

Monodispersed Metal (Hydrous) Oxides—A Fascinating Field of Colloid Science

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The quest of colloid chemists for ways of preparing particles of uniform size and shape is as old as colloid science itself. The interest in making "monodispersed" sols is not based solely on the esthetic appeal of such systems, although that often represents a strong motivation in human endeavors. Well-defined dispersions are also essential for the evaluation of the optical, magnetic, electrokinetic, or adsorptive properties of colloidal matter as well as for the theoretical interpretation of the interactions that involve such particles. Sols containing uniform *spheres* are of particular interest because they allow the determination of the particle size distribution, the number concentration, and the optical properties of a dispersion *in situ*. Furthermore, theoretical treatments of heterogeneous systems frequently utilize spherical symmetry; thus, sols of monodispersed spheres serve as useful model systems. Nature has shown that uniform colloidal particles can form if the conditions are right; the beautiful iridescence of opals is due to their structure, which is an aggregate of regular microspheres of silica.

Scientists have produced numerous "monodispersed" sols of the elements gold, selenium and sulfur, of the inorganic compounds barium sulfate, silica, silver halides, lead iodate, calcium fluoride, etc., and of organic polymers such as latexes. The development of electron microscopy and, particularly, of scanning electron microscopy has given a great impetus to progress in this area of colloid discipline. Before the instrumentation for a direct observation of submicron particles became available, only indirect methods could be used for their characterization. These included visual observation of color changes, Tyndall effect, higher order Tyndall spectra, and ultramicroscopy.

Both physical and chemical processes have been employed to prepare colloidal dispersions of uniform particles, but few general principles have been developed. Although in many instances a systematic effort was invested in order to produce well-defined dispersions, serendipity played a great role. A notable exception is provided by the synthesis of colloidal latex polymers. Several techniques have been designed (emulsion polymerization being the most common) which can yield extraordinarily uniform colloidal spheres of different organic macromolecules. Because of their unique properties and usefulness in many applications, latexes have been the subject of rather extensive research, which has led to a reasonable understanding of the mechanisms of processes involved in particle formation.

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Uniform Colloidal Metal (Hydrous) Oxides¹

Few families of inorganic compounds are of greater significance than metal (hydrous) oxides. They appear in nature as many minerals and are used in numerous applications as catalysts, catalyst carriers, pigments, coatings, fillers, etc. The end products of corrosion of metals invariably consist of metal (hydrous) oxides of various compositions and morphologies. It is, therefore, no surprise that these compounds have been continuously investigated by chemists in general and by colloid scientists in particular. Specifically, the mechanism of precipitation of metal (hydrous) oxides has been extensively studied, but has turned out to be very elusive. The difficulty can be traced to the complexity of the solutions of most metal salts, especially those of polyvalent metal ions. The compositions of, and the concentration of different solutes in, such solutions are extremely sensitive to a number of parameters, among which the pH, temperature, and the presence of different anionic species play a dominant role. Consequently, the properties of metal (hydrous) oxides obtained by homogeneous precipitation depend strongly on the conditions of the environment in which these solids are generated. The above reasoning may explain why so very few successes in the preparation of "monodispersed" sols of such materials have been reported. Indeed, it appears that until recently the only truly uniform metal hydrous oxide obtained by homogeneous precipitation was the acicular β -FeOOH first reported by Heller and his associates.²

During the past few years, we have developed several procedures which can yield dispersions of (hydrous) oxides of a number of metals consisting of particles of narrow size distribution of varying chemical compositions and morphologies, including spheres.^{3,4} This account deals mainly with the principles and techniques involved in the preparation of such "monodispersed" colloids.

Homogeneous Precipitation

LaMer's qualitative explanation of the mechanism of formation of monodispersed sulfur sols by the decomposition of sodium thiosulfate in acidic solution is illustrated in Figure 1.^{5,6} The concentration of the molecularly dispersed sulfur slowly released from $\text{Na}_2\text{S}_2\text{O}_3$ increases until critical supersaturation is reached, at which time the nucleation of the solid (or

(1) The term "metal (hydrous) oxide" is taken here in a rather general sense to include oxides, hydroxides, hydrated oxides, oxyhydroxides, etc.

(2) J. H. L. Watson, W. Heller, and W. Wojtowicz, *J. Chem. Phys.*, **16**, 997 (1948); J. H. L. Watson, R. R. Cardell, Jr., and W. Heller, *J. Phys. Chem.*, **66**, 1757 (1962).

(3) E. Matijević, *Prog. Colloid Polym. Sci.*, **61**, 24 (1976).

(4) E. Matijević, *Pure Appl. Chem.*, **50**, 1193 (1978).

(5) V. K. LaMer and R. Dinegar, *J. Am. Chem. Soc.*, **72**, 4847 (1950).

(6) V. K. LaMer, *Ind. Eng. Chem.*, **44**, 1270 (1952).

