EFFECT OF AMMONIUM NITRATE IN THE AVERAGE SIZE REDUCTION OF NANOPARTICLES OF SILVER, NICKEL AND RUTHENIUM SYNTHESIZED FROM FLASH PYROLYSIS

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Abstract

Nanoparticles of silver in the size range of 100-200 nm were synthesized by flash pyrolysis. Ammonium nitrate was added to aqueous silver nitrate solution, and was subjected to flash pyrolysis in a reactor tube. The ammonia gas generated in the reactor tube by the disintegration of ammonium nitrate at pyrolysis temperature of 700-900 °C was effective in breaking the aerosol droplet produced from the atomizer. It was observed that ammonia gas released in the process acted as a surfactant by breaking the aerosol and the resulting nanoparticles synthesized were in the size range of 10-20 nm. The operating parameters such as the solution concentration and atomizer power were maintained the same with and without the usage of ammonium nitrate in silver nitrate and both the results were compared to see the impact of ammonium nitrate surfactant on the aerosol droplet in reducing the size of the nanoparticle. It was observed that for the same set of conditions, when ammonium nitrate was used, a considerable size reduction occurred from 200 nm to 20 nm due to the presence of ammonia gas in the reactor.

1. Introduction

Synthesizing nanoparticles in the size range of 10-20 nm was always a challenge. Flash pyrolysis technique was used to synthesize silver nanoparticles from aqueous silver nitrate solution. The control of particle size was vital in the synthesis of nanoparticles. The size of nanoparticle depends on the size of the aerosol droplet generated. The size and shape of aerosol droplet depends on the surface tension of the droplet. Surfactants can be used to reduce the effect of surface tension of the aerosol droplet. Since the size of the nanoparticle depends on the size of the aerosol emitted, it is essential to control the size of the aerosol droplet. Due to the weak surface tension, the bigger droplet can be broken down into smaller droplets.

Various researchers have studied the effect of surfactants. Yamada [1] observed the effects of surfactant on the periodic ordered porous silica films where the dielectric constant and refractive index decreased due to the effect of surfactants. Leneweit [2] studied the effect of surfactant on the stability of thin liquid film and observed that at small radius ‘r’ adsorbing monolayer was not in thermodynamic equilibrium but approached equilibrium at larger ‘r’. Otsubo [3] observed the surfactant effect on suspension rheology where the surfactant molecule acted as a displacer and lead to desorption of polymer chains from particle surfaces. Suspension viscosity was reduced if the bridging was low and the surfactant also increased the viscosity where the surfactant adsorption was high. According to Pan [4], addition of surfactant to alum sludge system decreased the filterability of the sludge. At optimum dosage, sludge dewatering rate was increased. Cationic surfactant acted as a conditioning aid for cationic polymer.

2. Background

The effect of surfactants in various applications has been investigated by many researchers in the past. Agble [5] studied the binary liquid systems and investigated the effect of surfactants on interfacial mass transfer. It was observed that measured molar fluxes increased due to the surfactant in the aqueous phase. Interfacial stability was
manipulated by the addition of surfactant. Zhang [6] observed that the surfactant adsorption inhibited the electron transfer process and changed the reactant concentration profile adjacent to the droplet. Bulk surfactant concentration was one of the factors that affected the reaction concentration. According to Dutta [7], dynamic film tension has less impact on bubble size of aerated mesophase and viscosity of the mesophase has a greater impact. This depends on the surfactant concentration.

Surfactants were used in various applications as well. Huang [8] used the surfactants in the flotation process to aid the solid liquid separation and observed that the addition of cationic surfactant to oppositely charged polyelectrolyte had more impact to sludge dewatering whereas the addition of the cationic surfactant to the cationic polyelectrolyte-conditioned sludge had least impact. Saylor [9] studied the effect of surfactant monolayers on the vortex rings and observed a maximum display of vortex velocity at immediate surfactant concentration. Clay [10] studied the effect of surfactant on the spreading of a viscous droplet. Static contact angle was allowed to vary with the surfactant concentration and temperature to speed up the droplet motion. It was observed that when the surfactant transport was allowed along the interface, it was possible to stop the movement of the droplet.

