

Introduction

The use of inexpensive, ultrafine (<10 nm) iron catalysts for the initial stage of direct coal liquefaction [1] and the conversion of model compounds [2] has attracted attention in recent years. An advantage of using iron is that its disposal after use is not likely to present environmental problems. Hence the development of nanometer-sized, iron-based catalysts could eliminate the need for the expensive catalyst recovery step associated with the more conventional catalysts based on elements such as Mo, Co, Ni and W. Recent studies [1] indicate that ultrafine iron-based catalysts could be active for the first step in coal liquefaction, i.e., solubilization, in concentrations as low as 3,500 ppm with respect to coal.

To support research on the synthesis and testing of iron-based catalysts, it is necessary to have techniques to determine the composition, structural characteristics, and particle size distribution of the catalyst precursor, and more importantly, of the phases during and after the reaction. In the case of iron-based catalysts, the characterization techniques include Mössbauer spectroscopy, magnetometry, XAFS, electron diffraction, XRD, and BET surface area measurement. This paper will attempt to analyze the information that could be obtained from the above techniques and provide comparative results where available.

Phases in Iron-Based Catalysts

It is frequently observed that an iron-based catalyst precursor that is not a sulfide is converted into a sulfided form during coal liquefaction if sufficient sulfur is present in the reaction mixture. The sulfur could be present in coal itself or added as H_2S or S.

A significant fraction of the inorganic sulfur in coal is found as pyrite (FeS_2) which is transformed into pyrrhotite ($Fe_{1-x}S$) under liquefaction conditions according to

$$FeS_2 + (1+x)H_2 \rightarrow Fe_{1-x}S + (1+x)H_2S \quad (1)$$

Depending on the reaction temperature and the partial pressures of H_2 and H_2S, different pyrrhotites characterized by the value of x (typically .07-.12) are observed. The transformation of pyrite to pyrrhotite is slow below 400°C [3].

To investigate the influence of low concentrations of iron-based catalysts, a coal with a minimal quantity of pyrite must be used. For this reason, recent investigations [1] have focussed on the liquefaction of the low-pyrite Blind Canyon coal from Utah [4], which contains only 0.02 wt% pyritic sulfur, compared to 2.1 wt% in Illinois #6 and 0.17 wt% in Wyodak coal.

The approach to attaining ultrafine particle catalysts has been to increase the dispersion of the precursor. Complexes of iron [5], sulfate-promoted oxides [1], and carbides [6] have been used as precursors. In direct liquefaction, in the presence of sufficient sulfur, pyrrhotites are formed, for example [1],

$$Fe_2O_3/SO_4 + S + H_2 \rightarrow Fe_{1-x}S + H_2S + (SO_2, H_2O \text{ etc.}) \quad (2)$$

For compositions ranging between FeS (troilite) and Fe_7S_8 (monoclinic pyrrhotite), the compounds are referred to generally as pyrrhotites [7]. These include Fe_9S_{10}, $Fe_{10}S_{11}$, and $Fe_{11}S_{12}$ which are hexagonal, as is FeS. The hexagonal pyrrhotites are characterized crystallographically by their superstructures of the hexagonal NiAs structure.

It should be mentioned that the above phases are "low-temperature" pyrrhotites. Above 308°C and below its maximum melting point of 1190°C, pyrrhotite exhibits a rather wide homogeneity range as a single solid solution $Fe_{1-x}S$ with the NiAs structure, extending from the stoichiometric FeS to a composition of approximately $Fe_{0.8}S$. Irrespective of the phases found at room temperature in used catalyst samples, it is evident that at liquefaction temperature (350-425°C) the solid solution $Fe_{1-x}S$ is expected. Therefore, *in situ* characterization of the catalyst at reaction condition, although difficult to perform, is desirable.

Mössbauer Relaxation Spectra

The technique of Mössbauer Spectroscopy can be used to detect iron-bearing phases in coal and in liquefaction catalysts [8]. Since the pyrrhotites show magnetic ordering, magnetic hyperfine splitting resulting in a sextet for each magnetically inequivalent Fe site is observed in the Mössbauer spectrum and can be used to identify the phases present [9, 10]. The spectra are frequently

interpreted in terms of three or four inequivalent Fe sites, which have internal magnetic fields in the range 230 to 300 kOe.

In magnetically ordered materials such as the pyrrhotites and Fe_2O_3, one would expect the sextet pattern to broaden and collapse to a quadruple doublet as the particle diameter decreases below a critical diameter, d_c. The corresponding particle volume is designated V_c. Below d_c, the particles exhibit superparamagnetic behavior owing to rapid relaxation of the particle spin system. V_c is given by

$$V_c = kT \ln(f_o/f_L) \ / \ K_o \tag{3}$$

where K_a is the magnetic anisotropy energy, f_L is the Larmor precession frequency of the ^{57}Fe nucleus, and f_o is a frequency factor which has to be determined for each phase. The particle size distribution can be obtained from an analysis of the Mössbauer relaxation spectra [11].