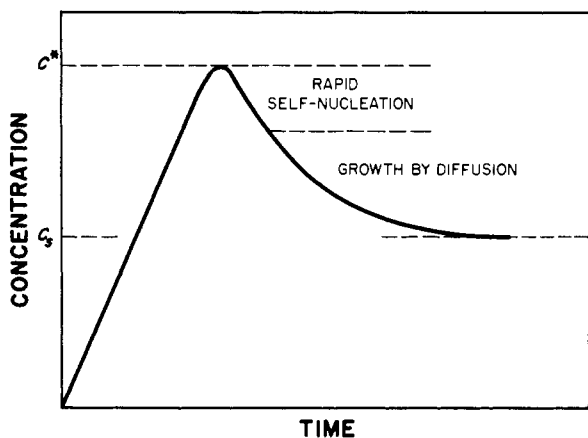
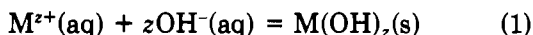


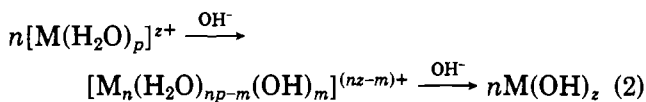
Figure 1. Schematic presentation of the concentration change with time of a particle forming solute species generated in situ before and after self-nucleation. C_s = solubility, C^* = critical supersaturation of the particle forming solute species.

supercooled liquid) sulfur takes place. The nuclei then grow by diffusion. Thus, the "secret" of the preparation of uniform particles lies in the controlled generation of solutes which eventually precipitate so that only one burst of nuclei occurs. The species contained in the particles must then continue to be formed at a rate which allows their removal by diffusion onto the existing particles so that no secondary nucleation may take place. Thus, the original nuclei grow uniformly, yielding monodispersed systems. Whereas the actual mechanism of the formation of LaMer sulfur sols appears to be somewhat more involved,⁷ the underlying principle certainly makes a lot of sense.

In order to apply the same ideas to generation of colloidal metal (hydrous) oxides, it is necessary to control the hydroxylation of metal ions (M^{z+}). It is quite obvious that the commonly written equation

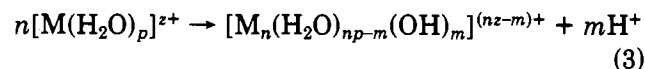


represents only the mass balance of a precipitation process. The appearance of the solid phase is preceded by the formation of dissolved metal complexes which include as ligands hydroxide ions and, possibly, other anions present in the solution. Assuming only hydroxylation, the mechanism of precipitation involves a scheme like



Obviously, the complexes act as precursors to nucleation and they affect the particle growth. The composition and rate of generation of these solutes will determine the chemical and physical natures of the resulting precipitate. Furthermore, not all complexes in solution need to participate in the formation of the solid phase. Since the compositions of solutions of a metal salt are often extremely sensitive to various parameters, it is obvious that a control of the precipitation of metal (hydrous) oxides would be a difficult task. Indeed, it seems almost impossible to assure reproducible precipitation by adding a base directly to an electrolyte solution.

Hydroxylation of metal ions can be greatly accelerated by raising solution temperature. Such forced hydrolysis can facilitate the formation of the complex precursors to nucleation of metal (hydrous) oxides. The process involves deprotonation of hydrated metal ions according to



By adjusting the initial pH of the solution and the temperature of aging, it should be possible to generate the complexes responsible for particle nucleation and growth under conditions schematically given in Figure 1. In principle, then, monodispersed metal (hydrous) oxides should result from the appropriate forced hydroxylation of solutions of metal salts. If other anions are incorporated in the complexes from which the particles are formed, the composition of the solid phase will so indicate.

Thus, the method requires an acidic solution containing a metal salt at a given concentration to be heated in order to produce hydroxide ligands in situ by deprotonation of bound water. The hydroxylation process can sometimes be accelerated by the homogeneous generation of hydroxide ion, such as by decomposition of urea. It is possible to reverse the procedure by starting with a solution of a stable metal complex, e.g., a metal chelate, at high pH. If the complex is then slowly decomposed by heating, the liberated metal ions will react with hydroxide ions to yield precursors of the solid phase. The latter procedure offers certain advantages over forced hydrolysis in that it allows a broader set of experimental conditions, e.g., addition of reducing or oxidizing agents into the system, changing ionic composition, and easier control of decomposition rate by choosing different ligands complexed with the same metal ion.

Forced Hydrolysis

All that is necessary to generate uniform particles of different metal (hydrous) oxides by forced hydrolysis is to keep acidified solutions of metal salts undisturbed at elevated temperatures for a definite period of time. The difficulty is that the conditions of salt concentration, pH, nature of the anion, temperature, etc., are in most cases very restrictive. With so many variables it takes a great deal of effort to establish the requirements illustrated by Figure 1. However, once the proper conditions are set, the reproducibility in generating "monodispersed" sols is rather good.

Figure 2 shows spherical particles of two different compositions obtained by forced hydrolysis; on the left (Figure 2a) is the electron micrograph of an amorphous aluminum hydroxide sol⁸ and on the right (b) a scanning electron micrograph of a hematite sol.⁹ The significant aspect is that this aluminum hydroxide was only obtained in the presence of sulfate ions and the hematite in the presence of chloride ions. Both solids contain the respective anions as contaminants which can be removed by extensive washing with water. Entirely different products result when the anions are changed in the two systems. Figure 2c shows the rather unique morphology of boehmite obtained by aging

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(9) E. Matijević and P. Scheiner, *J. Colloid Interface Sci.*, **63**, 509 (1978).

(7) R. L. Rowell, J. P. Kratochvil, and M. Kerker, *J. Colloid Interface Sci.*, **27**, 501 (1968).

