Characterization of hematite sols: correlation of size, shape and percentage yield

P D SAWANT

Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

MS received 13 October 1995; revised 27 June 1996

Abstract. α -Fe₂O₃ sols were prepared by forced hydrolysis method. The effect of time of aging, concentrations of ferric chloride and hydrochloric acid on the size, shape and percent yield were studied. Static light scattering was employed to determine the spherical shape, further confirmed by cryo-SEM technique.

Keywords. Hematite sols; forced hydrolysis; light scattering; cryo-SEM.

1. Introduction

The method of preparation of hematite sols of submicron size using forced hydrolysis technique was pioneered by Matijevic and Scheiner (1978). This method was further modified by Penner and Koopal (1986) for preparation of larger size, monodispersed sols on the small seed particles of the same sol. Microemulsion media have also been employed to prepare particles of sizes below 100 nm (Ayyub *et al* 1988). Spectral, physicochemical (Morris *et al* 1985), photocatalytic (Henglein 1987), magnetic (Muench *et al* 1981) and catalytic (Nozawa and Yoneda 1980) properties of α -Fe₂O₃ have been studied by several authors. It is known that the morphology and size of the particles depend on several factors such as pH, concentration of reactants, nature of medium, time and temperature of aging and nature of anion present in reactant salt solutions (Murphy *et al* 1976; Sugimoto and Matijevic 1980; Hamada and Matijevic 1982; Ozaki *et al* 1984, 1990; De Blanko *et al* 1986; Hamada and Matijevic 1990; Morales *et al* 1992; Baily *et al* 1993; Okana *et al* 1995). But a clear relationship between the reaction conditions and morphology of hematite particles has not emerged and their preparation remained an art.

In view of important applications of hematite in industry (Matijevic 1984), it is also necessary to evaluate the methods of preparation with percentage yield of formation in addition to size and shape. Therefore in the present paper, hematite sols prepared under different conditions were characterized with respect to size, shape and percentage yield of formation.

2. Experimental

2.1 Materials

Ferric chloride and hydrochloric acid used were of AR grade. Stock solutions were prepared using nanopure water and were filtered through 0.2 μ milli-Q filter paper before reaction.

2.2 Procedures

Size of hematite sols were measured using particle sizer (Brookhaven Instrument model B1-90) based on the principle of dynamic light scattering. Static light scattering experiments were performed on Brice-Phoenix Light Scattering Photometer using a source of 5 mW He/Ne laser light of wavelength $0.6328\ \mu$. Rayleigh–Gann theory in conjunction with Guinier law and $P(Q)$ formula for spherical particle was used to assess the shape and size of α -Fe₂O₃. These experiments were performed by taking sols in a round glass cell which was kept at the toluene bath to match the refractive indices glass and water. Scattered intensities were measured between angles 30 to 130° with respect to incident laser beam. The shapes obtained were independent of the size of particles. X-ray diffraction patterns were recorded on Philips X-ray diffractometer. Shapes of particles were monitored using fast-freeze-fracture technique of cryo-SEM on JEOL-JSM6400 model. When a sol sandwiched between two copper grids was plunged into the liquid freon, the sol got frozen at a rate of 10,000°K/sec. Due to fast freezing of the sol all motions of particles stopped instantaneously and thus it was possible to monitor the particles without any agglomeration. By fracturing of the upper grid it is possible to view the particles. Thus it avoids the drawbacks of drying methods.

Percentage yields were calculated from weight difference of filter paper alone and hematite deposited filter paper. The hematite sols were filtered through $0.05\ \mu$ or $0.22\ \mu$ milli-Q filter papers and were dried in an oven at 70°C, kept in desiccator to attain room temperature. The average of three readings were taken into consideration.

