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Synthesis and Characterization of Fine and Monodisperse Silver Particles of Uniform Shape

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Fine silver particles of uniform size and shape have been synthesized from silver nitrate in hot ethylene glycol. Quasi-spheric and monodisperse silver particles are produced only when particle sintering is prevented during the growth step. For this purpose, a protective agent, namely, polyvinylpirrolidone (PVP), was added to the system. Particle size increases with increasing temperature and PVP/silver nitrate weight ratio. Heterogeneous nucleation of metallic silver with a critical concentration of *in-situ* formed platinum nuclei produces monosize particles that have a rod-like shape. This drastic change in particle shape indicates that under these conditions PVP also acts as a crystal habit modifier. The thickness of rod-like particles changes when different PVP/silver nitrate weight ratios are used. Electron microscopy and X-ray diffraction techniques were used for particle characterization. The synthesis of metallic particles in liquid polyols, which act as both solvent and reducing agent, is a useful method for producing highly pure, fine, and monodisperse particles of uniform shape.

Introduction

Highly pure silver powders of fine, monosize, and uniformly shaped particles are increasingly needed for specific uses in many areas of technological importance, but especially in high-tech industrial applications. In the electronics industry, for example, they constitute the active part of conductive inks, pastes, and adhesives used in the manufacture of various electronic parts (*1*). Conductive silver pastes and inks form the basis of the thick-film technology for producing such electronic components as hybrid microcircuits (*2*) and the internal electrodes of multilayer ceramic capacitors (*3*).

Processes for the manufacture of silver powders involve a variety of methods ranging from chemical, physical (atomization and milling), and electrochemical to thermal decomposition. Each of these methods, however, produces particles of varying physical properties such as apparent density, surface area, particle size and shape, and particle size distribution. Particles with the smallest size, narrowest size distribution, and highest purity are those chemically produced by reduction of silver compounds or complexes in aqueous (*4*) or organic media (*5*). Although both inorganic and organic reducing agents are used for producing silver particles from solution, organic reducing agents present the advantage of forming finer particles (*1*).

In what is now known as the polyol process (*6, 7*), which is a newly developed chemical method for the synthesis of fine, highly pure, and monodisperse metallic par-

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ticles of uniform shape, liquid polyols such as diethylene glycol and ethylene glycol are used as both the solvent medium and reducing agent. Reduction of a metallic compound, nucleation of the metallic species, and growth of the metal particles in the polyol take place under strictly controlled reaction conditions. The polyol process has been successfully used for producing powders of cobalt, copper, nickel, and precious metals from many metallic compounds (7). Continuing with our research work on the synthesis of fine and monodisperse metallic particles of uniform shape using the polyol process, we report here the results on the synthesis and characterization of silver particles of specific size, shape, and narrow size distribution. This investigation was mainly undertaken for optimizing the reaction conditions required for producing monodisperse silver particles of uniform size and shape by reduction of silver nitrate in hot ethylene glycol, nucleation of the metallic silver by homogeneous and heterogeneous nucleation, and growth of the nuclei without sintering. The effect of such process variables as temperature, time, molar ratio of silver nitrate/ethlyene glycol, molar ratio of nucleating agent/metallic silver, weight ratio of protective agent/silver nitrate, and both mode and order of addition of reagents on the morphology, size distribution, and degree of sintering of the particles produced has been investigated in detail.

Experimental Materials and Methods

Materials

All chemicals used were reagent grade. Ethylene glycol and silver nitrate (Rectapur) were purchased from Prolabo. The organic compounds tested for their ability to prevent particle sintering included both surfactants and polymers such as sodium dodecyl sulfate (Rectapur, Prolabo), laurylamine (Aldrich), hydroxypropyl cellulose (Aldrich), polyvinyl alcohol (Prolabo), polyethylene glycol (Prolabo), and polyvinylpirrolidone (Aldrich). Hexachloroplatinic acid (Prolabo) was used as nucleating agent.

Methods

The synthesis of fine and monodisperse silver powders using the polyol process involves adding ethylene glycol solutions of silver nitrate and an organic protective agent to a given volume of hot ethylene glycol (EG) under stirring. For determining the optimum reaction conditions the following parameters were varied: silver nitrate/EG molar ratio, protective agent/silver nitrate weight ratio, and both temperature and time of the reaction.

