Colloid Polym Sci 273:939–946 (1995)

ORIGINAL CONTRIBUTION

V. Chhabra
M. Lal
A.N. Maitra
P. Ayyub

# Preparation of ultrafine high density gamma ferric oxide using aerosol OT microemulsions and its characterization

Received: 6 February 1995
Accepted: 19 April 1995

V. Chhabra · M. Lal · Dr. A.N. Maitra (✉)
Department of Chemistry
University of Delhi
110007 Delhi, India

P. Ayyub
Material Science Group
Tata Institute of Fundamental Research
400005 Bombay, India

**Abstract** Ultrafine gamma ferric oxide has been prepared by controlled heating of ferrous oxalate at a temperature range of 225° to 300 °C in moist air. Ferrous oxalate was prepared both in aqueous as well as in Aerosol OT microemulsion systems. It has been observed that the product is always a mixture of alpha and gamma ferric oxides which were characterized by TGA, DTA and XRD studies. Microemulsion mediated ferrous oxalate was found to yield more gamma ferric oxide than that from ferrous oxalate prepared in aqueous solution. However, the yield of gamma ferric oxide prepared through microemulsion mediated system depends on the size of the microemulsion droplets in which precursors have been participated as well as calcination temperature.

**Key words** Gamma ferric oxide – AOT microemulsion – ultrafine particles

## Introduction

Micelles, microemulsion and vesicles can be used as microreactor to carry out chemical reaction in confined geometries [1–2]. Henglein and coworkers [3–5] have pioneered the use of surfactant in the production of nanometer sized metal and semiconductor particles by radiolytic reduction and studied the influence of surfactant concentration on the nucleation and growth of particles. W/O microemulsions are particularly attractive reactive media for the preparation of metal particles of ultrafine dimensions. These microemulsions consist of nanometer sized water droplets which are dispersed in a continuous oil medium and stablized by surfactant accumulated at oil/water interface. Such microemulsions exhibit low polydispersity i.e. uniform droplet sizes. If ionic reactants are confined to the aqueous interior, they can be precipitated primarily to the dimension of the droplet. This is followed by transfer of precipitate from one droplet to another during the exchange process giving rise to larger particle size which may be defined as secondary growth. It has often been observed that the size of the precipitating particles is larger than the size of the aqueous core of the droplet in which the reaction occurs. The concept of preparing ultrafine particles in the aqueous core of reverse micellar system has been realised in different ways [6–14]. In most of these cases the precipitation were carried out within the aqueous core of reverse micellar droplets.

A critical parameter in the preparation of microemulsion is water/surfactant molar ratio i.e. ($W_0$) which controls the diameter of water droplets [15]. Lianos and others [16–17] studied the formation of cadmium sulphide particles in W/O microemulsion of AOT/Oil/Water in which they have found that the particle size increases with $W_0$ at constant cadmium ion concentration. An increase in cadmium ion concentration leads to decrease in particle size. These results were interpreted in terms of enhanced nucleation and less secondary growth at higher metal salt concentration [18]. Boutonnet et al. [19] studied the production of colloidal Pt, Pd, Rh and Ir particles in W/O microemulsion in which particles of size between 2 to 5 nm have been achieved.

The preparation of ultrafine solid material is necessary because below certain critical dimension the size of the particles governs a variety of interesting effects such as coherence or correlation length, mean free path, wavelength of elementary excitation etc [20]. Such phenomena are not only of basic physical interest but also have resulted in important technological applications. One of the important technical applications of such submicron fine particles is high density magnetic material which are widely used in audio and video applications, instrumentation and computer data storage. The magnetic material used extensively for these purposes are $\gamma$-$Fe_2O_3$, $Fe_3O_4$, Cobalt doped $\gamma$-$Fe_2O_3$, $CrO_2$ etc. Technology demands that the material used for high recording medium should be ultrafine, chemically homogenous stable with narrow size distribution and having a predetermined shape [21].