2.3 Preparation conditions

The sols were prepared using the method described by Matijevic (1985) under the following conditions:

- (I) Time of aging was varied from 6 to 48h; keeping FeCl₃ and HCl concentrations fixed as 20 mM and 3 mM respectively.
- (II) Four sets of solutions of 10 mM, 15 mM, 25 mM and 30 mM FeCl₃ were mixed with different concentrations of HCl and aged to 100°C for 24h and then immediately quenched into cold water.
- (III) Different concentrations of FeCl₃ solutions were mixed with 10 mM HCl and aged at 100°C for 24h and then immediately quenched into cold water.

3. Results and discussion

3.1 Variation of aging time

α -Fe₂O₃ sols were prepared by aging 20 mM FeCl₃ and 3 mM HCl solutions and quenched at different time intervals. The sizes of sols increased up to 24h of aging and a saturation in size (figure 1) was observed later up to 48h. This type of behaviour was previously observed for mixed oxides of cadmium and nickel particles (Quiben and Matijevic 1994) and for ellipsoidal hematite sol prepared from ferric nitrate and nitric acid (Okana *et al* 1995). The above behaviour indicates the aggregation of the particles with aging time.

Figure 1. Time of aging vs diameter of particles.

Figure 2. Concentration of HCl vs diameter of α -Fe₂O₃.

3.2 Variation of concentration of HCl

(A) α -Fe₂O₃ sols were prepared by aging solutions of 15 mM ferric chloride with different concentrations of hydrochloric acid at 100°C for 24h. No sol formation was observed for HCl concentrations 80 mM and above. This can be attributed to the excess concentration of HCl which suppressed the hydrolysis reaction (figures 2 and 3). Figure 2 shows the diameter of particles as a function of concentration of HCl. The diameter of the products formed first decreased and was the lowest at 10–15 mM of HCl; the size increased with concentration of HCl. In figure 3 percentage yields of the

Figure 3. Concentration of HCl vs percentage yield.

product formed as a function of HCl concentration are shown. Percentage yields first increased and was the highest at HCl concentration of 10–15 mM and then decreased. The above results indicate that the size was minimum with a maximum in percentage yield for HCl concentration of 10–15 mM. Figures 4A–D illustrate the morphology of α -Fe₂O₃ obtained from cryo-SEM by fast freeze-fracture technique. Changes in shape of α -Fe₂O₃ particles with concentration of HCl are indicated. The changes occurred in the morphology of α -Fe₂O₃ were in the following order: somewhat triangular to cubic to sphere to ellipsoidal. Similar type of shapes were reported previously at different concentrations of both FeCl₃ and HCl and in different media where sizes of the particles were also different and for which different mechanisms were suggested. Effect of HCl on the morphology of hematite particles were not fully established. Sphere and double-ellipsoid shapes were observed for 18 mM FeCl₃ and HCl concentrations of 10 mM and 50 mM respectively by Matijevic and Scheiner (1978). Combining our results with the work of Matijevic and Scheiner (1978), the shapes of hematite particles were changed in the following order: somewhat triangular to cubes to sphere to ellipsoidal to double-ellipsoidal. Baily *et al* (1993) indicated different growth patterns for cubes. They attributed the formation of cubes to the high concentration of all ions as 30-fold increase in the concentration of starting FeCl₃. In the present study we have obtained the cubes between somewhat triangular and spheres. The cubes were obtained relatively at low concentration of ferric chloride.

(B) A similar type of trends of size and percentage yield was observed when a set of sols prepared for various concentration of HCl for a fixed concentration of FeCl₃, 10 mM. Due to smaller sizes of particles it was not possible to check the gradual changes in shapes as observed in the first set. At high concentration of HCl (50 mM), ellipsoidal shaped particles (figure 4 E) were observed.

(C) When FeCl₃ concentration was maintained constant, as 25 mM and 30 mM, both size and yield increased and the highest yield was obtained for HCl concentration of

Figure 4. A-C.