A 0.025 silver nitrate/EG molar ratio was found to give the best results, and it was therefore used in all reactions. Addition of a protective agent is necessary for preventing particle sintering. Of all the organic chemicals tested for this purpose, polyvinylpirrolidone (PVP) gives the best protective action. It was dissolved in ethylene glycol and added drop by drop with the aid of a peristaltic pump. Under these conditions, the most satisfactory range of temperature is from 160 to 180°C. Metallic silver formed immediately after adding the silver nitrate solution to hot ethylene glycol, but the reaction was allowed to proceed for 15 min to ensure complete reduction of soluble silver species and allow for particle growth to the desired size. This method produces monodisperse quasi-spheric silver particles.

Monodisperse rod-like silver particles were synthesized as follows. A critical concentration of hexachloroplatinic acid dissolved in ethlyene glycol was added to ethylene glycol at 160°C before the addition of both the silver nitrate and PVP solutions. The silver nitrate/EG molar ratio was kept constant at 0.025 and the reaction time for 15 min. For investigating the effect of protective agent concentration on particle size, the PVP/silver nitrate weight ratio was varied from 0.2 to 4.0. The molar ratio of metallic nuclei/metallic silver was varied from 10^{-6} to 10^{-2}.

At the end of all reactions the suspension was cooled to room temperature, and the solids were separated from the supernatant by centrifugation. Subsequently, the solid product was washed with acetone and water several times until a clear solution was obtained. The particles were then dried at 40°C in air.

Characterization of the metallic particles was achieved through different techniques. Their X-ray diffraction patterns were obtained with a Philips X-ray powder diffractometer (model PW1729) using Cu$K\alpha$ radiation. The form and size of the final products were determined from microphotographs obtained with a Philips scanning electron microscope (model 505). The average particle size was determined upon feeding the microphotograph to a computer connected to an optical microscope. Particle size histograms were then computed using a computer program developed in our laboratories. The crystallographic structure of the rod-like silver particles and of the platinum nuclei was determined using a JEOL electron microscope (Model 200CX). The chemical analyses of the solid products were performed at the "Laboratoire d'Analyses Chimiques" of CNRS.

Results and Discussion

It is well known that the morphology, size distribution, and degree of sintering of metallic particles produced by reduction of metallic salts in solution depends on such reaction conditions as temperature, time, molar ratio of metallic salt/reducing agent, mode and order of addition of reagents, presence and type of protective agents, degree and type of agitation, and whether nucleation is homogeneous or whether it is heterogeneous. For optimizing the synthesis of silver particles of uniform size and form by homogeneous nucleation using the polyol process, the effect of several parameters on the silver yield, and the morphology, size, and degree of sintering of the particles, was investigated.

Homogeneous Nucleation of Silver Particles

Although the main objective of this investigation was the synthesis of fine and monodisperse silver powders, the silver yield of the reaction was chosen as the critical testing parameter for determining the optimum reaction temperature. First, the temperature was varied from 115 to 160°C while fixing the reaction time at 25 min and the silver nitrate/ethylene glycol molar ratio at 0.025. When the reaction temperature is below 150°C silver yields are smaller than 5%, but they increase significantly to 60% at 160°C. This last temperature, therefore, was selected to investigate the effect of reaction time on the yield of silver. By decreasing the reaction time to 15 and 5 min, silver yields decrease to 50% and 3%, respectively. These preliminary results indicated that silver yields increase with time at a fixed temperature, and also increase with temperature at a fixed time. The effect that both temperature and time have on silver yields clearly shows that silver production is controlled by the rate of Ag(I) reduction, which increases with temperature. All products obtained, however, show a high degree of particle sintering, a phenomenon that increases with both reaction temperature and time.