Preparation of $\gamma$-$Fe_2O_3$ from ferrous oxalate as precursor in aqueous medium has been reported by a number of authors [22–24]. The aqueous methods, of course, always yield uncontrolled particle growth and low volume susceptibility of the final product. The objective of the present work is to prepare high yield $\gamma$-$Fe_2O_3$ from ultrafine ferrous oxalate by using the concept of producing ultrafine colloidal particles of different sizes by varying the droplet size of the microemulsion. In this paper we have reported the precipitation of ferrous oxalate in the aqueous core of AOT microemulsion droplet dispersed in isooctane and ultimately igniting the ferrous oxalate at controlled temperature to yield $\gamma$-$Fe_2O_3$. In microemulsion, however, the secondary growth of the particles is considerably checked because the microreactor droplets are isolated from one another. We have also observed how the properties of microemulsion system like size, shape and interfacial rigidity of the droplet could control the yield and size of ultrafine magnetic particles.

## Experimental

### Materials

Aerosol OT, or AOT, i.e., sodium bis (2-ethylhexyl) sulphosuccinate, was purchased from Sigma and was used without further purification. Isooctane (SRL) of analytical grade was used without further drying. Analar quality Ferrous Ammonium Sulphate and Ammonium Oxalate were obtained from SRL (India). Analar cholesterol was procured from BDH England and was directly used without any further purification.

### Methods

#### *Sample preparation*

The preparation of colloidal ferrous oxalate was achieved by mixing equal volumes of two sets of 0.3 M AOT in isooctane, one with 0.3 M ferrous ammonium sulphate and the other with 0.3 M ammonium oxalate at desired $W_0$ value. The microemulsions were mixed under thorough stirring at 25 °C temperature. Schematic diagram for preparation of precursor ferrous oxalate particles in microemulsion is shown in Fig. 1. To vary the size and shape of the particles, samples of different $W_0$ were prepared from 20 to 40 (because it was found that under experimental conditions solution was clear within this $W_0$ range). The precipitated ferrous oxalate was separated from the reverse micellar solution by adding equal volume of acetone and then by centrifugation (5000 rpm for about 10 minutes). After washing the precipitate with acetone the materials were vaccum dried at about 50 °C. For the decomposition of the ferrous oxalate, the samples were calcined in the presence of dynamic air and water vapour at 225 °C or 300 °C for 15 minutes. The moist air passed after bubbling (at a rate of 60–65 ml $min^{-1}$) through water in a flask maintained at a temp of 50–60 °C. After 15 min, the moist air was replaced by dry nitrogen gas to remove any adhering moisture in the sample.

#### *Quasi elastic laser light scattering measurements*

Dynamic (quasi-elastic) laser light scattering measurements for determining the size was performed at 25 °C using Brookhaven 9000 USA Instrument with BI 200 SM goniometer. Air cooled argon ion laser was operated at 488 nm as a light source. The time dependence of the intensity autocorrelation function of the scattered intensity, $c(\mathcal{T}) = \langle I(0)I(\mathcal{T})\rangle$ was derived by using 136 channel digital photon correlator. Intensity correlation data were processed by using the method of cumulants. The translational diffusion coefficient ($\sigma_T$) of the reverse micellar droplets dispersed in isooctane as well as precursor particle dispersed in aqueous buffer (0.02 M ammonium acetate) was obtained from a nonlinear least square fit to the correlation curve using the decay equation.

$$c(\mathcal{T}) = \langle I\rangle^2[1 + b\exp(-2\Gamma_{\mathcal{T}})]$$

with $\Gamma = \sigma_T q^2$. Here $b$ and $q$ are known experimental constants and $\langle I\rangle^2$ is the $\mathcal{T} \to \infty$ value of the correlation function.

From the value of translational diffusion coefficient, the average hydrodynamic diameter, $D_h$ of the scattering