Figure 4. Cryo-SEM photographs of hematite particles observed in the sols prepared from 15 mM FeCl_3 with increasing concentration of HCl (given in bracket): (A) somewhat triangular (1 mM), (B) cubic (10 mM), (C) spherical (10 mM), (D) ellipsoidal (25 mM) and (E) ellipsoidal shape obtained in sol prepared from 10 mM FeCl_3 and 50 mM HCl.

35 mM and 50 mM respectively which then decreased as concentrations of HCl increased (figures 2 and 3). Decrease in size and increase in percentage yield at lower concentrations of HCl was not observed in these sets. Also the changes in shapes were not observed. This can be attributed to the increase in concentration of all the ions with the increase in concentration of FeCl_3 which in turn affects the kinetics and mechanisms of formation. Spherical particles were formed in the above sets at following

concentrations of ferric chloride and HCl.

[FeCl ₃]	[HCl]
15 mM	10 mM
25 mM	35 mM
30 mM	50 mM

Interestingly in all the above three sets, the percentage yield was found to be highest for spherical α -Fe₂O₃, for which reasons are not yet known. Spherical shape was observed at high concentrations of HCl in 25 mM FeCl₃ and 30 mM FeCl₃ whereas in 15 mM FeCl₃ it was observed at lower HCl concentration. The conversion of α -Fe₂O₃ from FeCl₃ in all these sets were found to be very low. The colour of the sols was observed to change from orange to red to yellowish with increase in the concentration of HCl and was reddish for the sol containing spherical particles.

3.3 Variation in concentration of ferric chloride

Concentration of ferric chloride was varied from 5 mM to 40 mM and HCl concentration was fixed at 10 mM. Both the size and percentage yield of the sols obtained showed a gradual increase with increase in concentration of FeCl₃. Nonspherical shapes were observed by SEM at higher concentrations of FeCl₃ except that of 15 mM concentration.

Thus the changes in shapes as well as in yields were predominantly observed when HCl was varied. Thus it is possible to tune the morphology by changing only the concentration of HCl. This suggests the requirement of suitable mechanisms which can explain changes in shapes of hematite. From the study of (II) and (III) it is observed that the yield of hematite is increased when FeCl₃ concentration is equal to or more than the HCl concentration.

3.4 Static light scattering

In these experiments emphasis was given for the spherical shape of the particles in sols. Rayleigh-Gan (1983) theory in conjunction with Guinier law (Guinier 1939; Guinier and Fornet 1965), $P(Q)$, form factor formula (Aragon and Pecora 1976) and Schulz distribution law (Schulz 1935) were used to find out the spherical shape and size of the particles. Spherical shape can be observed from the curve nature in the plot of Q^2 vs $1/(\text{scattered intensity})$, where Q is scattering wave vector. Polystyrene latex of size 300 nm was used as standard for these experiments. Static light scattering showed the gradual change in shape of α -Fe₂O₃ with HCl concentrations for FeCl₃ concentration of 30 mM (figure 5). Similar trend is also observed for sols prepared from 25 mM FeCl₃ and different concentration of HCl, hence not shown here. Since it was difficult to measure the aspect ratio of ellipsoidal particles from SEM micrographs, hence the ellipsoidal shape was not considered in these experiments. The sizes obtained were in good agreement with light scattering results.

4. Conclusions

Thus overall findings of the above study can be summarized as follows:

- (I) Hematite sols of different shapes can be obtained by varying the HCl concentration.

Figure 5. Plot of Q^2 vs $1/(\text{scattered intensity})$. Static light scattering shows the gradual change in shape of $\alpha\text{-Fe}_2\text{O}_3$. Concentration of FeCl_3 is fixed at 30 mM. HCl concentrations used are: 1: 15 mM, 2: 30 mM, 3: 40 mM, 4: 50 mM, 5: 70 mM. Spherical shape can be observed from the curve nature in above plot.