The effect of ammonia was studied earlier in various applications. Su [11] discussed the effect of ammonia as an adsorbant. A modification of the lattice parameter was observed in the case of NaBeta with the interaction of ammonia and methylamine. Butterworth [12] studied the effect of ammonia in the pathogenesis of the central nervous system complications of acute and chronic liver failure. Arterial ammonia blood concentrations were seen as good predictors of cerebral herniation incase of patients having acute liver failure. Abdoun [13] observed that intracellular protonation of ammonia tend to alkalinize the cytoplasm and the intracellular pH of polar and non polar cells gets affected by the cellular uptake of ammonia. According to Athawale [14], when acrylic acid-doped polyanilic polyaniline was exposed to saturated ammonia vapors, the resistance of polyaniline decreased due to the differences in the chemical interactions of the polymer with ammonia vapors. Feit [15] observed that ammonia suppresses chemotactic response of both ALC and pst cells. A higher concentration of ammonia was required to suppress the response to pst cells which is mediated by the unprotonated species of ammonia.

Researchers earlier used ammonia to study the various chemical behaviors. According to Kurakake [16], enzymatic hydrolysis was enhanced by pretreating bagasse, cornhusk and switchgrass with ammonia water. The performance of enzymatic hydrolysis was observed to improve. Chan [17] observed that the reduction in astrocytic uptake of neuronally-released glutamate and high extracellular glutamate levels was due to the effects of ammonia. According to Murthy [18], formation of free radicals in astrocytes can be induced by the elevated concentrations of ammonia. Free radical formation in the cells can be induced by pathophysiologial concentrations of ammonia. Igarashi [19] found that cytokine-induced apoptosis in gastric epithelial cells can be accelerated by ammonia. Bender [20] studied the effects of ammonia on GABA uptake and enhanced GABA release and found the extra cellular levels of GABA got elevated due to ammonia.
with a dysfunction of GABAergic neurotransmission. Though researchers have used ammonia in several applications, the effect of ammonia as a surfactant was not explored in detail. An attempt was made in this paper to study the effect of ammonia in breaking the surface tension of the aerosol droplet.

Ammonia gas can be induced into the reactor tube by heating up of ammonium nitrate. At high temperature of flash pyrolysis, ammonium nitrate can be disintegrated into ammonia and nitrate. Several researchers have used ammonium nitrate in various applications. The study done by Maheswari [21] showed that in the phase transitions of Langmuir films of amphiphilis-stearic acid, stearyl amine (STAM), searyl alcohol, dihexadecylphosphate and the quarternized ammonium salt octadecyldimethylammonium bromide at air/water interface, all other monolayers except for STAM exhibit a liquid expanded to liquid condensed transition with a a slight expansion in the presence of ammonium nitrate. Inazu [22] studied the decomposition of ammonium nitrate in aqueous solution where a series of experiements revealed that removal of ammonium and nitrate ion did not take place simultaneuosly through the independent reactions of two ions but was through the equimolecular reaction between the two. In the experiments done by Ortiz [23], environmentally relevant concentrations of ammonium nitrate (0 to 200 mg NO3- /L) were used to expose the embroys for 15 days. Hatching took place in this exposure limits.

Ammonium nitrate was used in combination with other chemicals in fertilizers as well. According to Brown [24], there will be extreme polarity in the ammonium nitrate-type explosives. Sasoh [25] used a mixture of ammonium nitrate and alcohol as a new type of propellant in ballistic experiments obtaining a increased ballistic performance with maximum energy. Ammonium nitrate was used to enhance the soil chemical properties. Harapiak [26] observed that most of the changes in the chemical soil properties were due to N fertilization by the addition of ammonium nitrate and urea. According to Flores [27], the deleterious effect of salinity can be reduced by using nutraient solutions with higher NH4+ concentrations. This contributes to the increase in the nitrogen assimilation. In the study done by Coolong [28], by using ammonium nitrate, flavour intensity and quality of onions can be influenced by nitrogen fertility levels.