From an analysis of the Mössbauer relaxation spectra, at temperatures from 10 K to 300 K, of a narrow-size range Fe_2O_3 with the particle diameter centered at 3.2 nm, and using K_a = 0.55 J/m^3 [12], Huffman et al [10] have determined that f_o = 10^{12} s^{-1}. The critical diameter d_c was determined to be 11.8 nm for Fe_2O_3 at 300 K.

Using the above parameters, the particle size range of Fe_2O_3/SO_4 precursors was determined [10] from the observed Mössbauer relaxation spectra. The size distribution showed that nearly 50% of the Fe was in particles that had diameters less than 11.8 nm. The methodology for determining particle size distribution of Fe_2O_3 and related compounds such as FeOOH from Mössbauer relaxation spectra appears to have been established.

In contrast to the above, Mössbauer spectra of pyrrhotites, attributing the unresolved lines to superparamgnetic particles, have been reported in only a few instances [13-15]. Even in these cases, only room temperature spectra were reported; hence the interpretation of the unresolved lines is not unequivocal.

A possible reason for the paucity of confirmed Mössbauer relaxation spectra in pyrrhotites could be the high value of the magnetic anisotropy energy; for example, K_a = 10 J/m^3 for Fe_7S_8 [16,17]. If f_o for Fe_7S_8 is the same as that for Fe_2O_3, one estimates the critical diameter of Fe_7S_8 as being d_c = 4 nm at 300 K. It would appear that the samples that have been examined by Mössbauer spectroscopy do not have pyrrhotite particles whose diameter is less than 4 nm.

Recent progress in the synthesis of fine particles using novel techniques, such as the microemulsion method [18], provides the possibility of synthesizing uniform-size pyrrhotite particles in the 4 nm range. It would then be possible to determine f_o for the pyrrhotites as was done in the case of Fe_2O_3, and use the value of f_o thus derived to estimate the pyrrhotite particle size in liquefaction catalysts.

Magnetometry

In favorable cases particle size distribution can be determined from a measurement of magnetization in a range of applied fields and temperatures [19]. The technique is applicable when the particles in the sample are super-

paramagnetic. In the range of temperatures in which the sample exhibits superparamagnetic behavior, the magnetization is a function of H/T and obeys the Langevin equation:

$$M/M_\infty = L(M_s VH/kT), \quad L(x) = \coth x - 1/x \tag{4}$$

where M_∞ and M_s are, respectively, the saturation and spontaneous magnetizations per unit volume, and V is the volume of the particle.

Using a SQUID magnetometer, Ibrahim et al. [19] have determined the particle size distribution of Fe_2O_3/SO_4 samples. A significant fraction of the sample consisted of particles in the 6-10 nm range. The results were in reasonable agreement with the particle size distribution obtained from Mössbauer relaxation spectra. The magnetometric method has not yet been used to determine the particle size of pyrrhotite samples.

XAFS Spectroscopy

Attempts are being made to use XAFS spectroscopy to obtain particle size information on Fe-based catalysts. The analysis of the XAFS spectra provides information on the interatomic distances and coordination numbers of the various neighbor shells to a given Fe atom. Spectra of bulk Fe_2O_3 were compared with those of the fine-particle Fe_2O_3/SO_4 catalyst precursor [10]. While the interatomic distances were similar for the two samples, the average coordination number of the catalyst precursor was significantly lower than that of the bulk sample. This indicated that the Fe atoms in the ultrafine particles that were on or near the surface had, on average, fewer Fe neighbors. Assuming a spherical shape for the particles, particle diameters in the range 1.2-1.8 nm were obtained. The significantly smaller particle diameter obtained using this technique was attributed to the possible nonspherical geometry of the particles.

XRD Line Broadening

The average crystallite dimension of small particles can be estimated from the line broadening of the Bragg peaks using the relation

$$d = 0.9\,\lambda \,/\, B \cos\theta \tag{5}$$

where d = crystallite size, λ = wavelength, B = peak width at half-maximum, and θ is the Bragg angle.

The technique has to be used with caution since faults or other defects can also result in line broadening [20]. Pollack and Spitler [21], who examined pyrrhotites produced in continuous liquefaction units, observed asymmetric Bragg peaks and attributed them to stacking disorder.

Ibrahim et al. [19] examined the XRD line broadening on the same sample of Fe_2O_3/SO_4 on which the Mössbauer and magnetometric studies were performed and found good agreement between the particle size obtained by the different techniques.