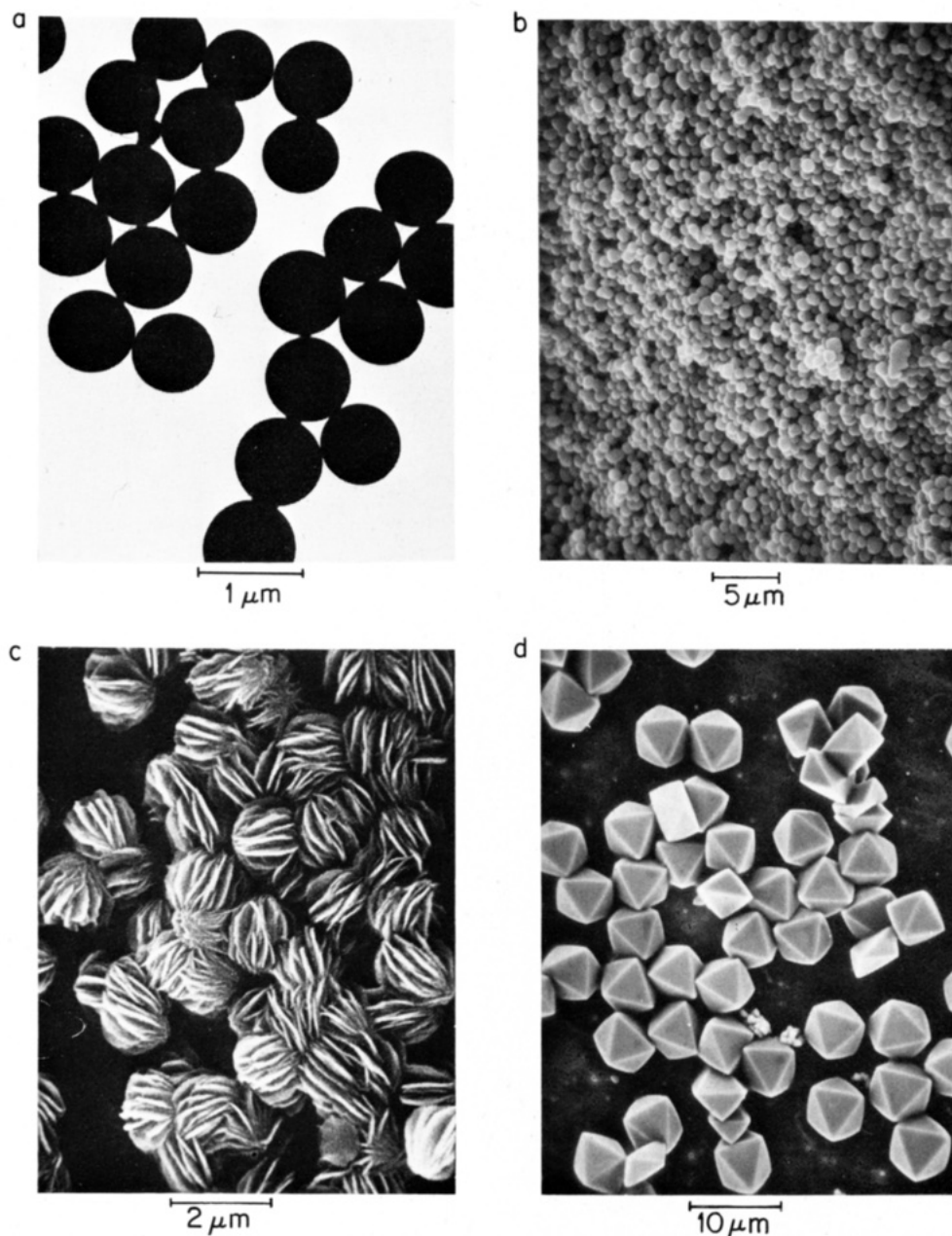


Figure 2. (a) Transmission electron micrograph (TEM) of aluminum hydroxide particles obtained by keeping for 48 h at 97 °C a 0.002 M solution of $\text{Al}_2(\text{SO}_4)_3$; (b) scanning electron micrograph (SEM) of hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles (0.032 M FeCl_3 + 0.005 M HCl solution aged at 100 °C for 2 weeks); (c) SEM of boehmite, $\alpha\text{-AlOOH}$, particles (0.0030 M solution of $\text{Al}(\text{ClO}_4)_3$ aged at 125 °C for 12 h); (d) SEM of alunite [$\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2\text{H}_2\text{O}$] particles (0.18 M $\text{Fe}(\text{NO}_3)_3$ + 0.27 M $(\text{NH}_4)_2\text{SO}_4$ solution aged at 80 °C for 1.5 h).

acidic solutions of aluminum perchlorate¹⁰ and Figure 2d represents the colloidal particles of alunite [$\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2\text{H}_2\text{O}$] crystallized on heating acidic solutions of ferric sulfate.^{11,12} In the latter case the sulfate ion is permanently incorporated in the particles and cannot be removed by rinsing.

Similar results have been found with some other metal ions. Thus, spherical amorphous particles of chromium hydroxide are generated by hydrothermal aging of solutions containing sulfate¹³ or phosphate

ions¹⁴ but not in the presence of chloride, nitrate, or acetate ions. On the other hand, slow hydrolysis of highly acidic titanium(IV) solutions in the presence of sulfate ions yielded spherical rutile particles.¹⁵ Now, why should forced hydrolysis yield amorphous particles in some cases and crystalline particles in other cases, and what is the role of the anions in this process? Also, how can particles be crystalline, yet spherical?