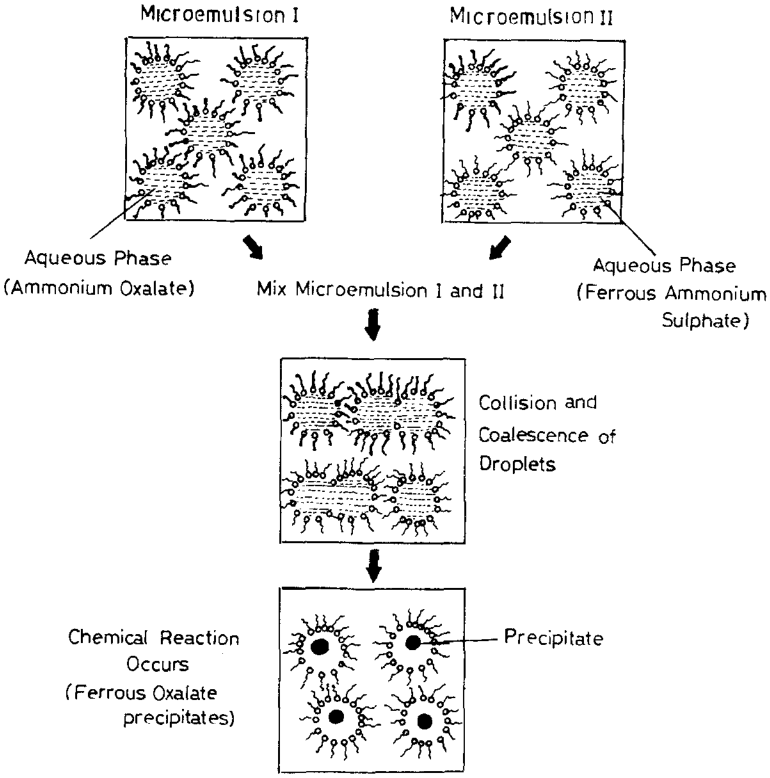


**Fig. 1** Schematic diagram for preparation of precursor ferrous oxalate particles in microemulsion

particles was calculated by Stokes–Einstein relationship:

$$D_h = kT/3\pi\eta\sigma_T ,$$

where $k$ is Boltzman's constant and $\eta$ is the viscosity of the solvent at an absolute temperature $T$. The diameter $D_h$ represents equivalent spherical diameter of the microemulsion droplet in which the precursor has been precipitated.

### *Thermal analysis*

The thermogravimetric (TG) and differential thermal analysis (DTA) curves in air were recorded on RIGAKU 8150 thermal analyser. All the experiments were carried out under identical conditions: heating rate 5 °C/min, mass of the sample approx 10 mg.

### *X-Ray diffraction studies*

The products of isothermal decomposition of $FeC_2O_4 \cdot 2H_2O$ were analysed by powder X-Ray diffraction (XRD) method using CuK$\alpha$ ($\lambda = 1.54$ Å) on RIGAKU instrument. Identifications were made by comparing the experimental '*d*' values and relative peak intensities with those reported in the ATSM powder data files.

### *TEM studies*

Transmission electron microscopy (TEM) was used to study the size and shape of the calcined particles. TEM of these samples was done by ultrasonically dispersing the powder in methanol prior to depositing it onto a carbon coated TEM grid.

### *Particle surface area studies*

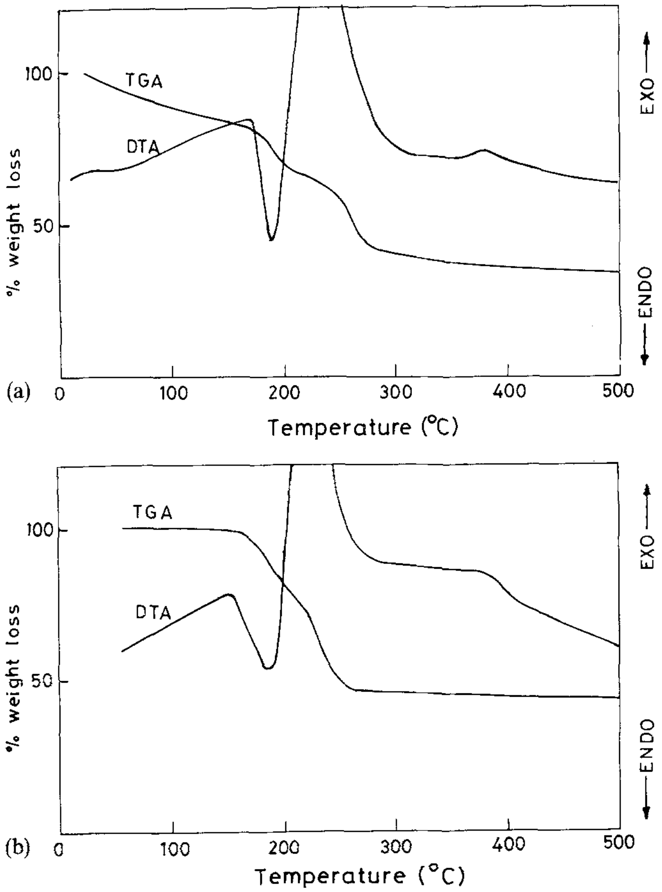
The total surface area of the particles was measured using Quantasorb BET surface area analyzer by Quantasorb Corporation. Previously adsorbed gases were removed prior to the measurement by degassing the samples in nitrogen gas at 110 °C for 2 h. A known mixture of nitrogen (adsorbent) and helium (carrier) gas was passed through the sample cell. When the sample cell is immersed in liquid nitrogen, the sample adsorb nitrogen. The amount of nitrogen adsorbed was measured for different nitrogen/helium ratios and the surface area was calculated using BET equation.