Typical silver powders obtained by reduction of silver nitrate in ethylene glycol at 160°C are shown in the microphotograph presented in Fig. 1. These powders are polydisperse and show a wide range of forms arising from the sintering of quasi-spheric individual particles. Because of the relatively high temperature used in the synthesis of these particles, their brownian motion and mobility of surface atoms increase, thus enhancing the probability of particle colli-

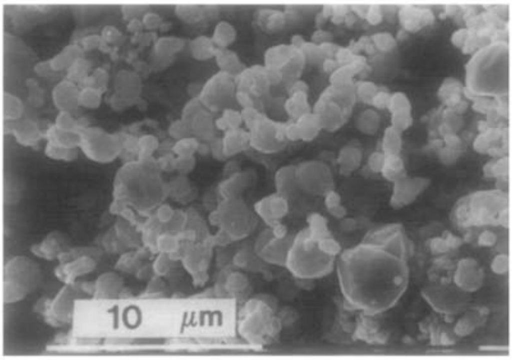

FIG. 1. Microphotograph of sintered silver particles obtained by reduction of silver nitrate in ethylene glycol at 160°C.

sion, adhesion, and subsequent coalescence by sintering. Particle coalescence by sintering is the means by which the system tries to attain thermodynamic equilibrium by reducing its total surface area. Since a number of organic materials are known to function as protective agents for preventing the sintering of colloids (*8*, *9*), we have investigated the effect that the addition of such chemicals as sodium dodecyl sulfate, laurylamine, hydroxypropyl cellulose, polyvinyl alcohol, polyethylene glycol, and polyvinylpirrolidone has on the morphology, size, and degree of sintering of silver particles. Of all the additives used, PVP exhibited the best protecting properties.

The reaction scheme for producing fine and monodisperse silver powders using the polyol process involves the reduction of the soluble silver species by ethylene glycol, nucleation of metallic silver, and growth of the individual nuclei in the presence of a suitable protective agent. Addition of this chemical is essential for preventing the coalescence of the nuclei during the growth step. Upon addition of the ethylene glycol–silver nitrate solution to hot ethylene glycol, the soluble Ag(I) species are reduced to metallic silver. As the reaction proceeds, the concentration of metallic silver in solution increases, reaches the saturation concentration, then supersaturation and finally the nucleation concentration. Spontaneous nucleation then takes place very rapidly and many nuclei are formed in a short time, lowering the silver concentration below the nucleation and supersaturation levels into the saturation concentration region. The nuclei then grow by deposition of metallic silver until the system reaches the saturation concentration. At the end of the growth period, all metal particles have grown at almost the same rate and the system exhibits a narrow size distribution. It is during the nucleation and growth steps that particle-particle adhesion and sintering must be prevented. In aggregation processes, particle coalescence by sintering is one of the main mechanisms by which the free energy of the system is lowered as a consequence of the decrease in interfacial area (*10*). Hindering particle coalescence is therefore very critical in the production of monodisperse metallic powders by the polyol process. Prevention of particle sintering is achieved by adding a critical dosage of an organic protective agent whose function is to cover the particles, thus effectively eliminating any possibility of silver particle–silver particle bond formation. The presence of this agent at the solid/liquid interface, however, does not interfere with the silver diffusion-surface deposition process since the particles grow to a definite size.

The amount, mode and order of protective agent addition was found to be very critical for avoiding particle sintering while allowing for particle growth. When the full dosage is added in the solid form, at room temperature or at intervals during the course of the reaction, particle sintering is not prevented. The protective agent was therefore added as an ethylene glycol solution. If this solution is added before or after more than 1 min of the addition of the silver nitrate solution, however, particle sintering also occurs. These findings confirm that agglomeration and subsequent coalescence of nuclei occur very early in the growth step. Dropwise addition of the protective agent solution using a burette also proved to be unsatisfactory for complete prevention of particle sintering, but it helped in lowering the degree of sintering of the product. It was therefore decided to add the PVP solution drop by drop with the aid of a peristaltic pump, starting at the time of silver nitrate addition. Using this technique we were able to produce monodisperse silver powders with a narrow size distribution.

For increasing the average particle size, the reaction temperature was varied from 160°C up to the boiling temperature of the solvent, namely, 194°C. At this temperature, the reduction of silver nitrate is observed to occur instantaneously. Although silver yields are very high and the average particle size increases when silver nitrate is reduced in boiling ethylene glycol, the product obtained is polydisperse, shows a high degree of sintering and, therefore, a wide variety of particle shapes. Silver yields obtained in the range of temperature from 160 to 180°C were found to increase with temperature, but the degree of sintering of these products also increased.