The questions can be answered if one considers the solution chemistry of the hydrolyzing salts. If the hydrolysis products consist of discrete well-defined ionic complexes, as is the case with ferric sulfate¹² or ferric chloride¹⁶ systems, crystal growth will ensue, yielding

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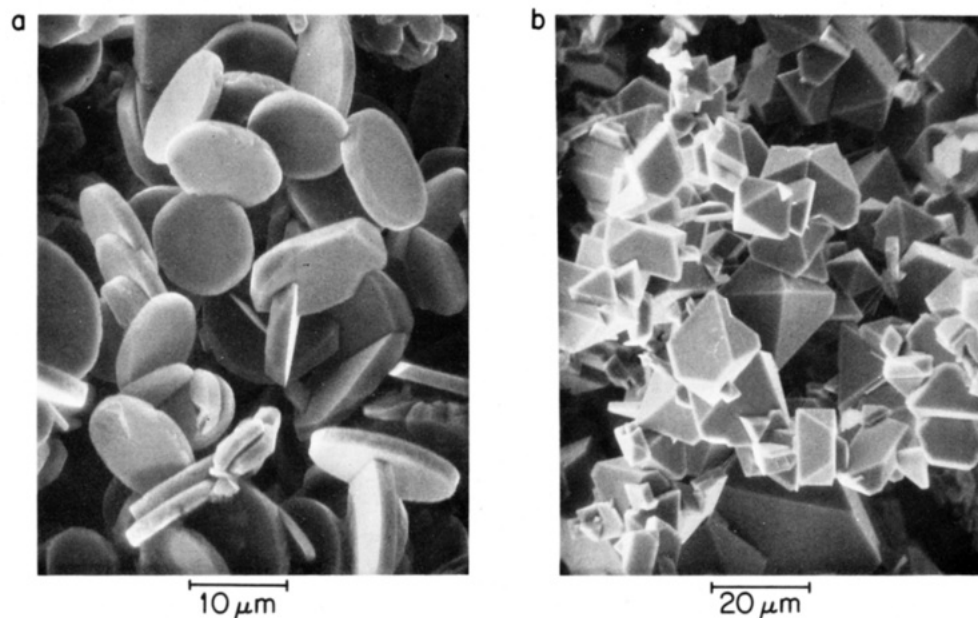


Figure 3. (a) SEM of hematite particles prepared by aging at 250 °C for 1 h a solution of the composition: 0.040 M $\text{Fe}(\text{NO}_3)_3$ + 0.20 M triethanolamine (TEA) + 1.20 M NaOH + 0.50 M H_2O_2 ; (b) SEM of magnetite particles (0.020 M $\text{Fe}(\text{NO}_3)_3$ + 0.40 M TEA + 2.4 M NaOH + 0.85 M N_2H_4 solution aged at 250 °C for 2 h).

particles of fixed stoichiometry and most often of well-defined crystal habits. If, on the other hand, the hydrolysis results in the formation of polymeric metal complexes, spherical amorphous particles will be produced just as with organic polymers. The typical case is that of chromium ion which is known to polymerize in solution on aging.¹⁷ Certain anions, such as sulfate or phosphate, may promote polymerization of the hydrolyzed species which does not take place in the presence of perchlorate, nitrate, or chloride ions that do not readily coordinate to form polynuclear complexes. Bridging of polymeric hydroxylated aluminum complexes by sulfate ion is believed to be responsible for the formation of spherical amorphous aluminum hydroxide. Since this anion does not coordinate into a strongly bound complex, it can be leached from the particles by dialysis or washing.

The question of the sphericity of crystalline hematite seems resolved by Hosemann,¹⁸ who showed the spheres to consist of much smaller subunits of ~40 nm in size. Similar evidence is now available for spherical magnetite, to be described below.

The examples offered here are just a few of the large number of different uniform metal (hydr)oxide systems that have been prepared by forced hydrolysis.^{3,4}

Thermal Decomposition of Complex Solutes

Various chelating agents such as triethanolamine (TEA), nitrilotriacetic acid (NTA), (ethylenedinitrilo)tetraacetic acid (EDTA) and some of its derivatives, gluconic acid, etc., in combination with different metals have been used to prepare metal (hydr)oxides by thermal decomposition of complexes in strongly alkaline solutions. Depending on the stability of the complex, the aging temperature varied between 100 and 250 °C. The composition and morphology of the particles formed were dependent on the experimental

conditions and, in some cases, on the presence of oxidizing or reducing agents. Only a few examples can be offered here to illustrate the wealth of the colloidal products which may be generated by thermal decomposition of metal chelate solutions.

Of all the chelating agents tested, the best-defined systems with the ferric ion were obtained in the presence of TEA. Figure 3a illustrates the unique disklike particles of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and Figure 3b shows rather well-developed crystals of magnetite. The conditions were quite similar except that in the latter case hydrazine was used instead of H_2O_2 .¹⁹

The procedure described is not limited to ferric (hydr)oxides, as illustrated by the following examples. Scanning electron micrographs in Figure 4 show copper oxide polyhedra (a), rodlike crystals of zinc oxide (b), vanadium pentoxide leaflets (c), and elemental nickel spherulites (d).²⁰ The last case is interesting since H_2O_2 acts as a reducing agent, which is indeed possible in a solution of high pH. Similar dispersions of nickel are also obtained when H_2O_2 is replaced by hydrazine. Hydrous oxides of other metals in addition to those shown in Figure 4 can be obtained by the same technique. In all cases the particle size, shape, and composition could be modified over a wide range by altering the anions and the ionic strength of the aged solutions.^{19,20}

Phase Transformation

Figure 5a shows a partial conversion of spherical hematite into octahedral magnetite on heating at 250 °C a strongly alkaline suspension containing hydrazine. The starting material is the same as illustrated in Figure 2b. On prolonged aging, the entire amount of hematite is recrystallized into magnetite.²⁰ Similar phase transformation takes place if disklike rather than spherical $\alpha\text{-Fe}_2\text{O}_3$ particles are used. The recrystallization process is accelerated by adding a chelating agent

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(17) H. T. Hall and H. Eyring, *J. Am. Chem. Soc.*, **72**, 782 (1950).