## Results and discussion

### Thermal studies

The representative TG and DTA curves for $FeC_2O_4 \cdot 2H_2O$ obtained from aqueous medium and from microemulsion are shown in Fig. 2. The TG curve shows a continuous mass loss in the temperature range of 170 °C to 280 °C (total loss $\approx$ 60%, corresponding to the formation of $Fe_2O_3$). The DTA consists of an endothermic dehydration peak at 190 °C and two exothermic peaks around 245° and 380 °C respectively. The first exotherm corresponds to an oxidative decomposition while the second one is relatively weak in intensity. There is no mass loss corresponding the second peak which has been accounted for in terms of a phase transition rather than any chemical change [22–25]. There is no further weight loss taking place even on countinuing the heating upto 500 °C beyond the temperature range of the second peak. Interestingly, the intensity of the second peak was found to be independent of the size of the aqueous core of the microemulsion droplet in which the precursor ferrous oxalate has been precipitated.

**Fig. 2** TGA/DTA (in air) of ferrous oxalate precipitated in (a) aqueous solution (b) microemulsion system



### XRD characterization

To ascertain the nature of phase transition corresponding to the second peak (discussed as above), we have made detailed XRD studies of the product calcined at different temperatures. The sample calcined at and above 400 °C always yielded $\alpha$-$Fe_2O_3$ irrespective of the nature of preparation of precursor ferrous oxalate. However the compounds were calcined at 225° and 300 °C, the temperature range between the beginning of the first peak (200 °C) and just before the appearance of the second peak in DTA diagram. Everytime, after calcining the samples, the moist air was replaced by nitrogen gas to remove the water. Dull, reddish brown, coarse products obtained were identified from XRD spectra as mixture of $\alpha$-$Fe_2O_3$ and $\gamma$-$Fe_2O_3$. The XRD pattern of these samples is sharp and samples seems to be highly crystalline. When the precursors are precipitated in a small droplet ($W_0 = 20$) the calcined product does not contain significant amount of $\alpha$ and $\gamma$-$Fe_2O_3$ and it is mainly amorphous. This is believed to be due to very small size of the precursor particle as well as of the final product [25].

X-ray diffractograms of ferric oxide obtained from aqueous medium as well as from AOT microemulsions at different $W_0$ and at different calcination temperatures are shown in Figs. 3 and 4. The characteristic relative intensities for '*d*' values at 2.95, 2.78, 2.52, 2.08, 1.61 and 1.48 responsible for $\gamma$-$Fe_2O_3$ obtained in the spectra of the present samples were matched with those reported in ASTM files. Since the XRD pattern also shows peaks corresponding to $\alpha$-$Fe_2O_3$, it is indicative that the product is always mixture of $\alpha$ and $\gamma$-$Fe_2O_3$. The ratio of $\alpha$ and $\gamma$-$Fe_2O_3$ were calculated from the area under the maximum intensity peaks corresponding to $\gamma$-$Fe_2O_3$ ($d = 2.514$) and $\alpha$-$Fe_2O_3$ ($d = 2.700$). It is interesting to note that at a particular calcination temperature the ratio of $\gamma/\alpha$ is not only different in the compounds prepared in aqueous and in microemulsion media but also this ratio varies with the size of the microemulsion droplets in which the precursor ferrous oxalate has been precipitated.

