

## CHEMICAL SYNTHESIS OF NANOPHASE MATERIALS

K.J. Klabunde, J.V. Stark, O. Koper, C. Mohs, A. Khaleel, G. Glavee,  
D. Zhang, C.M. Sorensen, G.C. Hadjipanayis  
*Departments of Chemistry and Physics*  
*Kansas State University*  
*Manhattan, Kansas 66506*  
*USA*

*Department of Physics*  
*University of Delaware*  
*Newark, Delaware 19716*

**ABSTRACT.** A short review of important methods for the chemical synthesis of nanoscale particles is presented: transition metal ion reduction by sodium borohydride in aqueous and nonaqueous solvents, nonaqueous reduction using alkali metals, precipitation of metal ions by hydroxide ion, aerogel synthesis, reverse micelle techniques, gas phase aerosol methods, and metal vapor deposition. Nucleation in cold matrices is discussed. Emphasis is placed on chemical reaction stoichiometries, reaction conditions, and isolation techniques. The uses of nanophase materials as novel chemical reagents is considered along with their unusual physical properties.

### 1. Introduction

Chemistry is the study of atoms and molecules, species that are far less than 1 nm in size. Solid state physics is the study of materials containing  $10^{20}$  or more atoms/molecules, essentially, infinite arrays. The range of 1-100 nm size particles defines a new field where neither quantum chemistry nor nonclassical laws of physics hold. For any nanoscale particle, 10 to 100,000 atom/molecules may be involved. Thus, a broad, new field is being developed that requires the cooperation of chemists, physicists, and engineers. And chemists need to be at the forefront in the synthesis of such novel materials. Therefore, it is appropriate that a tutorial/review of current chemical synthesis methods be presented herein. The topics are separated mainly by synthetic technique, and broadly include reduction, precipitation, pyrolysis, aerosol, and vapor deposition in cold matrices. Nanoscale metals, metal borides, metal nitrides, and metal oxides are the products of these chemical syntheses, but the scope could be still broader, and really is only limited by the insight and skill of the synthetic chemist.

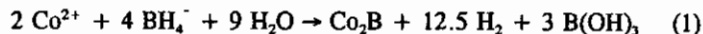
### 2. Reduction of Metal Ions

#### 2.1 BOROHYDRIDE REDUCTIONS

Although reduction of transition metal ions by  $\text{BH}_4^-$  has been known since the 1950's, the detailed chemistry is not well understood.<sup>1</sup> Indeed, seemingly small changes in procedure can cause the product to be completely different. For example, simply through mixing procedures and product handling the final product of the  $\text{CoCl}_2$  reduction with  $\text{NaBH}_4$  in water is Co nanoscale metal particles,  $\text{Co}_2\text{B}$ , or  $\text{Co}(\text{BO}_2)_2$ .<sup>2</sup>

1

For the first time a reasonable understanding of this complex chemistry is beginning to emerge. The complete stoichiometry of  $\text{Co}^{2+}$  reduction in aqueous solution was determined as and is shown by eq. 1.<sup>3</sup>



The primary product is cobalt boride, and an aquatic dimer species  $[(\text{H}_2\text{O})_2\text{CoOH}(\text{BH}_2)\text{OHC}(\text{H}_2\text{O})_3]^{3+}$  is believed to be an important intermediate. Unexpectedly, it was found that reduction of  $\text{CoBr}_2$  under non-aqueous conditions (in dry diglyme,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ) yielded nanoscale cobalt metal.<sup>4</sup> In this case, a diglyme solvated  $\text{Co}(\text{BH}_4)_2$  species is believed to be an important intermediate. This borohydride complex is stable at lower temperatures such as  $-78^\circ\text{C}$ , but upon warming to room temperature decomposes to  $\text{Co(s)} + \text{H}_2 + \text{B}_2\text{H}_6$ .<sup>4</sup>

In addition to being able to control whether  $\text{Co(s)}$  or  $\text{Co}_2\text{B(s)}$  is the product, several other experimental parameters were clarified: (i) care to work under inert atmosphere is important, since oxidation can "fool" an investigator, eg. the exothermic reaction (where  $\text{Co}_2\text{B}$  is actually the primary product, but  $\text{Co(s)}$  can be formed by a secondary reaction).

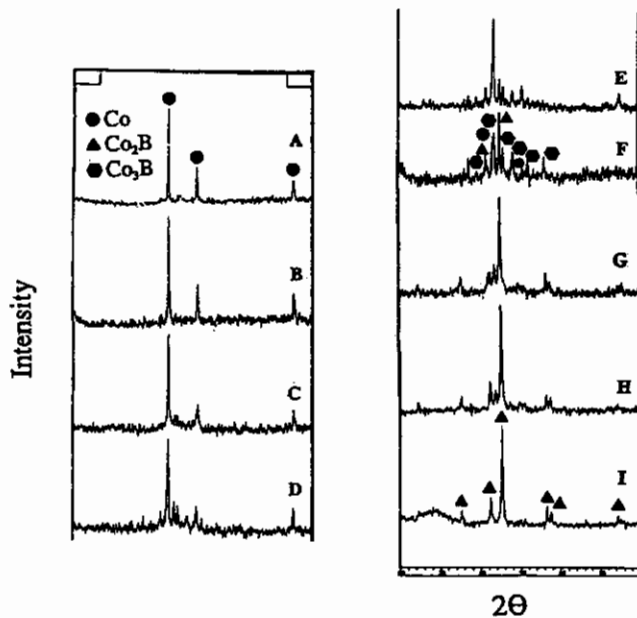
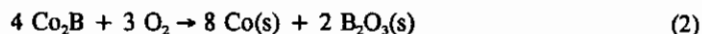
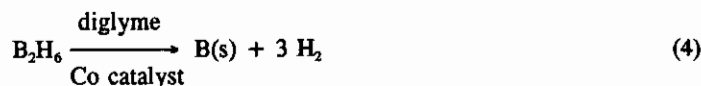
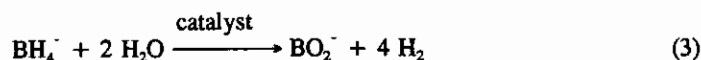
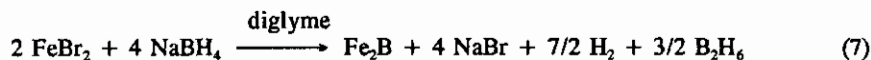
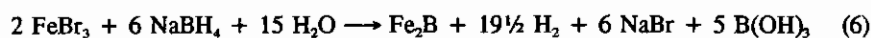
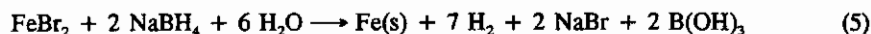


Figure 1. Powder X-ray diffraction of products from reactions in which different amounts of  $\text{H}_2\text{O}$  are added to diglyme solution of  $\text{CoBr}_2$ : (A) pure diglyme; (B) 2 mmol of  $\text{H}_2\text{O}$ ; (C) 8 mmol of  $\text{H}_2\text{O}$ ; (D) 64 mmol of  $\text{H}_2\text{O}$ ; (E) 2048 mmol of  $\text{H}_2\text{O}$ ; (F) 6100 mmol of  $\text{H}_2\text{O}$ ; (G) a 50 mL  $\text{H}_2\text{O}$  solution of  $\text{CoBr}_2$  reacted with 50 mL of diglyme solution of  $\text{NaBH}_4$ ; (H)  $\text{CoBr}_2$  solution in 100 mL of  $\text{H}_2\text{O}$  and 12 mL of diglyme reacted with a 25 mL diglyme solution of  $\text{NaBH}_4$ ; (I) pure  $\text{H}_2\text{O}$ . Samples were heat processed at  $500^\circ\text{C}$ .<sup>4</sup>