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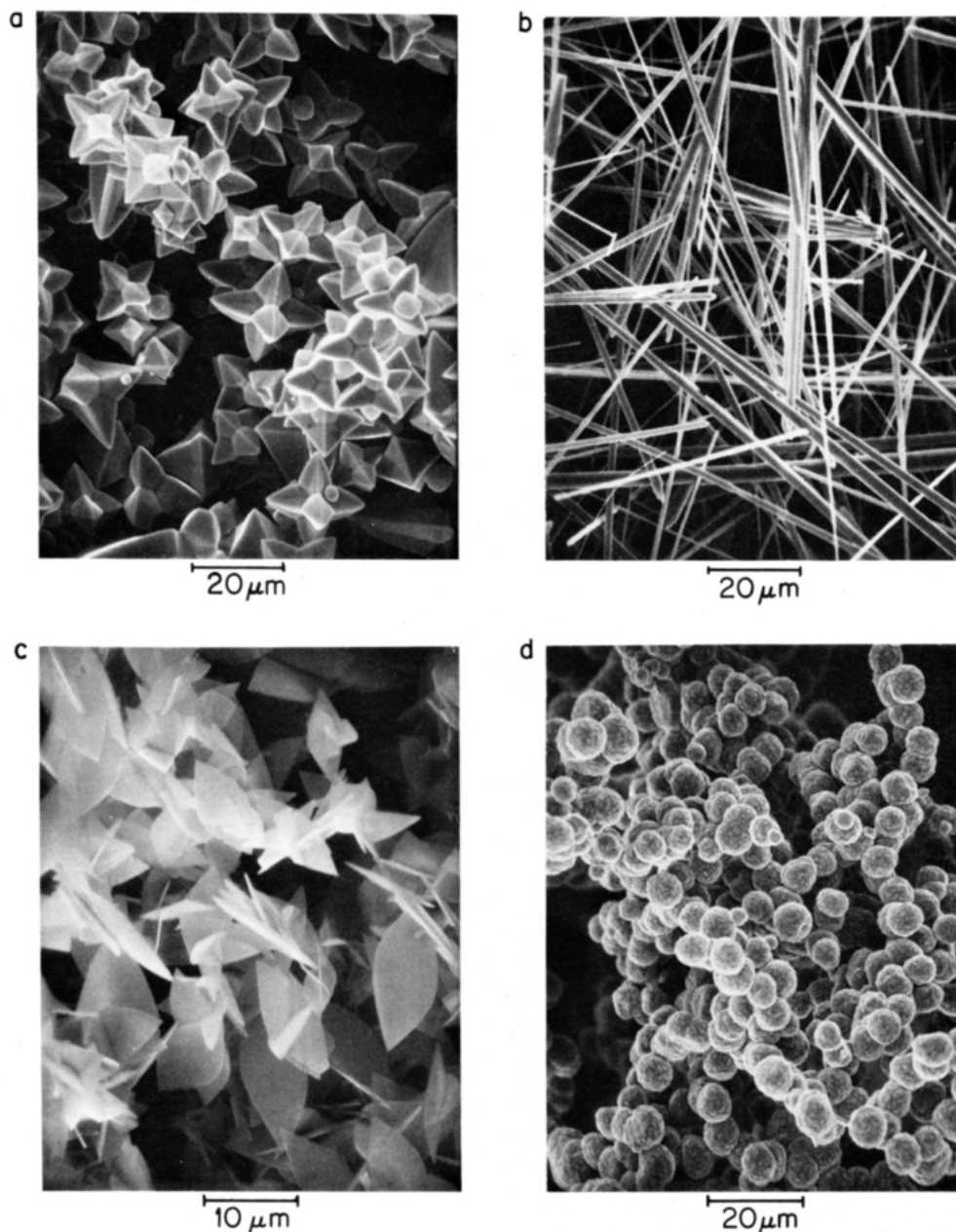


Figure 4. (a) SEM of copper oxide, CuO , particles ($0.040 \text{ M Cu(NO}_3)_2 + 0.20 \text{ M HEDTA} + 1.20 \text{ M NaOH}$ solution aged at 100°C for 70 min); (b) SEM of zinc oxide particles ($0.040 \text{ M Zn(NO}_3)_2 + 0.20 \text{ M TEA} + 1.2 \text{ M NaOH} + 0.85 \text{ M N}_2\text{H}_4$ solution aged at 250°C for 2 h); (c) SEM of vanadium oxide particles ($0.040 \text{ M Na}_3\text{VO}_4 + 0.20 \text{ M HEDTA} + 1.20 \text{ M NaOH} + 0.85 \text{ M N}_2\text{H}_4$ aged at 250°C for 3 h); (d) SEM of elemental nickel particles ($0.040 \text{ M NiCl}_2 + 0.20 \text{ M HEDTA} + 1.2 \text{ M NaOH} + 0.5 \text{ M H}_2\text{O}_2$ solution aged at 250°C for 2 h).

to the dispersion that is aged, but the final product is the same.

