temperature.

As mentioned previously, the electrical conductivity of TCNQ charge-transfer complexes has been of interest for some time. The compounds of interest in this study have conductivities in the range typical for semiconductors. The conductivity of TCNQ charge-transfer complexes is believed to be associated with the degree of electron transfer from the donor to the TCNQ. As discussed by Torrance,[8] one suggested mechanism for the conductivity in TCNQ complexes involves a mixed-valence compound with two distinct TCNQ species of different oxidation state in the structure, $TCNQ^0$, and $TCNQ^-$. Delocalization over these distinctly different species then is proposed to lead to high conductivity. $Cu(TCNQ)_2$ is such a compound, with both $TCNQ^0$ and $TCNQ^-$ species in the structure. However, the conductivities of $Cu(TCNQ)_2$ and CuTCNQ (which has only $TCNQ^-$ in the structure) are essentially identical. Thus at least in this case the existence of two oxidation states of TCNQ in the $Cu(TCNQ)_2$ structure does not appear to have any effect on the conductivity.

The correlation of the shape of the intensity on the high-binding-energy side of the core level peaks with the conductivity of the compounds is what one would expect if the valence state involved in the satellite observed for $TCNQ^0$ is the one that eventually leads to conductivity. Essentially what we are observing is the development of a continuous band from an intially localized excited state.

Summary

The X-ray photoelectron spectra presented here for the charge-transfer complexes of TCNQ have provided several insights into the bonding and properties of these compounds. The points we would like to stress are as follows:

The TCNQ moiety in LiTCNQ, $Ni(TCNQ)_2{\cdot}3H_2O$, and CuTCNQ exists as the $TCNQ^-$ species.

The oxidation state of Cu is +1 in both CuTCNQ and $Cu(TCNQ)_2$.

The $Cu(TCNQ)_2$ compound consists of one $TCNQ^-$ species and one $TCNQ^0$ species. Since the conductivities of CuTCNQ and $Cu(TCNQ)_2$ are essentially identical, the importance of a mixed-valence mechanism for conductivity is questionable for these compounds.

The C 1s spectra of the charge-transfer compounds are consistent with a more complex chemical environment than in $TCNQ^0$ and can be described by the assumption that the carbon atoms that interact most directly with the electron donor give rise to a low-binding-energy shoulder of the C 1s spectra. The fitted spectra indicate a 2.3-eV binding energy shift between the extra-ring carbons in $TCNQ^0$ and this most strongly interacting carbon.

The evolution of the localized shakeup peak observed in the N 1s and C 1s spectra of TCNQ into a continuous high-binding-energy tail for CuTCNQ is consistent with the development of a band that involves the excited valence orbital responsible for the shakeup feature. This is consistent with our previous assignment of the $TCNQ^0$ shakeup feature to a final-state excitaion involving the lowest unoccupied molecular orbital of TCNQ.

As was pointed out in the Introduction, the spectra presented here will also provide comparisons that should help greatly in the understanding of the chemistry of few-layer-thick films of TCNQ on the transition metals Cu and Ni. Experiments on such thin films are under way in our laboratory.

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Uniform Colloidal Zinc Compounds of Various Morphologies

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The preparation of finely dispersed zinc compounds consisting of uniform particles is described. Aging at elevated temperatures (~90 °C) of aqueous solutions of zinc nitrate or zinc chloride in the presence of urea resulted in precipitation of uniform rodlike basic zinc carbonate particles. These solids show X-ray characteristics of crystalline hydrozincite. In the presence of sulfate ions amorphous spherical particles of narrow size distribution of the same chemical composition are generated. On calcination both kinds of solids change to zinc oxide yet retain the original shape. In the presence of NaH_2PO_4 and urea, aqueous zinc salt solutions on aging yield rather uniform amorphous spherical zinc basic phosphate particles, which on calcination lose water.

Introduction

Solid zinc compounds are used in numerous applications. For example, zinc hydroxide carbonate, naturally occurring as hydrozincite, is of interest as such but also as a precursor to zinc oxide.[1-3] Catalytic activities of zinc carbonate in hydrogenation of oils,[4] in polymerization of cyclic ethers, and in synthesis of acetonitrile[5] have been reported. These materials have been used as fillers in rubber manufacture, pigments, storage batteries, etc. They are also common products of corrosion of zinc in moist air.