Typical silver particles obtained at 180°C and in the presence of a 1.6 : 1 PVP/silver nitrate weight ratio are shown in the microphotograph presented in Fig. 2a. These particles are quasi-spheric, very uniform in size, and present no sintering. Their size distribution is given by the histogram shown in Fig. 2b, and one can clearly see that this powder has a narrow size distribution. The average diameter of these particles was estimated to be 0.81 μm; the standard deviation has a value of 0.13 μm. The X-ray diffraction pattern of this material, which is presented in Fig. 3, shows the peaks characteristic of metallic silver. The chemical analysis of these powders gave the following results (% by weight): %C, 0.14–0.28: %N, 0.05–0.10: %O, 0.11–0.16. In spite of the use of PVP as protective agent, silver powders produced by the polyol process are of acceptable chemical purity, since the residual protective agent residing on the surfaces of the particles is removed during the washing step.

Next, the amount of added protective agent was varied for investigating the effect of surface coverage on particle sintering and size. The addition of a critical PVP dosage was found to be necessary for increasing the particle size while inhibiting sintering. Dosage additions below and above this critical value result in chaotic particle growth, which occurs by sintering. The effect that temperature and protective agent concentration have on particle size, degree of dispersion and silver yield is summarized in Table 1. Analysis of these data reveal that by a judicious control of the reaction parameters, the silver suspensions produced using the polyol process contain particles with the desired size and a narrow size distribution.

The effect of varying silver nitrate/ethylene glycol molar ratios on the final desired characteristics of silver particles synthesized at 160°C was also investigated. As this molar ratio was varied from 0.025 to 0.2, the degree of particle sintering was observed to increase, and therefore the lowest value was chosen as the working molar ratio. Again, this observation seems to indicate that control of the initial number of nuclei formed and their subsequent growth without aggregation and coalescence is essential for preparing monodisperse silver systems. When the initial concentration of silver nitrate is high, the rate of silver reduction seems to be higher than the rate of nucleation. As a consequence, once the system reaches the nucleation step the concentration of soluble metallic silver remains above the nucleation concentration for a long time, which increases the nucleation period and produces a polydisperse system. Under these conditions of high nuclei concentration, the total surface area of the system increases signifi-

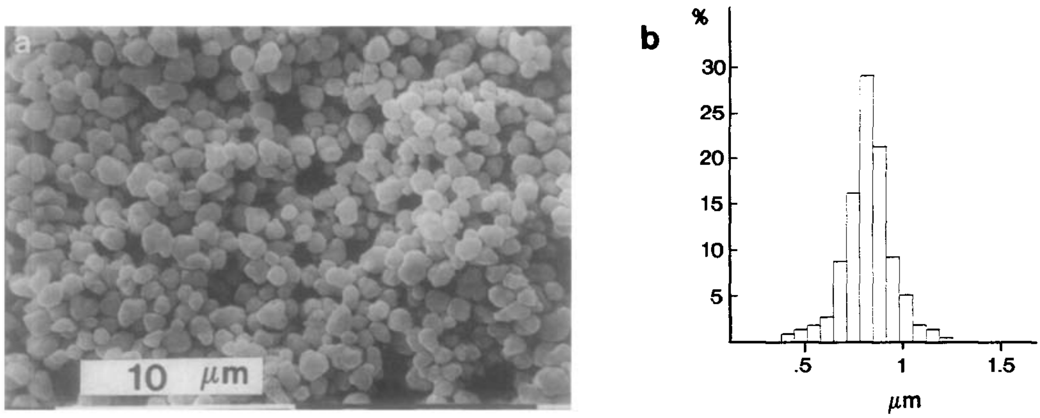

FIG. 2. (a) Microphotograph of quasi-spheric monodisperse silver particles obtained by reduction of silver nitrate in ethylene glycol at 180°C and in the presence of a 1.6 : 1 PVP/silver nitrate weight ratio. (b) Historgram of the size distribution of these particles. $d_m = 0.81$ μm; $\sigma = 0.13$ μm.

cantly, the degree of protective agent coverage of the nuclei decreases, their separation distance is considerably reduced and the probability of particle–particle collision and adhesion increases. Since the rate of aggregation is in general determined by the frequency of collisions and the probability of cohesion during collision (*11*), silver particle coalescence is promoted in concentrated suspensions and they then grow by sintering and not by deposition of metallic silver atoms on their surfaces.