The spherical particles in Figure 5b are also magnetite; however, the preparation procedure is entirely different. This dispersion was obtained by crystallization of ferrous hydroxide gel containing a small excess of FeSO_4 and a mild oxidizing agent such as nitrate ion at 90°C for 4 h.²¹ The modal particle diameter can be altered by adjusting the amount of free FeSO_4 in the system. This is apparently the only procedure that yields magnetite dispersions of reasonably uniform spheres described heretofore in the literature.

At present it is not possible to offer a general principle that would allow a prediction of the feasibility of phase transformation processes in preparing well-de-

fined metal (hydrous) oxides. For example, the mechanisms of formation of the two magnetite dispersions shown here are quite different. It was established that the spherical hematite particles dissolved and then magnetite crystallized in the system illustrated in Figure 5a, whereas contact recrystallization took place in the formation of the spherical magnetite (Figure 5b).

Chemical Reactions in Aerosols

So far, aerosols have found few applications in the preparation of matter in the colloidal state. Nevertheless, they represent a logical route for generation of spherical particles if starting materials are dispersed droplets which can be solidified by chemical reactions. Indeed, we have shown that using aerosols may prove to be a viable procedure for obtaining uniform spheres of metal (hydrous) oxides. Two obvious prerequisites

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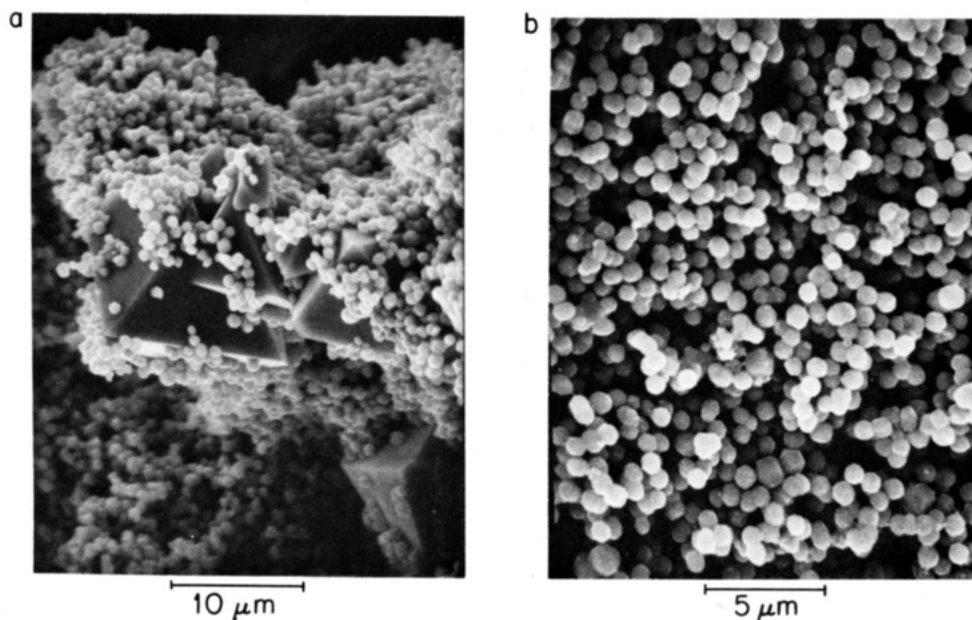


Figure 5. (a) Recrystallization of spherical hematite particles (described in Figure 2b) into magnetite by heating at 250 °C for 1 h a suspension of α - Fe_2O_3 in the presence of 0.20 M TEA + 1.20 M NaOH + 0.85 M N_2H_4 ; (b) SEM of magnetite particles prepared by aging at 90 °C for 4 h a ferrous hydroxide gel containing a 5.0×10^{-3} M excess of FeSO_4 . Reprinted with permission from ref 48. Copyright 1977, Academic Press.

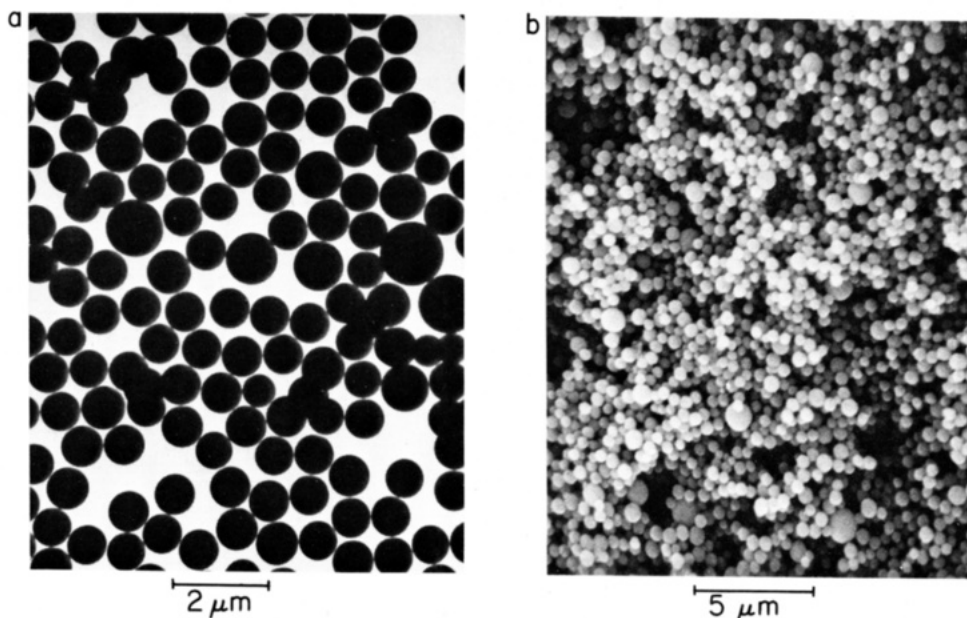


Figure 6. (a) TEM of titanium dioxide (TiO_2) particles obtained by the hydrolysis with water vapor of titanium(IV) ethoxide aerosol droplets; (b) SEM of aluminum oxide particles obtained by the hydrolysis with water vapor of aluminum *sec*-butoxide aerosol droplets.

are that the droplets are of narrow size distribution and that they can chemically react with a vapor. The first condition can be met by using properly designed aerosol generators²² or nebulizers which yield monodispersed liquid aerosols. The second condition is fulfilled with metal compounds, such as titanium tetrachloride or various metal alkoxides, which react readily with water vapor.