(ii) The proportion of water added can progressively change the product from Co(s) (non-aqueous) to Co<sub>2</sub>B (aqueous medium), but the water must have sufficient time to aquate the Co<sup>2+</sup> species in order for Co<sub>2</sub>B to be a product (see Figure 1). (iii) Co<sub>2</sub>B and Co(s) nanoscale particles serve as catalysts for NaBH<sub>4</sub> reaction with water, eqn. 3. (iv) Co(s) nanoscale particles can serve as a catalyst for B<sub>2</sub>H<sub>6</sub> decomposition (eq. 4).<sup>4</sup>



It is clear that the detailed study of Co<sup>2+</sup> reduction under aqueous and non-aqueous conditions has been quite educational. Naturally, it is important to determine if other transition metal ions will behave similarly. For example, it has been found that Ni<sup>2+</sup> behaves similarly to Co<sup>2+</sup>. However, with Cu<sup>+</sup>, only Cu(s) is the product under aqueous or non-aqueous conditions. With iron, the results are quite unexpected, however, with aqueous conditions yielding Fe(s) and non-aqueous yielding Fe<sub>2</sub>B(s) (opposite to the cobalt results). Indeed, it has been shown that Fe<sup>2+</sup> and Fe<sup>3+</sup> can behave differently, as shown by eq. 5-7.



There is also evidence that Fe<sup>•</sup> (atoms or small clusters) partially react with water to yield iron oxides.

Researchers are continually pushing the limits of the BH<sub>4</sub><sup>-</sup>/M<sup>n+</sup> system. There is confusion in the literature about what can be reduced with borohydride. Our experience suggests that BH<sub>4</sub><sup>-</sup> cannot be used to reduce aqueous metal ions with E<sup>•</sup> lower than about -1.0 volt. Also, with aqueous systems the thermodynamically favorable oxidation of borohydride (or finely divided boron) by water is a competing process. Unfortunately, predictions based on thermodynamics ΔH<sup>•</sup><sub>rxn</sub> are not very reliable, especially since ΔH<sup>•</sup><sub>f</sub> for metal borides are small values and solvation energies of reactants and products are difficult to evaluate. And obviously, kinetic parameters are just as important as thermodynamic parameters. In such complex reactions it is necessary to study each metal ion in some detail and determine how the final outcome can be controlled. Stoichiometries, method of addition of reagents, effect of water, reaction rate, work up procedure, catalytic properties of the nanoscale product particles and other parameters are of importance.

Based on experience and literature, Table I predicts what metal ions can be reduced to the metallic state (or to metal borides) by BH<sub>4</sub><sup>-</sup> and the more powerful AlH<sub>4</sub><sup>-</sup>. Although the list of metal ions that can be reduced is not extensive, quite a few of the more important ones (Fe<sup>3+/2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Pd<sup>2+</sup>, Pt<sup>2+</sup>, etc.) are reducible. Indeed, this chemistry has already allowed the synthesis of several very interesting nanoscale magnetic particles,<sup>5-7</sup> and it seems that the next important phase will be the production of bimetallic alloy and/or bimetallic core-shell particles.<sup>8</sup>

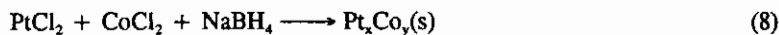
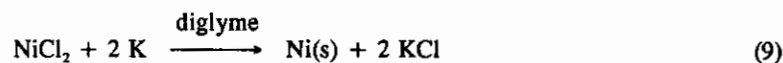


TABLE I. Metal ions that can or cannot be reduced to metals (or metal borides) by  $\text{BH}_4^-$  and  $\text{AlH}_4^-$

Metal Ion	$\text{BH}_4^-$	$\text{AlH}_4^-$
$\text{Ti}^{4+}$	NO	NO
$\text{V}^{3+}$	NO	NO
$\text{Cr}^{3+}$	NO	NO
$\text{Mn}^{2+}$	NO	YES
$\text{Fe}^{2+}$	YES	YES
$\text{Fe}^{3+}, \text{Ru}^{3+}, \text{Os}^{3+}$	YES	YES
$\text{Co}^{2+}, \text{Rh}^{3+}, \text{Ir}^{3+}$	YES	YES
$\text{Ni}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}$	YES	YES
$\text{Cu}^+, \text{Ag}^+, \text{Au}^+$	YES	YES
$\text{Cu}^{2+}, \text{Au}^{3+}$	YES	YES
Lanthanide ions	NO	NO
Actinide ions	NO	NO

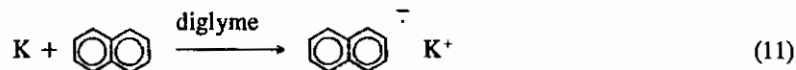
## 2.2 ALKALI METAL (Li, Na, K) REDUCTIONS

Rieke and coworkers<sup>9,10</sup> have described several ways to use the high reducing potential of alkali metals for preparing nanoscale metal particles under mild, solution phase conditions. Again, it is imperative that anaerobic conditions be maintained during these experiments. Usually, a head of pure argon gas is employed along with dry, pure ether solvents (diglyme, THF, diethylether, dimethoxyethane). The solvent must be chosen such that it dissolves at least part of the metal halide. Thus, polar organic solvents that do not react with the alkali metal are necessary. Examples are shown in equations 9 and 10.

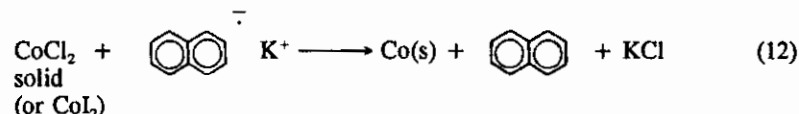


Generally what is obtained from these reductions is nearly amorphous metal deposited on microcrystals of potassium halide. The metals are extremely reactive with oxygen and a variety of organic compounds, and, in fact, the main thrust of the work has been to develop new organic chemistry using the activated metals.

A significant modification of this procedure has been developed where naphthalene is added to a diglyme solution of potassium. The naphthalene is soluble in the diglyme but has a high enough electron affinity that K metal transfers electrons to it, producing potassium naphthalide. In this way the potassium is brought up into solution (equation 11).



A dark colored slush is formed that reacts rapidly with added anhydrous salts (equation 12).



The final product is again nanoscale Co particles dispersed on KCl microcrystals. The naphthalene can be washed away with excess solvent.

These methods have been used successfully for many metal salt  $\longrightarrow$  metal reductions, with metals such as Mg, Al, Ni, Pd, Cu, Co, and In.

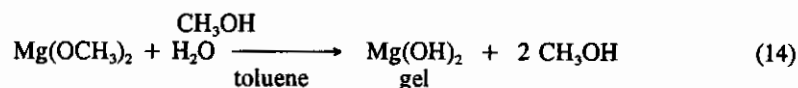
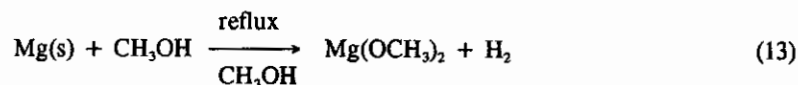
### 3. Precipitation of Metal Hydroxides and Oxides

#### 3.1 AEROGEL/XEROGEL METHODS

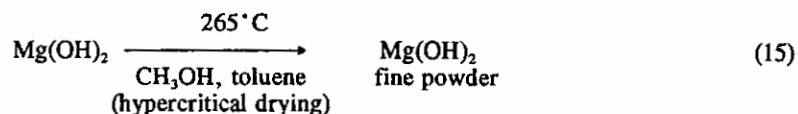
Direct precipitation of aqueous metal ions by addition of hydroxide ion suffers from the need to dry the gel precipitate. This dehydration process usually causes severe sintering and damage to pore structure. This is because the solvent, water, causes a vapor-liquid interface within the capillaries inside the gel network and results in surface tension creating concave menisci inside the network. As the menisci reduce in the gel body, the buildup of tensile force acting on the walls of the pores causes considerable shrinkage of the gel network. The resultant product is often hard and glassy and is often called a "xerogel".