Zinc oxide has been employed traditionally in rubber and paint industries, for coatings, in ceramics, and in production of varistors. It is an intrinsic semiconductor[6] and exhibits high piezoelectricity.[7]

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(1) Krause, A.; Plura, I. *Monatsh. Chem.* **1965**, *96*, 1581.
(2) Utsugi, H.; Tamiya, K. *Nippon Kagaku Zasshi* **1965**, *86*, 699.
(3) Shekhter, A. B.; Moshkovskii, S. H. *Dokl. Akad. Nauk SSSR* **1950**, *72*, 339.
(4) Teruyama, K.; Kobashi, A.; Nobori, H. *J. Chem. Soc. Jpn., Ind. Chem. Sect.* **1951**, *54*, 401.
(5) Ishiguro, T.; Kitamura, E.; Kubota, S.; Tabata, N. *J. Pharm. Soc. Jpn.* **1962**, *72*, 607.
(6) Greenwood, N. N. *Ionic Crystals, Lattice Defects and Nonstoichiometry*; Butterworths: London, 1969.

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Table I. X-ray Diffraction Patterns

material	*d* at λ = 1.5418 Å							
	Rodlike Particles and Hydrozincite, $Zn_5(OH)_6(CO_3)_2$[19]							
own sample[a]	6.75	3.71		2.88	2.73	2.47		1.62
hydrozincite	6.77	3.66	3.14	2.85	2.72	2.48	1.92	1.69
	ZnO Obtained by Calcination of Zinc Basic Carbonate[20,21]							
own sample[b]	2.72	2.59	2.47	1.91	1.61	1.47		
lit.	2.82	2.60	2.48	1.91	1.63	1.48		

[a] Sample illustrated in Figure 1B dried at 60 °C for 24 h. Essentially the same results were obtained with other powders. [b] Prepared by calcination of the zinc basic carbonate at 300 °C for 4 h.

Zinc phosphates are used as catalysts,[8-12] phosphors,[13,14] coatings,[15] painting pretreatment of structural iron and steel,[16] corrosion prevention,[16-18] and for other applications. In many of these uses, it is advantageous to have powders consisting of finely dispersed solids, uniform in size and shape.

This work describes procedures by which zinc basic carbonate, zinc oxide, and zinc phosphate can be prepared as particles of narrow size distribution and in different morphologies. These well-defined materials have been characterized by various techniques.

Experimental Section

Materials. All solutions of reagent grade chemicals were filtered through 0.22-μm pore size Nuclepore membranes to eliminate possible particle contaminants. To avoid hydrolysis on storage of aqueous zinc salt solutions, we made fresh preparations every month. Much longer aging times impair the reproducibility of the results. Most precipitation experiments were carried out in test tubes that were tightly sealed with screw-caps during aging.

Preparation of Colloidal Particles. Zinc Basic Carbonates. Colloidal particles of zinc basic carbonates were obtained by aging aqueous zinc salt solutions in the presence of urea at elevated temperatures (≤90 °C). The heating was carried out in a constant-temperature oven for various periods of time. On termination of the aging process, the systems were quenched to room temperature, the resulting dispersions were treated in an ultrasonic bath, and finally the particles were separated and washed at least twice with doubly distilled water.

Zinc Oxide. Zinc oxide powders were prepared by calcination of zinc basic carbonate powders in a tube furnace (LLI Carbolite) at 300 °C for 4 h. During this process chemical composition changed but not the particle morphology.

Zinc Phosphate. Well-defined zinc phosphate particles were generated by aging for 3 h at 90 °C solutions of zinc salts (nitrate, chloride, or sulfate) in the presence of urea and sodium dihydrogen phosphate.

Results

Zinc Basic Carbonates. The composition, size, and shape of the particles obtained by aging zinc salt solutions in the presence of urea depended strongly on a number of parameters, among which the most important ones were the concentration of urea, pH, and the nature and the concentration of anions present in the system. Since the anions played a decisive role, $Zn(NO_3)_2$, $ZnCl_2$, and $ZnSO_4$ were used in the experiments. Zinc nitrate and zinc chloride solutions gave rather similar results; therefore, most of the data to be reported below refer to the former electrolyte.

Table II. Infrared Spectra of Zinc Basic Carbonates Compiled from the Literature,[22,23] Rodlike Particles Obtained in $Zn(NO_3)_2$ Solutions (Figure 1B), and Spherical Particles Obtained in $ZnSO_4$ Solutions (Figure 3A)

hydrozincite (lit.), cm^{-1}	rodlike particles, cm^{-1}	spherical particles, cm^{-1}	
3300–3260	3400 vs	3400 vs	$\nu_1\nu_2$, OH, H_2O
1515–1400	1500	1500 vs	
	1425 vs	1380 vs	ν_3, CO_3
1050	1050 m	1068 m	ν_1, CO_3
837	870 m	830 m	ν_2, CO_3
738–710	712 w	710 w	ν_4, CO_3

The concentrations of zinc salts investigated ranged between 1×10^{-3} and 1×10^{-2} mol dm^{-3}, while that of urea was varied between $\sim 10^{-1}$ and 6×10^{-3} mol dm^{-3}. The constant temperature of aging was controlled from 50 to 90 °C at times as short as 1 h and as long as 24 h. It was established that the optimum temperature was 90 °C and that no observable change in the resulting particles could be noted after 3 h of heating.