To check the effect of calcination temperature on the yield of $\gamma$-$Fe_2O_3$ the precursor particles, prepared at various $W_0$ were calcined at two different temperatures, 225 °C which is the beginning of the formation of $\gamma$-$Fe_2O_3$, and 300 °C which is the beginning of decomposition of $\gamma$-$Fe_2O_3$. The dependence of $\gamma/\alpha$ ratio with droplet size at different calcination temperatures as well as the size of the precursor particles is shown in Table 1. It appears from the

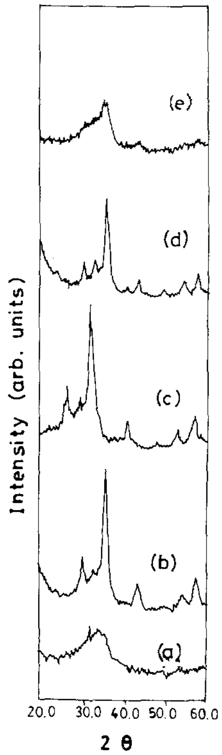


**Fig. 3** X-ray diffractograms of calcined product at 225 °C prepared through microemulsion (a) $W_0 = 20$ (b) $W_0 = 25$ (c) $W_0 = 30$ (d) $W_0 = 35$ (e) $W_0 = 40$

**Table 1** $\gamma/\alpha$ Ratio of $Fe_2O_3$ microparticles as a function of $W_0$ in oxalic acid (0.3 M)/AOT/isooctane

| $W_0$ | Droplet diameter ($D_h$) nm | Mean spherical diameter of the precursor particles (nm) | $\gamma/\alpha$ ratio 225 °C | $\gamma/\alpha$ ratio 300 °C |
|---|---|---|---|---|
| 20 | 9.0 (8.8) | 73 | amorphous | 1.28 |
| 25 | 11.0 (10.4) | – | 10.08 | 1.39 |
| 30 | 12.1 (12.4) | 92 | 10.00 | 1.62 |
| 35 | 15.0 (15.2) | – | 9.75 | 1.66 |
| 40 | 17.5 (19.6) | 138 | 9.53 | 2.00 |

The droplet size for water/AOT/isooctane given in the parenthesis are from ref. [15].

results that the droplet size of the AOT microemulsion strongly influences the $\gamma/\alpha$ composition of the calcined products. In our results it has been observed that $\gamma/\alpha$ ratio decreases with the increase of $W_0$ at the onset of formation of $\gamma$-$Fe_2O_3$ at 225 °C while a reverse trend is obtained when the calcination temperature is increased to 300 °C. We think that at temperature corresponding to the onset of formation of $\gamma$-$Fe_2O_3$, the metastable $\gamma$-$Fe_2O_3$ nucleate in preference of $\alpha$-$Fe_2O_3$ and the larger precursor particles need higher temperature for conversion to $\alpha$-$Fe_2O_3$ while the smaller particles are easily transformed to stable $\alpha$-$Fe_2O_3$ at higher temperature.

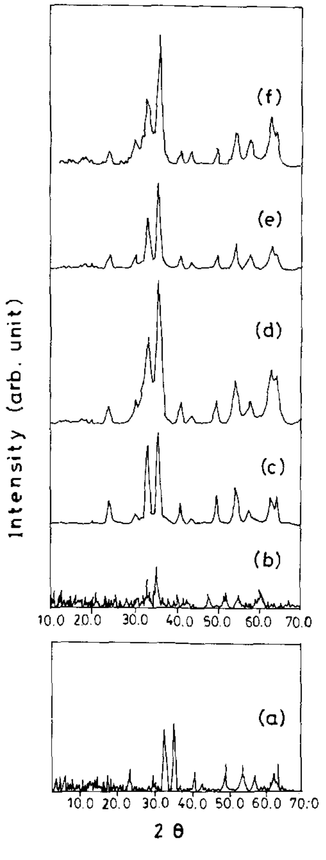


**Fig. 4** X-ray diffractograms of calcined product at 300 °C obtained through (a) aqueous and microemulsion (b) $W_0 = 20$ (c) $W_0 = 25$ (d) $W_0 = 30$ (e) $W_0 = 35$ (f) $W_0 = 40$