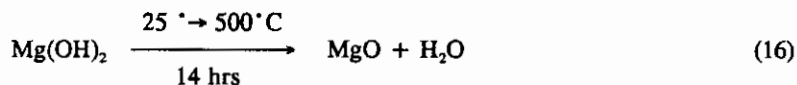
To better preserve the texture of the wet gel, the vapor interface inside the pores must be eliminated during the drying process. This can be done by heating in a high pressure autoclave above the critical temperature of the water and venting the water in its gaseous-fluid state. This hypercritical drying method was first described by Kistler.<sup>11</sup> Improvements were made by Teichner and coworkers<sup>12</sup> by replacing much of the water with alcohols. The resultant materials are called "aerogels".<sup>12,13</sup> Further improvements have been possible by adding less polar organic solvents.<sup>14</sup>

A good example of a successful preparation of Mg(OH)<sub>2</sub> (900 m<sup>2</sup>/g, 3.3 nm crystallites) and MgO (400 m<sup>2</sup>/g, 4.2 nm crystallites) is shown below (eq. 13-16).



20:100 methanol:toluene solvent ratio





Further study of the nanoscale MgO particles indicated that a fairly monodisperse material had been obtained, and the 4 nm crystallites were individual, spheroid particles. This was in contrast to more conventional samples of large particle size (Figure 2).<sup>15</sup> The two samples exhibited intrinsically different surface chemistry. Although both possessed the same average number of surface -OH groups/nm<sup>2</sup> (3.5-3.6), the smaller crystallites apparently had -OH groups on its edges, allowing more linear OAl-Et<sub>2</sub> groups to form, compared with the larger crystallites (eq. 17-18).

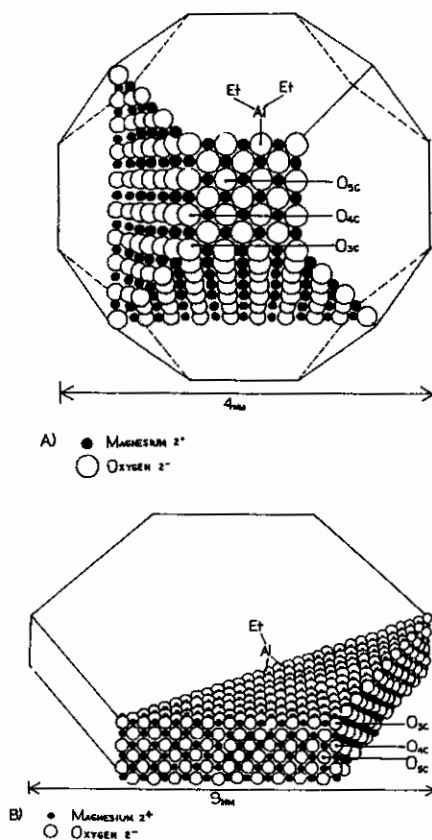
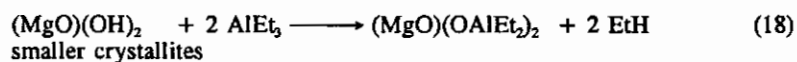
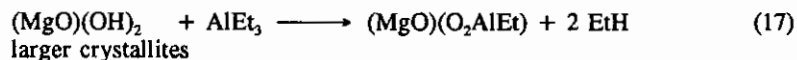
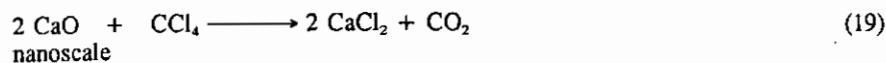


Figure 2. Idealized illustration of (A) Nanoscale MgO produced by an aerogel procedure, and (B) aqueous precipitation and dehydration (conventional) method.<sup>15</sup>

In other words, more geminal pair reactions of -OH with AlEt<sub>3</sub> occurred on the larger crystallites. Furthermore, the edge bound -OH groups were slightly less acidic, and the surface oxide anions were less basic. The smaller particles also absorbed less pyridine/nm<sup>2</sup>. Overall, the results show that particle size can have intrinsic effects on surface chemistry. The frequency of edge and corner sites vs. planes can be very important, and nanoscale ionic crystallites tend to possess more edge and corner sites than larger ones. Other types of reactive defects may also be more prevalent on smaller crystallites.

The aerogel procedure is most useful for the common metal oxides, and has been used very successfully for MgO, CaO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>. These nanoscale materials have low bulk densities (as low as 0.1 g/cm<sup>3</sup>), can be translucent or transparent, and generally have low thermal conductivities and unusual acoustic properties. They have found various applications including detectors for radiation, superinsulators, solar concentrators, coatings, glass precursors, catalysts and insecticides.

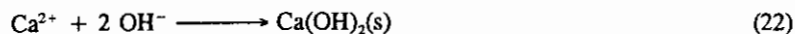
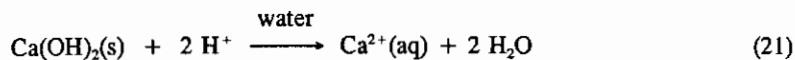
More recently nanoscale MgO, CaO, Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>/MgO have been found to be effective destructive adsorbents for toxic chemicals.<sup>16</sup> Because surface areas are so high, and reactive edge and other defect sites so prevalent, these materials can undergo surface reactions at nearly stoichiometric capacities. Thus, large amounts of toxic organophosphorus, organosulfur, and organochlorine compounds can be detoxified. For example, see equations 19-20.



Such results promise that nanoscale metal oxides can serve as reagents for environmental cleanup of hazardous waste, perhaps as an alternative to incineration.

### 3.2 DIRECT PRECIPITATION AND DIGESTION

The stability of solutions of aqueous metal ions is very dependent on pH. Very often metal halides, oxides, and hydroxides are soluble in acidic solutions.



The controlled precipitation of metal hydroxides is possible by careful manipulation of pH. Furthermore, particle size can be controlled by a second step where the metal hydroxide is converted to an oxide by heat treatment in aqueous solution, a process called digestion. Using this approach small particles can be prepared which span a broad size range and yet retain uniformity of composition, crystallinity, and morphology.<sup>17,18</sup>

Co-precipitation of two metal hydroxides/oxides simultaneously, if carefully done, can lead to varying sizes of bimetallic metal oxides, such as ferrites. For example manganese ferrite (MnFe<sub>2</sub>O<sub>4</sub>) nanoscale particles ranging from 5-180 nm have been prepared from Fe<sup>3+</sup> and Fe<sup>2+</sup> solutions with Mn<sup>2+</sup>.<sup>18</sup> Macroscopically, particle size can be controlled by adjusting the ratio of metal ion in solution to hydroxide concentration. Microscopically, further control can be achieved by the digestion procedure. Upon digestion nanocrystalline material formed and final particle size was a maximum at a [metal ion]/[OH<sup>-</sup>] ratio of about 0.32. However, higher

ratios showed a sharp decrease. Figure 3 clearly demonstrates the difference in magnetic ordering for undigested and digested samples.