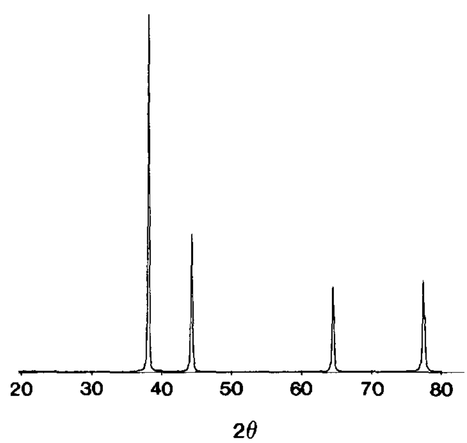

FIG. 3. X-ray diffraction pattern of the silver powder obtained by reduction of silver nitrate in ethylene glycol at 160°C.

Heterogeneous Nucleation of Silver Particles

Replacing homogeneous nucleation by heterogeneous nucleation in the polyol process reduces the size of metallic particles (*12*). At a critical concentration of platinum nuclei and in the presence of the organic protective agent, however, we have found that both the size and shape of silver particles changes drastically. The selective adsorption of this surface active chemical on a particular plane or edge of the nuclei determines the particle shape and dimensions. The quasi-spheric shape of silver particles obtained by homogeneous nucleation is observed to change into a rod-like shape when a critical concentration of hexachloroplatinic acid is added to hot ethylene glycol before the addition of both the silver nitrate and the PVP solutions. *In-situ* reduction of this nucleating agent provides the nuclei for the deposition of metallic silver on those planes not covered by the PVP, which acts in this system as both protective agent and crystal habit modifier, thus inducing an ani-

TABLE I

THE INFLUENCE OF TEMPERATURE AND SURFACTANT/$AgNO_3$ WEIGHT RATIO ON SILVER YIELD, AND SIZE AND DEGREE OF DISPERSION OF QUASI-SPHERIC SILVER PARTICLES PRODUCED USING THE POLYOL PROCESS

T(°C)	Surfactant/$AgNO_3$ weight ratio	Size (μm)	Degree of dispersion	Yield (%)
	1:1	0.37 (σ = 0.09)	Monodisperse	91
160	1.2:1	0.3–1	Aggregated	94
	1.6:1	0.3–1	Aggregated	90
	1:1	0.3–1	Aggregated	93
170	1.2:1	0.64 (σ = 0.13)	Monodisperse	94
	1.6:1	0.3–1.8	Aggregated	93
	1:1	0.3–1.3	Aggregated	95
180	1.2:1	0.3–1.3	Aggregated	94
	1.6:1	0.81 (σ = 0.13)	Monodisperse	92

sotropic growth of the silver particles. JEOL microphotographs of platinum nuclei show that these particles have an average size of 50 Å (see Fig. 4).

Figure 5 presents a microphotograph of the type of silver particles synthesized by heterogeneous nucleation of silver in ethylene glycol at 160°C and in the presence of a 2:1 PVP/silver nitrate weight ratio. The molar ratio of platinum nuclei/metallic silver used is 0.001. These silver particles have a rod-like shape, a range of particle size from about 3- to 5-μm long and 0.1- to 0.5-μm thick, and show no sintering. Their electron diffraction pattern is characteristic of silver metal and indicates that the particles are placed down the (110) plane. Different silver particles were obtained by increasing or decreasing the critical value of the platinum nuclei/metallic silver molar ratio, namely, 0.001. In the first case, the product obtained

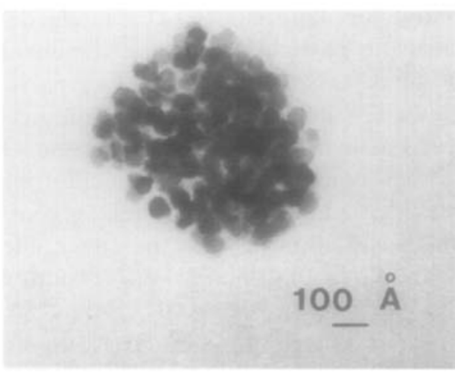

FIG. 4. Microphotograph of the platinum nuclei used for the production of rod-like silver particles.