Although the precipitation takes place initially within the aqueous nanophase of the microemulsion droplets, the final size of precursor particles always grows larger than that of the aqueous nanophase. This could be explained from the interdroplet interaction which allows intermixing of the aqueous electrolytes including the precipitates leading to the secondary growth of the precipitates and formation of larger particle size. This would definitely influence the composition of calcined ferric oxide product. In order to observe the influence of interdroplet interaction on the size of precursor particles and finally on the composition of the calcined product, the precursor ferrous oxalate has been precipitated in AOT microemulsion containing cholesterol. Cholesterol is known to condense with the surfactant hydrocarbon chains rigidifying the droplet interface and thereby reducing the interdroplet interaction [26–27]. Dynamic laser light scattering measurements of the size of microemulsion droplets containing different amount of cholesterol indicated that there is no significant change of droplet size with the addition of cholesterol (Fig. 5). The precursor ferrous oxalate in a series of microemulsion solutions containing fixed amount of water ($W_0 = 40$) but varied amount of cholesterol dissolved into them were prepared. These compounds were calcined at 300 °C for 15 min. Figure 5 shows that the ratio of $\gamma/\alpha$-$Fe_2O_3$ obtained from these products decreases with

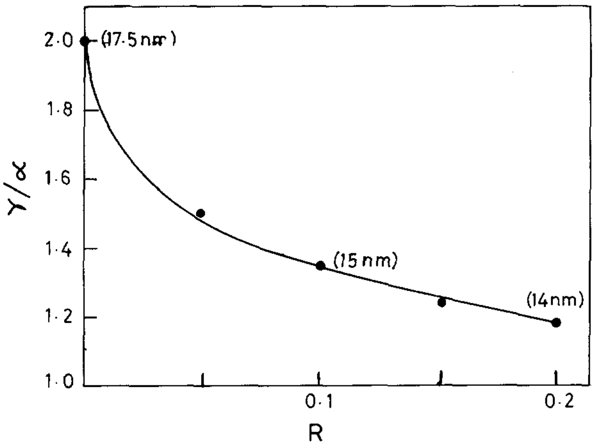


**Fig. 5** The dependence of the ratio of $\gamma/\alpha$ $Fe_2O_3$ in the final product on cholesterol content [R] of microemulsion in which ferrous oxalate has been precipitated. [R] = [Cholesterol]/[AOT], $W_0 = 40$. The sizes of cholesterol containing droplets are indicated within the parenthesis

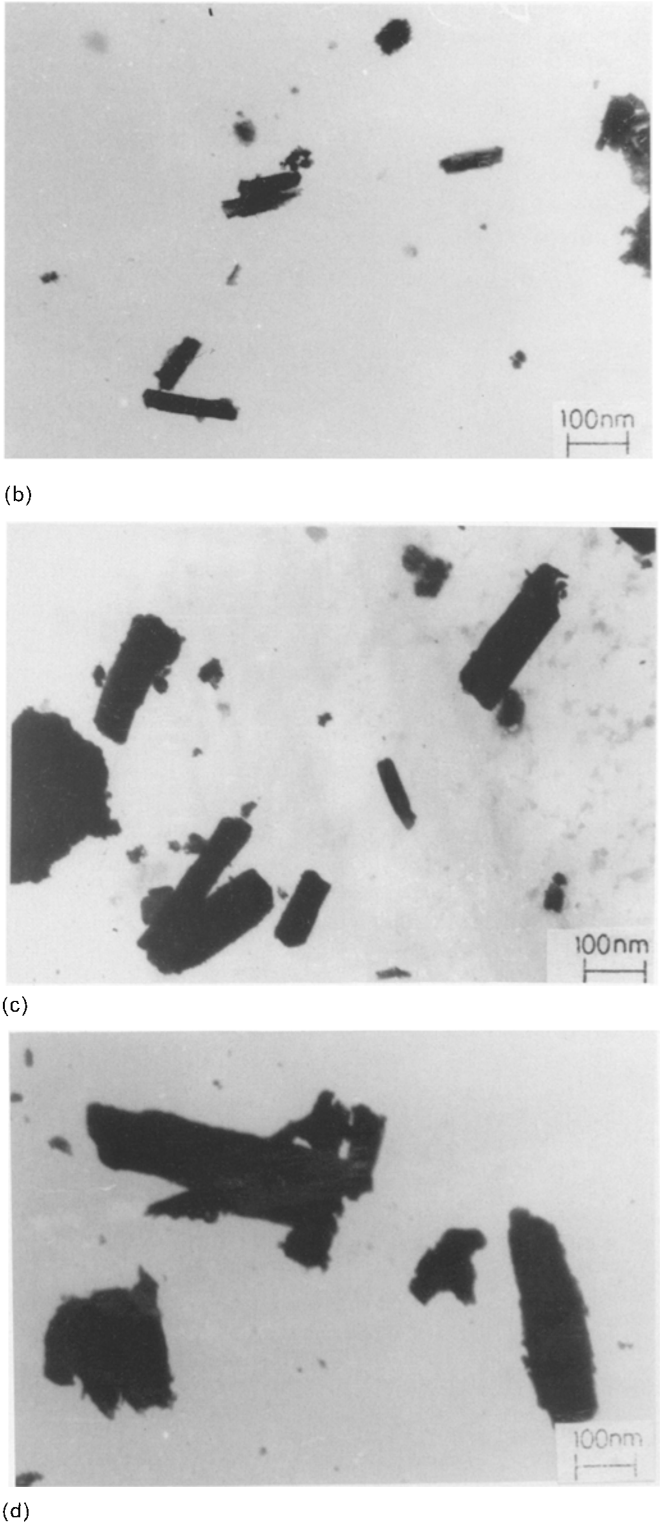
increasing concentration of cholesterol. The interfacial rigidity in presence of cholesterol and subsequent decrease in interdroplet interaction are responsible for reduction of secondary growth and consequently the particle size of the precursor. These smaller precursor particles produce higher yield of $\alpha$-$Fe_2O_3$ when calcined at 300 °C.