Chemical equations can be written as follows:

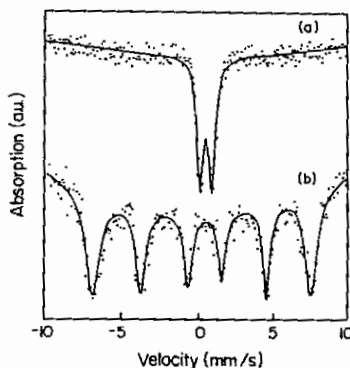
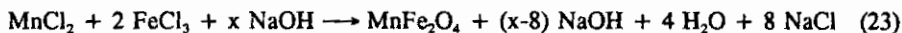


Figure 3. Mossbauer spectra for undigested manganese ferrite (a) and digested (b) samples.<sup>18</sup> (The metal ion/OH<sup>-</sup> ratio was 0.20).

#### 4. Reverse Micelle Techniques

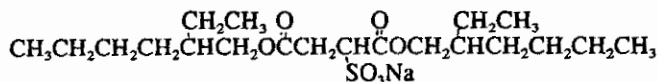
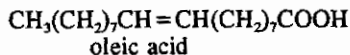
Micelles are normally considered as hydrocarbon molecules in a sea of water, but made compatible with the water by polar tail groups. The nonpolar tails can organize around an oil-like particle.

Reverse micelles, sometimes called inverted micelles, are also made up of hydrocarbon molecules with polar head groups, and these "surfactants" are placed in a sea of oil. In this way the polar head groups organize and form a small cavity that would be "water loving".

In recent years reverse micelles have been useful for the preparation of inorganic nanophase particles. This is done by allowing the hydrophilic cavities to fill with water, and these small water pools can hold and dissolve inorganic salts that can be converted to insoluble inorganic nanoparticles within the cavity. In fact, the cavity size can help dictate the size of the final particle. Since choice of surfactant, concentration, and other parameters can help determine the cavities size, some control of size of the resultant nanoparticle is possible.

Recently, reverse micelles have been used to prepare very small, nearly monodisperse, particles of Pt,<sup>19</sup> Au,<sup>20</sup> Fe boride,<sup>21</sup> Co boride,<sup>22</sup> Ni boride,<sup>23</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>24</sup> and CdS.<sup>25,26,27</sup>

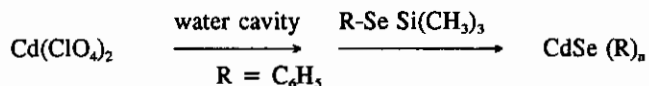
Surfactant molecules used in such work can have quite a varied structure. Two examples are shown below.



bis(2-ethylhexyl)sulfosuccinate sodium salt(aerosol OT, AOT)

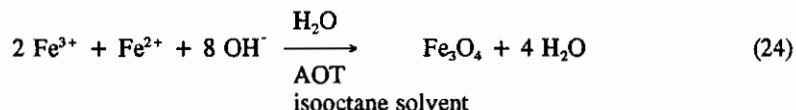


Herein two interesting chemical systems will be described as examples: in one case  $\text{Cd}(\text{ClO}_4)_2$  was allowed to dissolve in the water cavities, and selenium donating reagents  $(\text{CH}_3)_3\text{Si-Se-Si}(\text{CH}_3)_3$  or  $\text{C}_6\text{H}_5\text{SeSi}(\text{CH}_3)_3$  were added in heptane solution. In this way  $\text{Cd}^{2+}$  captures  $\text{Se}^{2-}$ , and CdSe crystallites grow inside the cavities. If desired, a phenyl capping could be carried out by using  $\text{C}_6\text{H}_5\text{SeSi}(\text{CH}_3)_3$ .<sup>27a</sup>



Similar methodology has been used to make core-shell structures of CdSe coated with ZnS, or ZnS coated with CdSe.<sup>27b</sup>

In a second example, superparamagnetic  $\text{Fe}_3\text{O}_4$  particles were prepared by the reaction of  $\text{FeCl}_3/\text{FeCl}_2/\text{NaOH}$  within the water filled cavities of AOT in isooctane solvent.<sup>28</sup>



Interestingly, the molar ratios of water to AOT were critical in determining particle size of the  $\text{Fe}_3\text{O}_4$  formed. These particles were extremely small while in the water cavities, about 1-2 nm as determined indirectly by Dynamic Light Scattering. After removal of the  $\text{Fe}_3\text{O}_4$  followed by drying, particle sizes according to TEM were 5-20 nm, and these dried particles exhibited ferromagnetism.

The molar ratios of water to AOT used were 3.7, 8.4, 11.1, and 14.9 and molar concentrations of iron salts were 0.1 to 0.2 molar. These ratios proved to be important and appear to control the micelle cavity size and final particle size of the  $\text{Fe}_3\text{O}_4$ .

## 5. Aerosol Methods

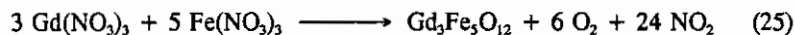
The chemical aspects of the aerosol spray pyrolysis method for production of fine particles is also of interest. Aerosol synthesis and processing methods are attractive due to the simplicity of flexibility of the approach.<sup>29</sup> In addition, the purity of the particles prepared can be very high.

In this method metal salts are dissolved in a solvent, usually water, the solution is nebulized, and during the gas phase flight to a collector surface, the droplets are dried and pyrolyzed. In this way whatever salt components are in the droplet at the beginning of the flight will remain and become one particle. Thus, mixed metal oxides are readily formed with controllable composition. A typical example is in the preparation of gadolinium iron garnet particles,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ .<sup>30</sup> For the preparation of such a composition,  $\text{Gd}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  crystals were dissolved in water at Ge:Fe atomic ratios of 3:5, and the total concentrations were varied so that final particle size could be varied.

The nebulizer, aerosol formation, dryer, and product collection have been described in detail.<sup>30,31</sup>

The chemistry involved in such pyrolysis procedures is complex and deserves some discussion. Very high temperatures are used, often 800°C or higher. Usually, nitrogen is employed as a flow gas so that oxygen is not present to act as an oxidizer. The only reagents present, therefore, are those in the small water-salt droplet. Since metal oxides are usually the desired product, the pyrolytic reaction within the water droplet must allow release of unwanted

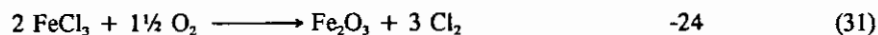
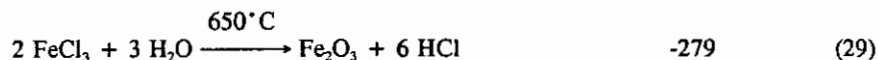
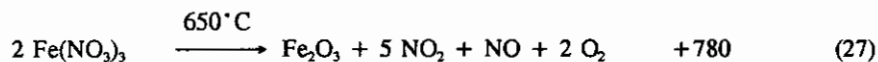
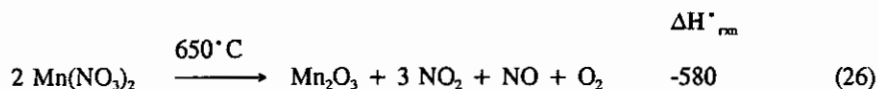
reagents as gases. For this reason, nitrate salts are usually the anions of choice; for the gadolinium iron garnet, as an example, the following balanced chemical reaction may occur.