Under these conditions (3 h at 90 °C) rodlike particles were obtained over a given concentration range of reactants as illustrated in Figure 1A. In most cases bundles of fiberlike particles were also present in varying amounts in so generated dispersions. These aggregates could be eliminated to a large extent by acidifying the zinc salt solutions before aging. The transmission electron micrograph in Figure 1B illustrates particles produced in the presence of 5×10^{-5} mol dm^{-3} HNO_3. The addition of HCl to $ZnCl_2$ solutions containing urea had a similar beneficial effect on the resulting dispersions.

Domains in Figure 2 summarize the conditions that produced essentially rodlike particles, either dispersed (N) or aggregated (A), as a function of the concentrations of $Zn(NO_3)_2$ and urea (lower part). The effect of the acid at constant $Zn(NO_3)_2$ concentration on the resulting solids is given in the upper part of the same figure. It is apparent that the aggregation occurs randomly, and it may depend on small changes in the experimental conditions.

The particle composition was evaluated by X-ray diffraction (XRD) and infrared spectroscopy. Table I shows that the XRD pattern of a powder consisting of rodlike particles, dried at 60 °C for 24 h, is in a reasonably good agreement with the reported data on hydrozincite, $Zn_5(OH)_6(CO_3)_2$.[19] Samples pretreated at higher temperature

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(7) Hutson, A. R. *Phys. Rev. Lett.* **1960**, *4*, 505.

(8) Moellerstedt, B. O. P., Stockholms Superfosfat Fabriks AB, Swedish Patent 124669, Apr 19, 1949.

(9) Topsoe, H. F. A., Stockholms Superfosfat Fabriks AB, Swedish Patent 127558, Mar 14, 1950.

(10) Bailey, F. E., Jr., Union Carbide Corp.; U.S. Patent 3274129, Sept 20, 1966.

(11) Fukui, K.; Yuasa, S.; Kagiya, T.; Shimizu, T.; Sano, T. Sumitomo Chemical Co., British Patent 1017669, Jan 19, 1966.

(12) Szonyi, A. J.; Graydon, W. F. *Can. J. Chem. Eng.* **1962**, *40*, 183.

(13) Koller, L. R.; Coghill, H. D., General Electric Co., U.S. Patent 3016307, Jan 9, 1962.

(14) Feldman, C. *Rept. NRL Prog. May 1957*; pp 1–8.

(15) Frisch, H. R. U.S. Patent 2530458, Nov 21, 1950.

(16) Eickhoff, A. J. *Proc. Am. Soc. Testing Mater.* **1949**, *49*, 311.

(17) Meyer, G. *Dtsch. Farben-Z.* **1965**, *19*, 183.

(18) Müller, J. *Chemie (Prague)* **1949**, *5*, 17.

(19) Ghose, S. *Acta Crystallogr.* **1964**, *17*, 1051.

(20) Laudise, R. A.; Ballman, A. A. *J. Phys. Chem.* **1960**, *64*, 688.

(21) Kohanty, G. P.; Azaroff, L. V. *J. Chem. Phys.* **1961**, *35*, 1268.

(22) Nakamoto, K. *The Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978; pp 125–130.