## Particle size analysis

The TEM pictures of the products prepared from aqueous medium showed irregular shapes whereas in case of microemulsion uniform needle-shaped particles were obtained (Fig. 6). From the figure it is apparent that the size of these particles are strongly dependent on the size of these microemulsion droplets. The TEM pictures show that in aque-

**Fig. 6** Transmission electron micrograph of ferric oxide prepared through (a) aqueous and microemulsion (b) $W_0 = 20$ (c) $W_0 = 30$ (d) $W_0 = 40$

(a)



(b)

(c)

(d)

ous medium particles are in the range of 1–8 $\mu$m while it is of 0.1–0.5 $\mu$m in case of products obtained from microemulsion mediated systems. This shows that the size of the microemulsion droplets has direct influence on the size of the final calcined ferric oxide particles. The elongated particles prepared through microemulsion support acicular shape of $\gamma$-$Fe_2O_3$. We think that the larger precursor particles are formed through the secondary growth of the precipitates during the clustering of the droplets. This resulted the formation of irregular non spherical particles which on calcination assume elongated shape.

The BET specific surface area (SSA) of the ferric oxide product (calcined at 255 °C) obtained through microemulsion medium was also found to be dependent on the size of microemulsion droplet in which the precursor particles has been precipitated. The SSA of the calcined particles corresponding to different microemulsion droplet size are shown in Table 2. The SSA of the calcined product was reduced from 155 $m^2/gm$ to 145 $m^2/gm$ when the droplet size was increased from 9 nm to 17.5 nm. A simple estimation for the expected size of $\gamma$-$Fe_2O_3$ particle produced by this technique can be done as follows. For the case of $W_0 = 40$ the droplet diameter is 17.5 nm, which gives the diameter of the aqueous core to be about 15.5 nm. A 15.5 nm sized aqueous droplet of ferrous ammonium sulphate (0.3 M solution) can be shown to contain 351 Fe atoms. The corresponding $Fe_2O_3$ particles has an ESD value of 8.1 nm (Table 2) giving rise to 3794 Fe atom which is about 10 times the number of Fe atom present in each microemulsion droplet. It can be concluded from the results that atleast 10 microemulsion droplets form a cluster to give a large size precipitate of ferrous oxalate and subsequent $Fe_2O_3$ particles since we do not expect any sintering of particles at the formation temperature 225 °C.