It is clear that when nitrate salts are used, the gaseous products are highly oxidizing; in fact, "excess"  $\text{O}_2$  probably is a product. This would suggest that nitrate counterions will always ensure that the highest oxidation states of the metal ions will be obtained. However, if mixed oxidation states (of metals with variable stable oxidation states) are desired, then nitrate is not the anion of choice. Indeed, in these cases, halide anions or mixtures of halide/nitrate salts may be better choices. An example is the synthesis of manganese ferrites such as  $\text{MnFe}_2\text{O}_4$ .<sup>32</sup> In this substance, the Mn ion is in a  $2^+$  state. When  $\text{Fe}(\text{NO}_3)_3/\text{Mn}(\text{NO}_3)_2$  precursors were used, a "chemical segregation" occurred where  $\text{Mn}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were formed. Obviously "overoxidation" occurred. When  $\text{Fe}(\text{NO}_3)_3/\text{MnCl}_2$  was used,  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  still were the products. However, when  $\text{FeCl}_3/\text{Mn}(\text{NO}_3)_2$  solutions were used, some  $\text{MnFe}_2\text{O}_4$  was formed along with  $\text{Mn}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Mn}_3\text{O}_4$ .

When only chloride salts,  $\text{FeCl}_3/\text{MnCl}_2$  were used, the best results were obtained and  $\text{MnFe}_2\text{O}_4$  was the major product. However, it was necessary to inject a small amount of air into the flowing aerosol stream for optimal results.

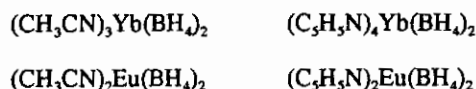
It would appear that just the right amount of oxidizing power and a delicate balance of the following high temperature chemical reactions is needed. These are somewhat speculative, since very little quantitative study of these high temperature processes has been carried out. As the reactions are written, thermochemical calculations based on standard enthalpies of formation  $\Delta H_f^\circ$  of all components were possible (eq. 26-31).



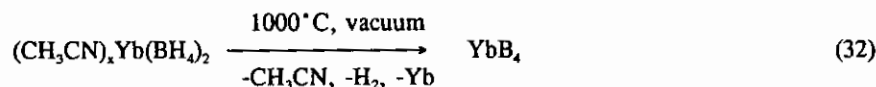
When a balanced combination can be used so that MnO and  $\text{Fe}_2\text{O}_3$  can be formed simultaneously in the hot droplet,  $\text{MnFe}_2\text{O}_4$  formation is favored. What can be learned from these considerations is that choice of precursor or mixture of precursors is extremely important. Balance of cations is needed for appropriate stoichiometry, but choice of anion is vitally important to control oxidation state.

## 6. Pyrolysis of Inorganic/Organometallic Compounds

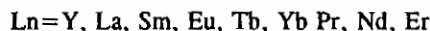
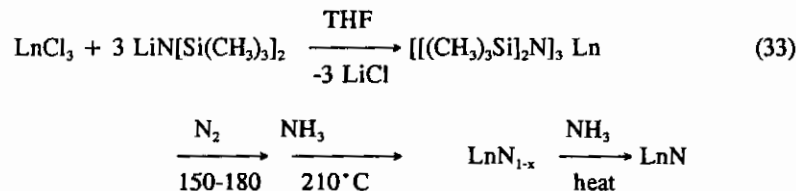
Some recent results on the straight pyrolysis of new inorganic/organometallic compounds should also be mentioned here because of the considerable promise of obtaining rare earth borides and nitrides. For example, Shore and coworkers<sup>33</sup> have prepared several complexes of  $\text{BH}_4^-$  and thoroughly characterized them.



When metal ions are "nonreducible" such as lanthanides, then stable  $\text{BH}_4^-$  complexes can be prepared and isolated. Upon pyrolysis, lanthanum borides could be produced, eq. 32:



LaDuca and Wolczanski<sup>34</sup> have prepared lanthanum nitrides by pyrolysis of silylamino complexes, eq. 33:

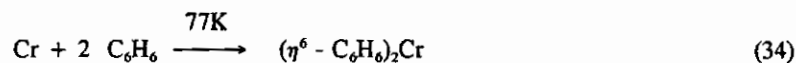


Depending on the metal ion involved, temperatures for the final step ranged from 475-850°C and crystallite sizes ranged from 20-27 nm.

## 7. Vapor Deposition in Matrices

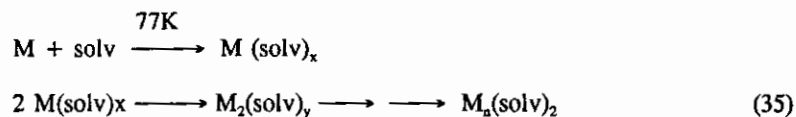
### 7.1 SOLVATED METAL ATOM DISPERSION

7.1.1. *Nanoscale Metal Particles.* The codeposition of metal vapor (atoms) with the vapor of an organic compound has allowed the synthesis of multitude of a new organometallic compounds. A classic example is the direct synthesis of bis(benzene)chromium (0), eq. 34.<sup>35</sup>



Generally such experiments have been carried out where excess organic reagent is codeposited with metal vapor at 77K in a "metal atom-vapor reactor".<sup>36</sup>

When an organic matrix material is chosen that only weakly interacts with the metal atoms of choice, low temperature "solvated metal atoms" can be prepared. Upon warming towards room temperature, the solvate decomposes and metal-metal bonds begin to reform, eq. 35.



As this process proceeds in the cold liquid (usually around 100-150 K), the mobility of the growing particle decreases, and solvent reordering continually occurs. The consequences are that particle growth is stopped.

In selected cases, beautiful nonaqueous colloidal solutions can be prepared in this way; for example, gold is prepared in acetone where the particle size of the gold is about 6 nm, and these are held in solution indefinitely by the solvation effects of the polar organic solvent.<sup>37</sup>

Several metals including Pd, Pt, and Au can be used to prepare such nonaqueous metal colloids.<sup>38,39</sup> Solvents can be varied, although polarity is important. Good results were obtained with acetone, ethanol and isopropyl alcohol. Even fluoroorganic solvents such as  $(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2)_3\text{N}$  can be employed.<sup>40</sup>

Particle stabilization was shown to be due to solvation effects coupled with electrostatic effects. As is common for many colloidal solutions, the particles scavenged electrons creating a negatively charged particle which is then surrounded by counterions and solvent (Figure 4). A "double layer" electrical potential is thus produced, and these electrostatic effects discourage particle aggregation.

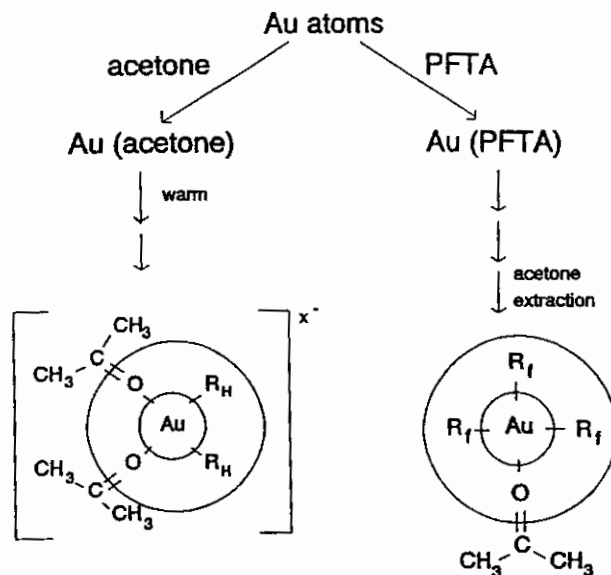


Figure 4. Gold atom agglomeration in acetone and in perfluorotri-n-butylamine (PFTA).<sup>39</sup> ( $R_H$  = fragments of acetone,  $R_f$  = fragments of PFTA)

A unique feature of these nonaqueous metal colloids is their "living" nature. Since only metal and pure solvent are present, there are few impurities to interfere. Upon solvent removal, large particles followed by thin metallic films can be produced by a process almost as simple as spray painting. Recently a detailed report on the adherence of gold films produced in this way showed that the substrate was very important.<sup>39</sup> For example, if polyphenylene sulfide was coated by spraying with a Au/acetone solution, a shiny, strongly adhering film was produced, and the adhesion was due to the strong ligating properties of the sulfur atoms in the polymer backbone that were on the surface (Figure 5).