Figure 6a shows a titanium dioxide powder prepared by the hydrolysis of droplets of an aerosol of titanium(IV) ethoxide. Analogous particles can be obtained with other alkoxides (e.g., titanium(IV) isopropoxide) or TiCl_4 .²³ Obviously, the modal particle diameter will

depend on the droplet size of the starting aerosol. Titanium dioxide so generated is rather pure, as no ionic species are involved in the reaction. The original powder is amorphous; on heating it crystallizes first into anatase and then into rutile, but the particles retain their spherical shape. The material is most readily dispersed in water with the particle charge depending on the pH.

When essentially the same procedure was used, colloidal spheres of aluminum hydroxide (Figure 6b) were prepared by hydrolysis of aluminum *sec*-butoxide.²⁴ Recently, mixed metal oxide powders were obtained by

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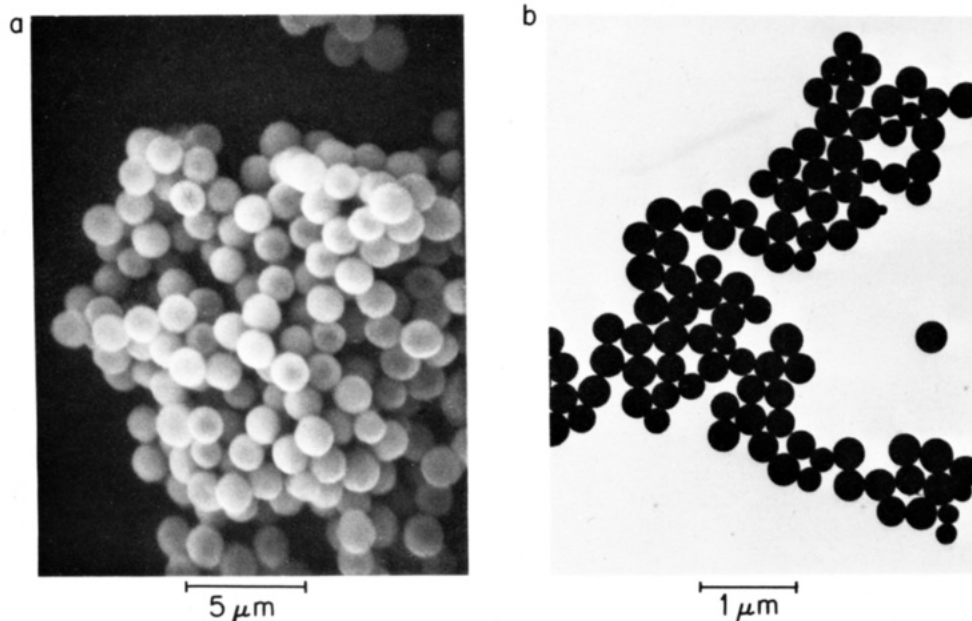


Figure 7. (a) SEM of cadmium sulfide particles obtained by aging at 26 °C for 36 h a solution of 0.0010 M $\text{Cd}(\text{NO}_3)_2$ + 0.0050 M CH_3CSNH_2 + HNO_3 to give a pH 0.75; (b) TEM of ferric phosphate particles obtained by aging at 40 °C for 24 h a solution of 0.00080 M $\text{Fe}(\text{ClO}_4)_3$ + 0.030 M H_3PO_4 .

hydrolysis of corresponding mixed alkoxide aerosols.²⁵

Other Systems

The principles of homogeneous precipitation are not restricted to metal (hydrous) oxides only. They should be applicable to the preparation of other colloidal dispersions provided that proper conditions can be established. For example, Figure 7a shows spherical particles of a cadmium sulfide sol, generated from acidic solution of cadmium nitrate in which thioacetamide was slowly decomposed at room temperature.²⁶

A ferric phosphate sol is illustrated in Figure 7b. The rather uniform precipitate is formed on heating a solution of ferric perchlorate and phosphoric acid for 24 h at a moderate temperature (40 °C).²⁷ The process is exceedingly sensitive to a small change in the parameters, and careful maintenance of experimental conditions is therefore needed to achieve reproducible results.

Studies with Monodispersed Metal (Hydrous) Oxides

As one would expect, the metal (hydrous) oxide dispersions exemplified in the previous sections have been employed in a variety of studies. Of particular interest is their use as model systems for metal corrosion products, pigments, and catalysts. It is not the purpose of this review to describe these works in detail; instead it will offer a few examples of the results obtained.