**Table 2** Particle size of $\gamma$-$Fe_2O_3$ particles obtained from AOT/isooctane microemulsion

| $W_0$ | S.S.A ($m^2/gm$) | ESD (Å) |
|---|---|---|
| 20 | 154.9 | 75.9 |
| 25 | 153.23 | 76.9 |
| 30 | 150.4 | 78.2 |
| 35 | 147.5 | 79.7 |
| 40 | 145.02 | 81.1 |

## Conclusion

AOT/water/isooctane microemulsion system can be effectively used for precipitation of ultrafine ferrous oxalate which on ignition in moist air at temperatures range of 225 °C and 300 °C gives ferric oxide containing mixture of $\alpha$-$Fe_2O_3$ and $\gamma$-$Fe_2O_3$. The yield of $\gamma$-$Fe_2O_3$ prepared through microemulsion mediated system is always found to be higher than that in aqueous medium. In microemulsion system the yield of $\gamma$-$Fe_2O_3$ depends on size of the droplet in which the precursor material is precipitated as well as calcination temperature. The size of the calcined product as measured from TEM as well as from BET shows that the size of these submicron size ferric oxide particles can be controlled by controlling the size of the microemulsion droplet in which the precursor has been precipitated.

**Acknowledgement** The authors (VC and ANM) are thankful to Prof M. Multani and his group for XRD and BET experiment at TIFR, Bombay and for extending all cooperation. Thanks are also due to Dr A.K. Bhatnagar, R&D centre, Indian Oil Corporation, Faridabad for using XRD facility and to Dr Dinesh, Head USIC, Delhi University for SEM and TGA experiments. The work has been financially supported by Department of Science and Technology, New Delhi.

## References

1. Fendler HJ (1987) Chem Rev 87:877
2. Lufimpadio N, Nagy JB, Derouane EG (1986) In: Mittal KL, Lindman B (eds) Surfactants in solution, Vol 3. Plenum NY, pp 483
3. Henglein A (1988) in 'Topics in Current Chemistry' Springer Berlin, 143:113
4. Haase M, Weller H, Henglein A (1988) Ber Bnusenges Phys Chem 92:1103
5. Kumar A, Henglein A, Weller H (1989) J Phys Chem 93:2262
6. Nagy JB, Gourgue A, Derouane EG in 'Preperation of Catalysts' Poncelet G, Grange P, Jacobs PA Eds, (1983) Vol III, pp 193, Elsevier, Amsterdam
7. Kurihara K, Kizling J, Stenius P, Fendler JH (1983) J Amer Chem Soc 105:2574
8. Gobe M, Kon-no K, Kandori K, Kitahara A (1983) J Colloid Interface Sci 93:293
9. Kandori K, Kon-no K, Kitahara A (1988) J Colloid Interface Sci 122:78
10. Chew CH, Gan LM, Shah DO (1990) J Dispersion Sci & Tech 11:593
11. Kon-no K, Koide M, Kitahara A (1984) J Chem Soc Japan 6:815
12. Ayyub P, Maitra AN, Shah DO (1990) Physica C 168:571
13. Pillai V, Kumar P, Shah DO (1992) J Magn Mag Mater 116:L-299
14. Chhabra V, Pillai V, Mishra BK, Morrone A, Shah DO (1994) Langmuir (*Communicated*)
15. Maitra A (1984) J Phys Chem 88:5122
16. Lianos P, Thomas JK (1986) Chem Phys Lett 125:299
17. Motte L, Lebrun A, Pileni MP (1992) Prog Colloid Polym Sci (Trends colloid Interface Sci IV) 89:99
18. Lianos P, Thomas JK (1987) J Colloid Interface Sci 117:505
19. Boutonnet M, Kizling J, Stenius P (1982) Colloids and Surfaces, 5:209
20. Rao CNR (1974) in Solid State Chemistry, MARCEL DEKKER, INC New York

Colloid & Polymer Science, Vol. 273, No. 10 (1995)

21. Craik DJ (1975) in 'Magnetic Oxide' Parts 1&2, Wiley & Sons NY
22. Brown RA, Bevan SC (1966) J Inor Nucl Chem 28:387
23. Rao V, Shashimohan AL, Biswas AB (1974) J Material Sci 9:430
24. Rane KS, Nikumbh AK, Mukhedkar AJ (1981) J Material Sci 16:2387
25. Ayyub P, Multani M, Barma M, Palkar VR, Vijayraghavan (1988) J Physc C 21:2245
26. Maitra AN, Dinesh, Patanjali PK, Varshney M (1986) Colloid and Surfaces 20:211
27. Maitra AN, Patanjali PK (1986) in 'Surfactants in Solution' Eds Mittal KL, Bothoral P, Plenum Press NY, pp 581