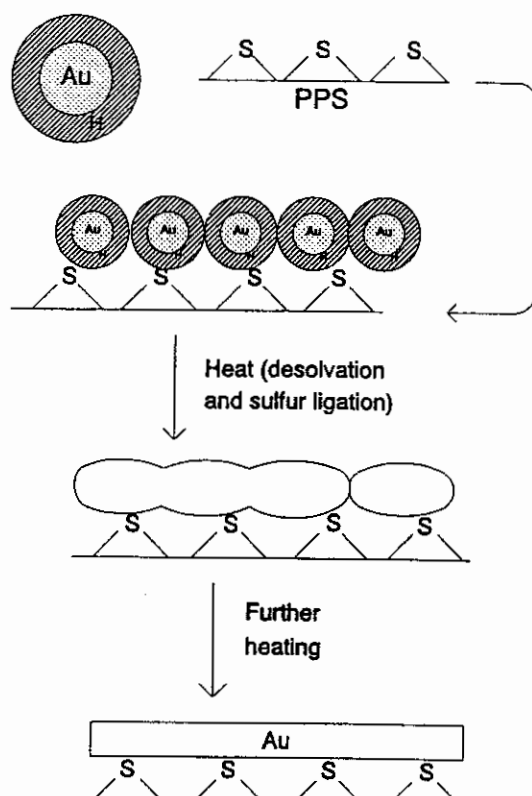


Figure 5. Gold-acetone colloidal solution used to prepare a gold film on polyphenylene sulfide. (H refers to acetone solvation).<sup>39</sup>

In addition to colloidal solutions, ultrafine metallic powders can be produced by the SMAD procedure.<sup>41,42</sup> Final particle size can be controlled by solvent choice (alkanes, ethers, or aromatic molecules), dilution effects and warm-up rates (77K→300K). For example fine powders of Cr, Mn, Fe, Co, Ni, Pd, Cu, Zn, Sn, Pb, and other metals have been prepared. Such particles have crystallite sizes ranging from 3-10 nm and exhibit extremely high surface reactivities.<sup>41-43</sup>

**7.1.2 Nanoscale Particles of Immiscible Metals** Of very recent interest has been the application of the SMAD method for producing metastable alloys of immiscible metals. The approach is to use atom clustering at low temperature in a matrix material that is relatively inert. In this way kinetic control of cluster growth should prevail. Thus, two metals can be vaporized simultaneously and trapped in codepositing pentane at 77K. When such a matrix is warmed, atom migration takes place. For example Fe-Li metastable alloy particles can be prepared and are stable up to room temperature.<sup>44-45</sup> During their preparation, slight phase segregation occurs in such a way that very small Fe particles are imbedded in solid Li (Figure 7). Upon heat treatment further phase segregation takes place so that larger Fe crystallites form and are protected by a Li metal coating. Thus, a core-shell structure forms with Fe as the core. This mode of phase segregation is apparently controlled by metal-metal bond strength. Since Fe-Fe bonds are stronger than Li-Li or Fe-Li, the Fe-Fe bonds form irreversibly, and the iron cluster grows and becomes protected (Figure 6).

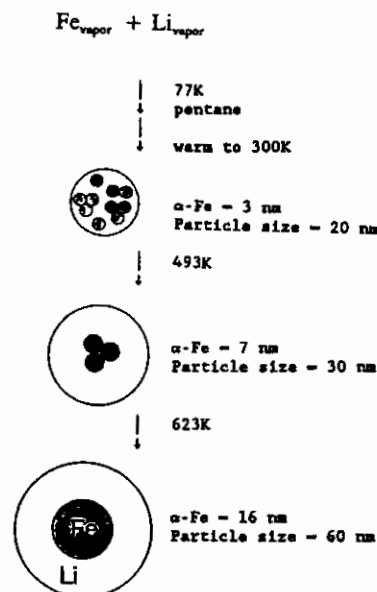


Figure 6. Fe-Li "Plum Pudding" structure.<sup>44</sup>

A similar codeposition scheme works well with Fe-Mg combinations.<sup>46</sup> Again, upon heating, a core-shell structure is formed with the center Fe crystallite protected by a Mg coating. Upon exposure to air, a thin MgO coating forms on the Mg and the system becomes impervious to further oxidation.



The preparation of these core-shell structures with a "sacrificial metal" (Li and Mg are able to scavenge any oxygen and thereby protect the Fe from oxidation) has allowed for the first time a study of the magnetic properties of nanoscale iron particles that do not possess a coating of a magnetic metal oxide. The results and comparisons have been extremely interesting. As

shown in Table 2, the coercivity ( $H_c$ ) of Fe-Mg particles is extremely low and does not seem to depend on size. Likewise, the saturation magnetization ( $M_s$ ) is near that of bulk iron. In contrast, a series of iron oxide coated nanoscale Fe crystallites exhibited much higher  $H_c$  that were quite dependent on temperature.<sup>47</sup> In addition  $M_s$  values were low. It would appear that the coating material is the key parameter in affecting magnetic properties of nanoscale iron particles.

These results have inspired a search for methods to produce other types of coatings and to measure effects on magnetic properties. To date, iron core-shell structures of Fe/Li, Fe/Mg, Fe/Fe<sub>3</sub>O<sub>4</sub>, Fe/FeS, and Fe/Ag have been prepared.

In the Fe/FeS case, a long chain thiol was used to cap the Fe particles, and upon heating an FeS coating was formed. This represents an antiferromagnetic coating. In the Fe/Ag case, silver and iron vapors were co-deposited (these metals are immiscible in the bulk at high temperature). Unfortunately, in this instance, a clean phase segregation forming a predictable morphology did not occur. Instead, all combinations were produced and the result was a complex mixture of Fe/Ag particles where most of the Fe was not protected from oxidation. Table II summarizes some magnetic properties of these systems.

TABLE II - Magnetic Properties of Core-Shell Iron Particles.

Sample	$\alpha$ -Fe Crystallite size (nm)	Coercivity $H_c$ at 10K (O <sub>e</sub> )	Saturation Magnetization at 150K $M_s$ (emu/g)
Fe	2.0	670	146
Fe/Li	3.0	395	132
Fe/Mg	3.0	200	110
Fe/FeS	<5	1000	52
Fe/Fe <sub>3</sub> O <sub>4</sub>	2.5	3400	25
bulk $\alpha$ -Fe	—	<50	220

## 8. Conclusions

The synthesis and characterization of nanoscale particles is truly an interdisciplinary field. Chemists, physicists, and engineers will need to work closely together in order to bring these fascinating materials to the forefront of science and technology. In this short tutorial/review, some of the important chemical aspects have been emphasized. It would be prudent to emphasize, from a chemist's point of view, that the synthesis of nanoscale particles is a difficult challenge. Purity of reagents and solvents, concentrations, temperatures, nucleation/precipitation rates, and environmental oxidation must be carefully controlled. Complete elemental analysis and careful spectroscopic characterization must precede the study of fundamental physical properties. After all it is of little worth to carry out fundamental measurements on impure or poorly characterized systems.