Characterizations. Systems consisting of well-defined particles are particularly attractive for the assessment of various properties of metal (hydrous) oxides. One of their important characteristics is the pH dependence of the charge of the particles suspended in aqueous solutions and, specifically, the isoelectric point (iep). The available data showed that the latter quantity varied considerably as determined by different investigators on supposedly the same materials; for ex-

ample, the iep of titania was found to range from 2.7 to 7.2.²⁸⁻³⁰ The very pure spherical particles of titania obtained by the aerosol procedure,²³ which contained no ionic contaminations, have an iep of 4.5–5.2, which is well within the range of the “best data”.²⁸ Of particular interest would be a study of the dependence of electrokinetic properties of the same material on the size and shape of the suspended particles. The limited results on this relationship so far available are inconclusive.⁹ Monodispersed metal (hydrous) oxides offer the opportunity for such an investigation, although meaningful data can only be expected if the complete “histograms” of charges for each system are evaluated.

As was mentioned in the introduction, the availability of colloidal dispersions of metal (hydrous) oxides consisting of spherical particles made it possible to determine their size distribution *in situ* by light scattering.^{8,13,31} It is advantageous not to remove suspended material from its environment in order to avoid possible changes in particles that may take place on collection, drying, heating, exposure to different radiation (e.g., electron beams), etc. Thus, the change of the particle size of chromium hydroxide was followed as a function of the time of aging, and the growth mechanism could be deduced from the data.³² It was also shown by measurements of light scattering that no change in the size of suspended particles takes place on altering their charge when pH is varied.¹⁴

Another important application of these systems is in the determination of their optical properties. For example, spherical particles of hematite were used for establishing the absorption index of $\alpha\text{-Fe}_2\text{O}_3$.³³ This

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(26) D. A. Wilhelmy and E. Matijević, to be published.

(27) R. B. Wilhelmy and E. Matijević, to be published.

iron oxide is a common pigment, yet the literature data on its optical properties were in error; this has now been corrected through the availability of "monodispersed" sols. Color calculations, carried out with the new values of the absorption index, agreed well with visual observations.³³

One of unresolved questions about metal (hydrous) oxides is how their magnetic properties depend on their particle size. This problem has been studied by using hematite sols with spheres of different modal diameters.³⁴ It was found that the magnetic susceptibility increases rather abruptly once the particle diameter, d , becomes less than 100 nm. When $d > 100$ nm the magnetic susceptibility of these particles is equal to that of bulk α -Fe₂O₃.

On being dried most of the metal (hydrous) oxides retain their morphology, as confirmed by electron microscopy and by resuspension of the powdered metal (hydrous) oxides in aqueous solutions with subsequent light-scattering analysis. On extensive treatment at high temperatures the amorphous particles of chromium hydroxide develop micropores or mesopores of very narrow size distribution.³⁵

Interactions. In order to establish the chemical mechanism of particle formation and growth it is necessary to know the composition and the concentration of each species in solution and to establish which of these act as precursors to solid-phase nucleation. This arduous task was performed with several systems involving monodispersed metal (hydrous) oxides, specifically in the precipitation of chromium hydroxide³⁶ and of basic ferric sulfate.¹² Indeed, it could be shown in both cases that only selected complex solutes, out of a large number, are directly involved in reactions leading to particle nucleation and subsequent growth.

Owing to their well-defined morphologies and uniform size, the metal (hydrous) oxides described here are suitable adsorbents for a variety of solutes. Thus, the uptake of EDTA³⁷ and of hydroxamic acid trimers and polymers³⁸ on spherical hematite particles was studied in detail. As expected, the adsorption was strongly pH dependent. In addition, at certain chelating agent concentrations and pH, dissolution of the particles took place. In another study the adsorption of aspartic acid on spherical chromium hydroxide exceeded by orders of magnitude the amount that could be accommodated on the particle surface, leading to the conclusion that the solute was absorbed by the solids.³⁹ In contrast, the uptake of tryptophan on the same substrate was negligible. Furthermore, it was shown that the adsorption of a series of carboxylic acids derived from pyridine onto the same sols (hematite and chromium hydroxide) was related to the complexing power of these acids to the metal ions of the solids.⁴⁰

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Sols of spherical particles of aluminum hydroxide and chromium hydroxide were used in heterocoagulation studies with latexes⁴¹⁻⁴³ to test the existing theories of coagulation of unlike particles. The advantage of the metal hydroxide/latex mixtures is in that their constituents respond differently to changes of pH. Whereas the charge of the polymer latexes is little affected by pH, that of the metal hydroxide changes from positive to negative as the pH rises from below to above the iep. Thus, it is possible to investigate the interactions of the same particles but of different potentials just by varying the pH. The most recent work has shown that the double-layer theory explains the experimental data quite well⁴² if the electrostatic contribution is calculated by using the expression based on the two-dimensional solution of the Poisson-Boltzmann equation.⁴⁴

Adhesion of particles on plane surfaces may be treated as a special case of heterocoagulation of two spheres, by assuming that the radius of one of the spheres goes to infinity. Thus, monodispersed metal (hydrous) oxides lend themselves well to studies of the adhesion of particles on solid surfaces and of their detachment from such substrates. Systematic studies have been carried out with spherical chromium hydroxide and hematite sols on steel^{45,46} and of chromium hydroxide sols on glass.⁴⁷ Again, the experimental observations were in good agreement with double layer-calculations when the newly developed theory⁴⁴ for the sphere/plate interactions at close distance was taken into consideration.

Concluding Remarks

This Account has shown that several techniques are now available for preparation of metal (hydrous) oxide particles of uniform size and shape. Similar procedures may be applied to obtain other "monodispersed" metal compounds, such as sulfides. The newly developed systems should be of interest for a number of fundamental studies. Since the underlying principles are reasonably well understood, it should be possible to design conditions so that large quantities (at least of some) of these materials can be produced for various applications.

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