Ammonium nitrate was also used to study the influence in the root induction medium and polymerization reactions. Bennet [29] observed that ammonium nitrate had an influence on the rooting of the eucalyptus globulus by the presence of NH4+ in the root induction medium. The presence of ammonium nitrate decreased the pH. In the study done by Lutfor [30], the known free radical method initiated the grafting reactions where ceric ammonium nitrate acts as an initiator for graft copolymerization. Ammonium nitrate can be mixed with aqueous silver nitrate solution as it is soluble in aqueous silver nitrate. In this paper, ammonium nitrate was used to produce ammonia gas inside the reactor tube where the ammonia gas may act as a surfactant in breaking the aerosol by reducing the surface tension of the droplet. Since the ammonia gas can reduce the surface tension, of a droplet, it is important to induce ammonia at the point of emission of the aerosol inside the reactor tube.
3.0 Experimental Mechanism

Though ammonium nitrate had been used in various applications, its usage in the synthesis of nanoparticles in the size range of 10-20 nm has not been investigated. An attempt was made in these experiments to study the effect of ammonia gas in breaking the aerosol in order to generate smaller aerosols in the synthesis of nanoparticles by flash pyrolysis. In the synthesis of silver nanoparticles by flash pyrolysis using an atomizer and reactor assembly, it was observed that the particles were in the size range of 100-200 nm. Several aglomeres were also observed in the initial stages of the synthesis. This was probably due to the larger size of the aerosol droplet. When ammonium nitrate was mixed with silver nitrate solution, it was soluble in aqueous silver nitrate solution. Temperature at 800 °C was maintained by heating the reactor tube by a furnace. Thermocouples are used to measure the temperature of the reactor at various locations. At high temperature of flash pyrolysis, the mixture of aqueous silver nitrate and ammonium nitrate can disintegrate into silver, ammonia and nitrate gas. Since the reactor assembly was under vacuum, nitrates generated would go through the exhaust leaving behind aqueous silver particles and ammonia gas. Ammonia gas can break the aqueous silver aerosols into smaller aerosols. Due to the high temperature, water in the aqueous phase evaporates leaving behind silver particles. Argon gas flowing through the reactor tube can deposit these silver particles on the substrate at the bottom of the reactor tube. Quartz glass plates were used as sample substrates to collect the silver nanoparticles.

The technique was extended to other metal systems such as ruthenium chloride and Nickel chloride to synthesize the nanoparticles of ruthenium and nickel. The experiments were carried out with separate aqueous solutions of ruthenium chloride and nickel chloride. Initially the experiments were run without ammonium nitrate for silver nitrate, ruthenium chloride and nickel chloride. Later the experiments were performed by mixing ammonium nitrate in these solutions. The behavior of ammonia gas as a surfactant in reducing the surface tension of the aerosol thus breaking the aerosol into smaller droplets for various metal solutions in obtaining corresponding metal nanoparticles was investigated.

Silver, ruthenium and nickel nanoparticles thus synthesized by flash pyrolysis without ammonium nitrate were compared with the set of nanoparticles of silver, ruthenium and nickel synthesized by using ammonium nitrate. Reduction in size of the nanoparticles can be expected due to the nature of ammonia gas. Samples of nanoparticles of silver, ruthenium and nickel were collected on separate substrates of quartz plates at the bottom of the reactor which was kept perpendicular to the path of the deposition of nanoparticles. The reactor was cooled after the experiment, and the samples were removed. The samples obtained were later analyzed for the size and shape. The behavior of ammonia gas in breaking the aerosol particle would be the same for all the metal solutions, but the study of its effect in obtaining nanoparticles of smaller range was studied. How effectively ammonia gas can act as a surfactant in the sub-nano range within the contact time of few seconds at high temperature of flash pyrolysis was investigated. Since the size of aerosol generated from the atomizer was very small, the impact of ammonia gas on the aerosol was important in obtaining desired nanoparticle.
3.1 Sample Characterization

Formvar coated nickel grids were loaded on the quartz plates for obtaining the deposits of the nanoparticles and were kept inside the reactor tube. The samples of nickel grids were collected on a substrate of quartz plates at the bottom of the reactor, and their size and shape was characterized by using Transmission Electron Microscopy (TEM). Structure of samples less than 100 nm can be clearly seen in TEM. 200 mesh nickel grids with formvar coating were used as substrates for analyzing the samples under TEM. The samples are developed and the films obtained were analysed for particle size distribution. Every particle on the film was counted and their size is characterized based on their mean particle size and standard deviation.