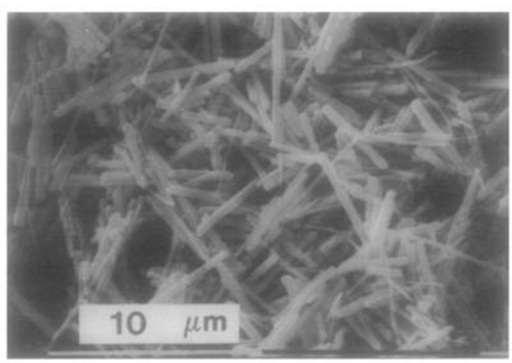

FIG. 5. Microphotograph of rod-like silver particles obtained by heterogeneous nucleation of silver in ethylene glycol at 160°C and in the presence of a 2:1 PVP/silver nitrate weight ratio. The platinum/silver molar ratio used was 0.001. Particle dimensions: 3 μm long and 0.5 μm thick.

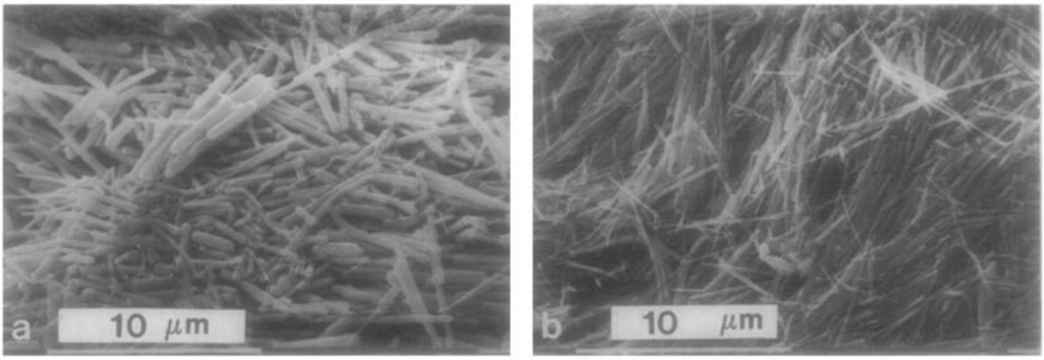

FIG. 6. Microphotgraphs of rod-like silver particles obtained using the polyol process and different PVP/silver nitrate weight ratios: (a) 1 : 1; (b) 4 : 1.

consists of a mixture of rod-like silver particles and quasi-spheric AgCl particles; in the second case only quasi-spheric silver particles are produced.

The thickness of the rod-like silver particles was found to change when the amount of added PVP varied. As shown in Fig. 6, considerably thinner rod-like silver particles are produced with high dosages of PVP. The particles shown in Fig. 6a are those produced in the presence of a 1 : 1 PVP/silver nitrate weight ratio; those in Fig. 6b were synthesized in the presence of a 4 : 1 PVP/silver nitrate weight ratio. The decrease in particle thickness is perhaps related to adsorption of excess PVP on some silver surfaces as well, thus inhibiting metallic silver deposition during the growth step.

Conclusions

Monodisperse quasi-spheric silver powders, with average particle sizes in the range of 0.37 to 0.81 μm, have been synthesized from silver nitrate in hot ethylene glycol and in the presence of a suitable organic protective agent, namely PVP. The dosage, mode, and order of addition of this protective agent is very critical for effectively preventing particle sintering. By covering the metallic surfaces and inhibiting particle–particle contact, the protective agent hinders agglomeration of the particles, which under the reaction conditions of the polyol process leads to particle coalescence by sintering. Particle size is highly dependent on both the reaction temperature and PVP/silver nitrate weight ratio. When homogeneous nucleation of metallic silver is replaced by heterogeneous nucleation, through the addition of a critical concentration of hexachloroplatinic acid before the addition of both the silver nitrate and PVP solutions, the particles formed show a drastic change in shape. This technique allows the production of monodisperse rod-like silver particles. By adsorbing on a specific plane of the foreign nuclei's surface, the protective agent also acts as crystal habit modifier and induces anisotropic growth of the particle. As a result, the metallic silver atoms deposit only on the bare surface of the nuclei. Rod-like silver particles with different thickness were produced by varying the PVP/silver nitrate weight ratio. The results of this investigation show that by a judicious control of the reaction conditions and use of a suitable protective agent, the polyol process is a useful and powerful method for the synthesis of highly pure metallic silver powders of uniform size, shape, and narrow size distribution.

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