Electron Microscopy

Transmission electron microscopy (TEM), in combination with electron microdiffraction, is being employed to examine the particle size distribution and the structural characteristics of iron-based catalysts. In the case of Fe_2O_3/SO_4, the particle size distribution measured by TEM was in agreement with the results from Mössbauer, magnetometry, and XRD line broadening [10].

BET Surface Area

Surface area measurement using the BET method requires a clean surface and is hence limited to the study of catalyst precursors. Pradhan et al. [1] found good correlation between the BET surface area and the average particle size from XRD and TEM on Fe_2O_3/SO_4 samples. In the BET method, nitrogen adsorption at pressures upto 0.1 MPa is frequently used. Lambert et al. [22] have described a more sensitive BET method for measuring the surface area of pyrrhotites using krypton as the adsorbate at -196°C and at pressures from 20 to 270 Pa.

Conclusions

A number of characterization techniques are being successfully used to determine the particle size of iron-based catalyst precursors. In particular, the methods to measure the particle size of Fe_2O_3 and related phases appear to be well established. There is a need to perform additional experimental and theoretical studies to develop methods to measure the particle size of pyrrhotites which seem to be catalytically very important. *In situ* techniques to measure particle size under reaction conditions have to be developed.

Acknowledgements

The author would like to thank M. Farcasiu, S.S. Pollack, G.P. Huffman, F.E. Huggins, K.R.P.M. Rao, B. Ganguly, M.S. Seehra and C.D. Stinespring for helpful discussions.

References

1. See for example, V.R. Pradhan, J.W. Tierney, and I. Wender, ACS Fuel Div. Preprints, **37**, 254 (1992).
2. M. Farcasiu, C. Smith, V.R. Pradhan, and I. Wender, Fuel Process. Tech. **29**, 199 (1991).
3. G.M. Schwab and J.J. Philnis, J. Am. Chem. Soc. **69**, 2588 (1947).
4. Available from the Penn State Coal Research Bank.
5. D.E. Herrick, J.W. Tierney, I. Wender, G.P. Huffman and F.E. Huggins, Energy and Fuels **4**, 231 (1990).
6. F. Derbyshire and T. Hager, ACS Fuel Chemistry Preprints, **37**, 312 (1992).
7. L.F. Power and H.A. Fine, Minerals Sci. Eng. **8**, 106 (1976).
8. See for example, P.A. Montano, Magn. Res. Rev. **7**, 175 (1982).
9. J.C. Ward, Rev. Pure and Appl. Chem. **20**, 175 (1970).
10. G.P. Huffman, B. Ganguly, J. Zhao, K.R.P.M. Rao, N. Shah, Z. Feng, M.M. Taghiei, F. Lu, I. Wender, V.R. Pradhan, J.W. Tierney, M.S. Seehra, M.M. Ibrahim, J. Shabtai, and E.M. Eyring, Energy and Fuels, in press.
11. V.U.S. Rao, F.E. Huggins and G.P. Huffman, J. Appl. Phys. 50, 2408 (1979).
12. A.M. van der Kraan, Phys. Stat. Sol. (a) **18**, 215 (1973).

13. P. Bussiere, A. Newman and B.K. Sharma, Hyperfine Interactions **42**, 1211 (1988).
14. M. Jamond, R. Bacaud, P.Bussiere, H. Charcosset, and B. Nickel-Pepin-Donat, **52**, 297 (1989).
15. W. Sihao, J. Keyu, W. Zhaoming, G. Jinsheng, W. Youqing, W. Zhen, L. Diwan, Y. Yongquin, and Z. Changgen, Hyperfine Interactions **58**, 2617 (1990).
16. M.J. Besnus, G. Munschy, A.J.P. Meyer, J. Appl. Phys. **39**, 903 (1968).
17. K. Adachi and K. Sato, J. Appl. Phys. **39**, 1343 (1968).
18. See for example, J.C. Linehan, R.M. Beam, D.W. Matson, J.L. Fulton, and A.E. Crump, ACS Fuel Div. Preprints, **37**, 488 (1992).
19. M.M. Ibrahim, J. Zhao, and M.S. Seehra, J. Mater. Res. **7**, 1856 (1992).
20. J.M. Stencel, V.U.S. Rao, J.R. Diehl, K.R. Rhee, A.G. Dhere, and R.J. DeAngelis, J. Catal. **84**, 109 (1983).
21. S.S. Pollack and C.A. Spitler, American Mineralogist 66, 1258 (1981).
22. J.M. Lambert, Jr., P.L. Walker, Jr., A.J. Perrotta, J.P. McCullough and H. Beuther, Fuel **62**, 1474 (1983).