- (II) Comparison of above results with references (Baily *et al* 1993; Okana *et al* 1995) showed that the ellipsoidal particles were forming where FeCl_3 concentration were much less than the concentration of HCl or HNO_3 .
- (III) The percentage yields of hematite obtained from forced hydrolysis of FeCl_3 were observed to be very low. High yields can be obtained by increasing FeCl_3 concentration but in turn it increases the size of hematite particles.
- (IV) The yields obtained for hematite sols of spherical shape was observed to be higher than other shapes. The colour of these sols were observed to be reddish.
- (V) Spherical particle formation and high yields were obtained when concentration of HCl was near to concentration of FeCl_3 .
- (VI) Static light scattering experiments used to determine the shapes and sizes of nanosize particles, which are in good agreement with light scattering and cryo-SEM.

Acknowledgements

Author wishes to thank Dr C Manohar, Mr P A Hassan and Mrs Janaky Narayanan for useful discussions and encouragement; Dr A K Sriraman for providing facilities; Dr J Bellare, B Kiran and M Haridas, IIT Bombay for their help in cryo-SEM and Prof. S D Samant, UDCT for useful suggestions; Dr Hemant Salunke for providing laser source. The author is also grateful to the Department of Atomic Energy (DAE), India for the financial support.

References

- Aragon S R and Pecora R 1976 *J. Chem. Phys.* **64** 2395
- Ayyub P, Multani M, Barma M, Palkar V R and Vijayaraghavan R 1988 *J. Phys. Chem: Solid State Phys.* **21** 2229

- Baily J K, Brinker C K and Mecortney M L 1993 *J. Colloids & Interface Sci.* **157** 1
- De Blanco E K, Blesa M A and Liberman S 1986 *J. React. Solids* **1** 189
- Guinier A 1939 *Ann. Phys.* **12** 161
- Guinier A and Fornet G 1965 *Small-angle scattering of X-rays* (New York: Wiley)
- Hamada S and Matijevic E 1982 *J. Chem. Soc. Faraday Trans. I* **78** 2147
- Hamada S and Matijevic E 1990 *J. Colloid & Interface Sci.* **137** 546
- Henglein A 1987 *Topics Curr. Chem.* **143** 113
- Kuo R J and Matijevic E 1980 *J. Colloids & Interface Sci.* **78** 407
- Matijevic E 1984 *Proc. 49 Spring natl. meeting*, (The Chem Soc of Japan)
- Matijevic E 1985 *Ann. Rev. Mater. Sci.* **15** 483
- Matijevic E and Scheiner P 1978 *J. Colloid & Interface Sci.* **63** 509
- Morales M P, Gonzales-Carreno T and Serna C J 1992 *J. Mater. Res.* **7** 2538
- Morris R W, Lauer Jr H V, Lowson C A, Gibbson Jr E K, Nace G A and Stewart C 1985 *J. Geophys. Res.* **90** 3126
- Muench G J, Arais S and Matijevic E 1981 *J. Appl. Phys.* **52** 493
- Murphy P J, Posner A M and Qrirk J P 1976 *J. Colloids & Interface Sci.* **54** 284
- Nozawa Y and Yoneda Y 1980 *Bull. Chem. Soc. Jap.* **53** 648
- Okana M, Morales M P and Serna C J 1995 *J. Colloids & Interface Sci.* **171** 85
- Ozaki M, Krathovil S and Matijevic E 1984 *J. Colloids & Interface Sci.* **102** 145
- Ozaki M, Ookoshi N and Matijevic E 1990 *J. Colloids & Interface Sci.* **137** 546
- Penner N H G and Koopal L K 1986 *Colloids and Surfaces* **19** 337
- Quihen J and Matijevic E 1994 *Colloids and Surfaces* **A82** 237
- Rayleigh-Gan Theory 1983 *In absorption and scattering of light by small particles* (ed.) C F Bohren (New York: Wiley)
- Sugimoto T and Matijevic E 1980 *J. Colloids & Interface Sci.* **74** 227
- Schulz G V 1935 *Z. Phys. Chem.* **43** 25