## 9. Acknowledgements

The authors gratefully acknowledge the financial support of the National Science Foundation, Army Research Office, and the Hazardous Waste Research Center of Kansas State University, and the Office of Naval Research through a subcontract from Professor Hadjipanayis.

## 10. References

1. a. Schlesinger, H.I., Brown, H.C., Finholt, A.E., Gilbreath, J.R., Hockstra, H.R., Hyde, E.K. (1953) "Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen", *J. Am. Chem. Soc.*, **75**, 215-219.
- b. Brown, H.C.; Brown, C.A. (1962) "New, Highly Active Metal Catalysts for the Hydrolysis of Borohydride", *J. Am. Chem. Soc.*, **84**, 1493-1494.
- c. Brown, H.C.; Brown, C.A. (1962) "A Simple Preparation of Highly Active Platinum Metal Catalysts for Catalytic Hydrogenation", *J. Am. Chem. Soc.*, **84**, 1494-1495.
2. Glavee, G.N., Klabunde, K.J. Sorensen, C.M. and Hadjipanayis, G.C. (1992) "Borohydride Reductions of Metal Ions. A New Understanding of the Chemistry Leading to Nanoscale Particles of Metals, Borides, and Metal Borates", *Langmuir*, **8**, 771-773.
3. Glavee, G.N., Klabunde, K.J., Sorensen, C.M. and Hadjipanayis, G.C. (1993), "Borohydride Reduction of Cobalt Ions in Water. Chemistry Leading to Nanoscale Metal, Boride, or Borate Particles," *Langmuir*, **9**, 162-169.
4. Glavee, G.N., Klabunde, K.J., Sorensen, C.M. and Hadjipanayis, G.C. (1993) "Sodium Borohydride Reduction of Cobalt Ions in Nonaqueous Media. Formation of Ultrafine Particles (Nanoscale) of Cobalt Metal", *Inorg. Chem.*, **32**, 474-477.
5. a. Van Wonerghem, J., Morup, S., Koch, C.J.W., Charles, S.W., and Wells, S. (1986) "Formation of Ultra-fine Amorphous Alloy Particles by Reduction in Aqueous Solution", *Nature*, **322**, 622-623.
- b. Linderoth, S., Morup, S., Meagher, A., Larsen, J., Bentzon, M.D., Clausen, B.S., Wells, S. and Charles, S.W., Koch, C.J.W. (1989) "Amorphous to Crystalline Transformation of Ultrafine Fe<sub>62</sub>B<sub>38</sub> Particles", *J. Magn. Magn. Mater.*, **81**, 138-146.
6. Corrias, A., Ennas, G., Licheri, G.C., Marongiu, G. and Paschina, G. (1990) "Amorphous Metallic Powders Prepared by Chemical Reduction of Metal Ions with Potassium Borohydride in Aqueous Solution" *Chem. Mater.* **2**, 363-366.
7. Yiping, L., Hadjipanayis, G.C., Sorensen, C.M., and Klabunde, K.J., (1989) "Magnetic and Structural Properties of Ultrafine Co-B Particles", *J. Magn. Magn. Mater.*, **79**, 321-326.
8. Yiping, L., Tang, Z.X., Hadjipanayis, G.C., unpublished work.
9. Rieke, R.D., (1977) "Preparation of Highly Reactive Metal Powders and Their Use in Organic and Organometallic Synthesis", *Acc. Chem. Res.*, **10**, 301-306.
10. Rochfort, G.L. and Rieke, R.D. (1986) "Preparation, Characterization, and Chemistry of Activated Cobalt", *Inorg. Chem.*, **25**, 348-355.
11. Kistler, S.S. (1932) "Coherent Expanded Aerogels", *J. Phys. Chem.*, **36**, 52-64.
12. Teichner, S.J., Nicolaon, G.A., Vicarini, M.A., Gardes, G.E.E. (1976) "Inorganic Oxide Aerogels", *Adv. Colloid Interface Sci.*, **5**, 245-273.
13. Gesser, H.D. and Goswami, P.C., (1989) "Aerogels and Related Porous Materials", *Chem. Rev.* **89**, 765-788.
14. Utamapanya, S., Klabunde, K.J. and Schlup, J.R. (1991), "Nano-scale Metal Oxide Particles/Clusters as Chemical Reagents. Synthesis and Properties of Ultra-High Surface Area Magnesium Hydroxide and Magnesium Oxide", *Chem. Materials*, **3**, 175-181.
15. Itoh, H., Utamapanya, S., Stark, J.V., Klabunde, K.J. and Schlup, J.R., (1993) "Nanoscale Metal Oxide Particles as Chemical Reagents. Intrinsic Effects of Particle Size on Hydroxyl Content and on Reactivity and Acid/Base Properties of Ultrafine



- Magnesium Oxide", *Chem. Materials*, **5**, 71-77.
16. a. Li, Y.X., Koper, O., Atteya, M. and Klabunde, K.J. (1992) "Adsorption and Decomposition of Organophosphorus Compounds on Nanoscale Metal Oxide Particles. In Situ GC-MS Studies of Pulsed Microreactions over Magnesium Oxide.", *Chem. Materials*, **4**, 323-330.
  - b. Koper, O., Li, Y.X., Klabunde, K.J., (1993), "Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide", *Chem. Materials*, **5**, 500-505.
  - c. Khaleel, A. and Hooker, P., unpublished work.
  17. a. Sugimoto, T. and Matijevic, E. (1980) "Formation of Uniform Spherical Magnetite Particles by Crystallization from Ferrous Hydroxide Gels", *J. Colloid Interface Sci.*, **74**, 227-243.
  - b. Tamura, H., and Matijevic, E., (1982), "Precipitation of Cobalt Ferrites", *J. Colloid Interface Sci.*, **90**, 100-109.
  - c. Fan, X.J. and Matijevic, E. (1988), "Preparation of Uniform Colloidal Strontium Ferrite Particles", *J. Am. Ceram. Soc.*, **71**, C60-C62.
  18. Tang, Z.X., Sorensen, C.M., Klabunde, K.J. and Hadjipanayis, G.C. (1991), "Preparation of Manganese Ferrite Fine Particles from Aqueous Solution", *J. Colloid Interface Sci.*, **146**, 38-52.
  19. Boutonnet, M., Kizling, J., Stenius, P. and Maire, G. (1982) "The Preparation of Monodisperse Colloidal Metal Particles from Microemulsions", *Colloids and Surfaces*, **5**, 209-225.
  20. Kurihara, K., Kizling, J., Stenius, P. and Fendler, J.H. (1983) "Laser and Pulse Radiolytically Induced Colloidal Gold Formation in Water and in Water-in-Oil Microemulsions", *J. Am. Chem. Soc.*, **105**, 2574-2579.
  21. Lufimadio, N., Nagy, J.B., Derouane, E.G., (1984) "Surfactants in Solution", in K.J. Mittal and B. Lindman, Editors, Plenum, New York, **3**, 1483.
  22. Ravet, I., Lufimadio, N., Gourgue, A. and Nagy, J.B. (1985) "Physico-Chemical Characterization of Reversed Micelles CTAB-1-Hexanol-water Containing Co(II) Ions", *Acta. Chim. Hung.*, **119**, 155-166
  23. Nagy, J.B., Gourgue, A. and Derouane, E.G. (1983) "Preparation of Monodispersed Nickel Boride Catalysts Using Reversed Micellar Systems", *Stud. Surf. Sci. Catal.*, *Preparation of Catalysts III*, **16**, 193-202.
  24. Gobe, M., Kon-No, K., Kandori, K. and Kitahara, A. (1983) "Preparation and Characterization of Monodisperse Magnetite Sols in W/O Microemulsion", *J. Colloid Interface Sci.*, **93**, 293-295.
  25. Meyer, M., Wallberg, C., Kurihara, K. and Fendler, J.H. (1984) "Photosensitized Charge Separation and Hydrogen Production in Reversed Micelle Entrapped Platinized Colloidal Cadmium Sulphide", *J. Chem. Soc. Chem. Comm.*, **90-91**.
  26. Lianos, P. and Thomas, J.K. (1986) "Cadmium Sulfide of Small Dimensions Produced in Inverted Micelles", *Chem. Phys. Lett.*, **125**, 299-302.
  27. a. Steigerwald, M.L., Alivisatos, A.P., Gibson, J.M., Haris, T.D., Kortan, R., Muller, A.J., Thayer, A.M., Duncan, T.M., Douglass, D.C. and Brus, L.E. (1988) "Surface Derivatization and Isolation of Semiconductor Cluster Molecules", *J. Am. Chem. Soc.*, **110**, 3046-3050.
  - b. Kortan, A.R., Hull, R., Opila, R.L., Bawendi, M.G., Steigerwald, M.L., Carroll, P.J. and Brus, L.E. (1990) "Nucleation and Growth of CdSe on ZnS Quantum Crystallite Seeds, and Vice Versa, in Inverse Micelle Media", *J. Am. Chem. Soc.*, **112**, 1327-1332.
  28. Lee, K.M., Sorensen, C.M., Klabunde, K.J. and Hadjipanayis, G.C. (1992) "Synthesis and Characterization of Stable Colloidal Fe<sub>3</sub>O<sub>4</sub> Particles in Water-In-Oil