3.2 Experimental Design

Experiments were carried out for various combinations of solution concentration and atomizer power as the concentration of the solution determines the number of atoms in the droplet. The vibration frequency of the atomizer was controlled by varying the atomizer power input. The set of experiments were run with the combination of parameters and the same combination of parameters was carried out for the set of experiments by mixing the solution with ammonium nitrate. The two results were compared. The same was carried out for ruthenium chloride and nickel chloride to synthesize nanoparticles of ruthenium and nickel. Finally, the nanoparticles of silver, nickel and ruthenium were compared to see the impact of ammonia gas on the aerosol droplet. The solution concentration was varied from $10^{-1}$N to $10^{-7}$N and atomizer power between 4W and 11W.

4.0 Results and Discussions

Effect of ammonium nitrate on the average particle size was studied. Three set of experimental conditions were selected and were run without using ammonium nitrate and their size was measured and characterized by TEM and tabulated. The same set of experiments was run for the second time with the same conditions and operating parameters using ammonium nitrate. The difference in the average particle size can be seen in the reduction of size when ammonium nitrate was used. Table 1 shows the comparison of the size of the silver nanoparticles performed without ammonium nitrate and with ammonium nitrate. The drop in average particle size was observed when ammonium nitrate was used. The set of experiments whose average particle size was above 200 nm without the usage of ammonium nitrate was selected to see the impact of ammonium nitrate on the average particle size. The corresponding particle size distribution images of TEM are listed in the Appendix.

Experiments were performed using other metal systems such as ruthenium chloride and nickel chloride to synthesize the nanoparticles of ruthenium and nickel. Ammonium nitrate was used in these two solutions. Table 2 shows the results of ruthenium nanoparticles synthesized from ruthenium chloride using ammonium nitrate.

Since the effect of ammonium nitrate was expected to bring down the particle size, solution concentration was kept high whereas atomizer power and reactor temperature were kept at lower limits. This gave the flexibility to operate the experiment at optimum reactor conditions. Nanoparticles of higher average size were synthesized
from higher concentration. However, average particle size of less than 50 nm was obtained with monodisperse particle size distribution. The same distribution was even observed for the particles less than 20 nm. The average particle size can also depend on the density of solution which varies with the nature of solution.

For example, the behavior of silver nitrate can be different from ruthenium chloride and nickel chloride. All three chemicals can also show a different behavioral pattern in the particle size distribution. This phenomenon was also investigated when the solutions were varied in synthesizing nanoparticles of various metals like silver, ruthenium and nickel. Table 3 shows the results of nickel nanoparticles synthesized from nickel chloride using ammonium nitrate.

The operating conditions were maintained similar to that of the set of experiments run with ruthenium chloride. This showed that nature of chemical or solution had a least impact on the distribution and average particle size. Both the solutions of ruthenium chloride and nickel chloride behaved in a similar way, as can be seen from the particle size distribution having almost the similar average particle size. The operating parameters and the effect of surfactant was dominant than the nature of solution or chemical.

5.0 Conclusions

Ammonia gas had a significant impact in reducing the average particle size. A significant difference was seen in the average size of the nanoparticle when ammonium nitrate was used. The size was reduced from 200-300 nm to 10-20 nm. However, smaller particles of less than 10 nm were also observed. Coalescence of particles was reduced. Monodisperse distribution of particles was observed. It can be concluded that smaller particles can be synthesized by inducing ammonia gas into the reactor chamber by mixing the solution with ammonium nitrate.

(1) Ammonium nitrate can be mixed with the solution to synthesize nanoparticles of less than 20 nm by the process of flash pyrolysis.

(2) Higher concentration and lower power can also be used to synthesize nanoparticles of less than 20 nm, as the effect of ammonia gas was significant in breaking the aerosol bubble in generating fine droplets.