- Microemulsions", *IEEE Trans. Magnetics*, 28, 3180-3182.
29. For examples of this method, see:
- a. Messing, G.L., Gardner, T.J. and Ciminelli, R.R. (1983) "Characteristics of EDS-Derived Powders" *Sci. of Ceram.*, 12, 117-124.
  - b. Zhang, S.C., Messing, G.L. and Borden, M. (1990) "Synthesis of Solid, Spherical Zirconia Particles by Spray Pyrolysis", *J. Am. Ceram. Soc.*, 73, 61-67.
  - c. Nonaka, K., Hayashi, S., Okada, K., Otsuka, N. and Yano, T. (1991) "Characterization and Control of Phase Segregation in the Fine Particles of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> Synthesized by the Spray Pyrolysis Method. *J. Mater. Res.* 6, 1750-1756.
  - d. Tang, Z.X., Nafis, S., Sorensen, C.M., Hadjipanayis, G.C. and Klabunde, K.J. (1989) "Magnetic Properties of Aerosol Synthesized Iron Oxide Particles", *J. Mag. Mag. Mater.*, 80, 285-289.
30. Xu, H.K., Sorensen, C.M., Klabunde, K.J. and Hadjipanayis, G.C. (1992) "Aerosol Synthesis of Gadolinium Iron Garnet Particles", *J. Mater. Res.*, 7, 712-716.
31. Tang, Z.X., Nafis, S., Sorensen, C.M., Hadjipanayis, G.C. and Klabunde, K.J. (1989) "Magnetic and Structural Properties of Aerosol Synthesized Barium Ferrite Particles", *IEEE Trans. Magnetics*, 25, 4236-4238.
32. Li, Q., Sorensen, C.M., Klabunde, K.J. and Hadjipanayis, G.C., unpublished results.
33. White III, J.P., Deng, H. and Shore, S.G. (1991) "Borohydride Complexes of Europium (II) and Ytterbium (II) and Their Conversion to Metal Borides. Structures of (L)<sub>4</sub>Yb[BH<sub>4</sub>]<sub>2</sub> (L = CH<sub>3</sub>CN, C<sub>2</sub>H<sub>5</sub>N)", *Inorg. Chem.*, 30, 2337-2342.
34. LaDuca, R.L. and Wolczanski, P.T. (1992) "Preparation of Lanthanide Nitrides via Ammonolysis of Molten {(Me<sub>3</sub>Si)<sub>2</sub>N}Ln: Onset of Crystallization Catalyzed by LiNH<sub>2</sub> and LiCl", *Inorg. Chem.*, 31, 1311-1313.
35. Timms, P.L. (1969) "The Formation of Complexes from Transition-Metal Vapours", *Chem. Comm.*, 1033.
36. Klabunde, K.J., (1980) "Chemistry of Free Atoms and Particles", Academic Press, San Diego.
37. Lin, S.T., Franklin, M.T. and Klabunde, K.J. (1986) "Non-Aqueous Colloidal Gold. Clustering of Metal Atoms in Organic Media. 12", *Langmuir*, 2, 259-260.
38. Cardenas-Trivino, G., Klabunde, K.J. and Dale, B. (1987) "Living Colloidal Palladium in Non-Aqueous Solvents, Formation, Stability and Film Forming Properties. Clustering of Metal Atoms in Organic Media 14", *Langmuir*, 3, 986-992.
39. Klabunde, K.J., Youngers, G., Zuckerman, E.B., Tan, B.J., Antrim, S. and Sherwood, P.M. (1992) "Living Colloidal Metal Particles in Non-Aqueous Solvents as Precursors for Thin Films by Chemical Liquid Deposition (CLD). Gold Coating on Glass, Metals, Silicon, and Organic Polymers Employing Organic and Fluororganic Solvents", *Eur. J. Solid State Inorganic Chem.*, 29, 227-260.
40. Zuckerman, E.B., Klabunde, K.J., Olivier, B.J. and Sorensen, C.M. (1989) "Non-Aqueous Perfluorocarbon-Derived Gold Colloids. Clustering of Metal Atoms in Fluorocarbon Media. 1.", *Chem. Materials*, 1, 12-14.
41. Klabunde, K.J. and Murdock, T.O. (1979) "Active Metal Slurries by Metal Vapor Techniques. Reactions with Alkyl- and Arylhalides", *J. Org. Chem.*, 44, 3901-3908.
42. Klabunde, K.J., Li, Y.X. and Tan, B.J. (1991) "Solvated Metal Atom Dispersed Catalysts", *Chem. Materials*, 3, 30-39.
43. Olsen, A.W., (1988) "Dispersions of Metal in Organic Media", Ph.D. Thesis, Kansas State University.
44. Glavee, G.N., Easom, K., Klabunde, K.J., Sorensen, C.M. and Hadjipanayis, G.C. (1992) "Clusters of Immiscible Metals. 2. Magnetic Properties of Iron-Lithium

- Bimetallic Particles", *Chem. Materials*, 4, 1360-1363.
45. Glavec, G.N., Kernizan, C.F., Klabunde, K.J., Sorensen, C.M. and Hadjipanayis, G.C. (1991) "Clusters of Immiscible Metals. Iron-Lithium Nano-scale Bimetallic Particle Synthesis and Behavior Under Thermal and Oxidative Treatments", *Chem. Material*, 3, 967-976.
  46. Zhang, D. (1991) unpublished work.
  47. Gangopadhyay, S., Hadjipanayis, G.C., Dale, B., Sorensen, C.M., Klabunde, K.J., Papaefthymiou, V., and Kostikas, A. (1992) "Magnetic Properties of Ultrafine Iron Particles", *Phys. Rev. B.*, 45, 9778-9787.
  48. Easom, K. (1992) "Preparation and Characterization of Ultrafine Iron Powders: Mössbauer and Magnetic Studies", Ph.D. Thesis, Kansas State Univeristy.