(3) However, clear and fine distribution of nanoparticles was seen in the case of solution with lower concentration and higher power.

(4) Agglomeration of nanoparticles was reduced when ammonium nitrate was used.

Nomenclature

°C unit of relative temperature, degrees Celcius
nm nanometer
TEM Transmission Electron Microscopy
SEM Scanning Electron Microscopy
N unit of measurement of concentration, Normality
W unit of power, watts
References


[19] Igarashi, M; Kitada, Y; Yoshiyama, H; Takagi, A; Miwa, T; Koga, Y; (2001). “Ammonia as an Accelerator of Tumor Necrosis Factor Alpha-Induced Apoptosis of Gastric Epithelial Cells in Helicobacter Pylori Infection.” Infection and Immunity 69(2): 816-821.


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Address

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Table captions

Table 1. Comparison of Average Particle Size With and Without Ammonium Nitrate
Table 2. Experimental Results for Ruthenium Nanoparticles Synthesized from Ruthenium Chloride Using Ammonium Nitrate.
Table 3. Experimental Results for Nickel Nanoparticles Synthesized from Nickel Chloride Using Ammonium Nitrate.

Table 1. Comparison of Average Particle Size With and Without Ammonium Nitrate

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Table 3. Experimental Results for Nickel Nanoparticles Synthesized from Nickel Chloride Using Ammonium Nitrate.

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Figure Captions

Figure 1. SEM image of particle size distribution of silver nanoparticle of 293.47 nm which was run without ammonium nitrate at $10^{-1}$N, 800 °C and 8W.

Figure 2. TEM image-01 of particle size distribution of silver nanoparticle of 13.61 nm which was run using ammonium nitrate at $10^{-1}$N, 800 °C and 8W.

Figure 3. TEM image-02 of particle size distribution of silver nanoparticle of 13.61 nm which was run using ammonium nitrate at $10^{-1}$N, 800 °C and 8W.

Figure 4. SEM image of particle size distribution of silver nanoparticle of 301.63 nm which was run without ammonium nitrate at $10^{-1}$N, 700 °C and 8W.
Figure 5. TEM image-01 of particle size distribution of silver nanoparticle of 16.21 nm which was run using ammonium nitrate at 10^{-1}N, 700 °C and 8W.

Figure 6. TEM image-02 of particle size distribution of silver nanoparticle of 16.21 nm which was run using ammonium nitrate at 10^{-1}N, 700 °C and 8W.

Figure 7. TEM image-01 of particle size distribution of ruthenium nanoparticle of 9.46 nm which was run using ammonium nitrate at 10^{-4}N, 700 °C and 5W.

Figure 8. TEM image-02 of particle size distribution of ruthenium nanoparticle of 9.46 nm which was run using ammonium nitrate at 10^{-4}N, 700 °C and 5W.

Figure 9. TEM image-01 of particle size distribution of ruthenium nanoparticle of 8.45 nm which was run using ammonium nitrate at 10^{-4}N, 700 °C and 5W.

Figure 10. TEM image-02 of particle size distribution of ruthenium nanoparticle of 8.45 nm which was run using ammonium nitrate at 10^{-4}N, 700 °C and 5W.

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Figure 6. TEM image-02 of particle size distribution of silver nanoparticle of 16.21 nm which was run using ammonium nitrate at $10^{-1}$N, 700 °C and 8W.

Figure 7. TEM image-01 of particle size distribution of ruthenium nanoparticle of 9.46 nm which was run using ammonium nitrate at $10^{-4}$N, 700 °C and 5W.
Figure 8. TEM image-02 of particle size distribution of ruthenium nanoparticle of 9.46 nm which was run using ammonium nitrate at $10^{-4}$N, 700 °C and 5W.

Figure 9. TEM image-01 of particle size distribution of ruthenium nanoparticle of 8.45 nm which was run using ammonium nitrate at $10^{-4}$N, 700 °C and 5W.
Figure 10. TEM image-02 of particle size distribution of ruthenium nanoparticle of 8.45 nm which was run using ammonium nitrate at $10^{-4}$N, 700 °C and 5W.