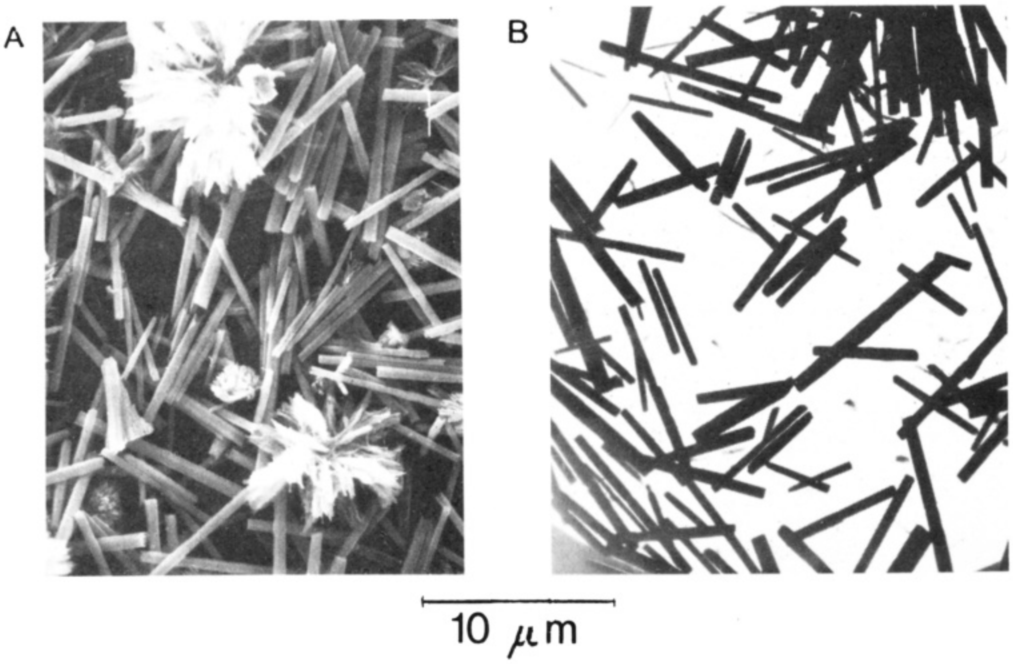

Figure 1. (A) Scanning electron micrograph (SEM) of zinc basic carbonate particles obtained by aging at 90 °C for 3 h a solution of 1.1×10^{-3} mol dm^{-3} $Zn(NO_3)_2$ and 8×10^{-3} mol dm^{-3} urea. (B) Transmission electron micrograph (TEM) of zinc basic carbonate particles obtained by aging at 90 °C for 3 h a solution of 1.1×10^{-3} mol dm^{-3} $Zn(NO_3)_2$, 8×10^{-3} mol dm^{-3} urea, and 5×10^{-5} mol dm^{-3} HNO_3.

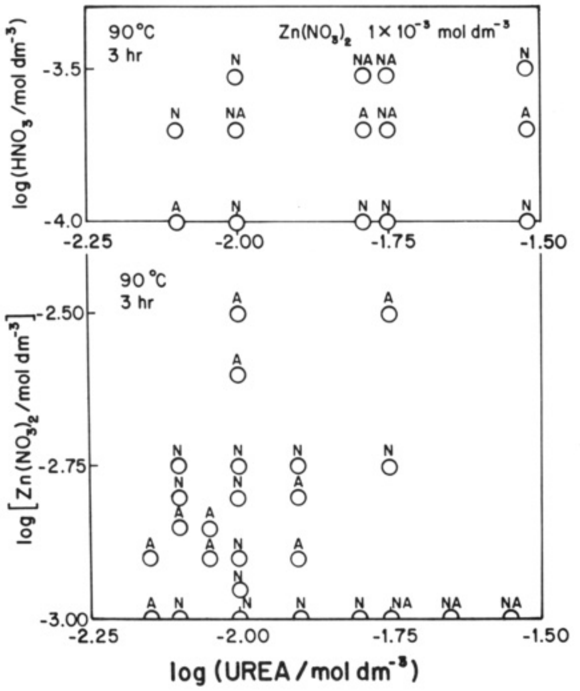

Figure 2. Lower: precipitation domain for solutions containing varying concentrations of $Zn(NO_3)_2$ and of urea aged at 90 °C for 3 h. Symbols designation: N, mostly needles; NA, needles and aggregated needles; A, mostly aggregated needles. Upper: precipitation domain for solutions containing a constant concentration of $Zn(NO_3)_2$ of 1×10^{-3} mol dm^{-3} and varying concentrations of urea and HNO_3.

(90 °C) indicate partial decomposition into zinc oxide.

Table II summarizes the information on infrared spectra (KBr) from various literature sources for zinc basic carbonates, which agree quite well with those obtained in this work.

When $ZnSO_4(H_2SO_4)$ was used as the electrolyte, particles of entirely different morphology were generated. For the zinc sulfate concentration range from 1×10^{-3} to 1×10^{-2} mol dm^{-3}, the amount of urea needed to prepare reasonably uniform particles over a relatively short aging time had to be increased to 2–3 mol dm^{-3}. All systems were acidified with 3×10^{-4} mol dm^{-3} sulfuric acid. The optimum aging conditions were 90 °C for 4 h in open tubes. Typical particles prepared by the described procedure are illustrated in the transmission electron micrograph Figure 3A, which are nearly spherical and rather small. Dispersions of similar properties were generated by using various concentrations of the reactants given above.

The IR spectra of these powders showed the same characteristic bands as those of the rodlike particles (Table II), confirming the composition of zinc basic carbonate. There were no discernible peaks in the X-ray diffraction pattern, indicating the amorphous nature of these solids.

Aging at lower temperatures (80 °C) produced gel-type precipitates which, on drying, showed an open-shell structure as illustrated by the scanning electron micrograph in Figure 3B.

Zinc Oxide. Zinc oxide was obtained by calcination of the zinc basic carbonate. Differential thermal analysis showed a clear endothermic reaction at 260 °C (Figure 4), which is in agreement with previously reported data for $Zn_5(OH)_6(CO_3)_2$.[24] This transformation was interpreted as the combined loss of water and carbon dioxide. Consequently, one would expect zinc oxide to form at calcination temperatures of ~300 °C. Indeed X-ray diffraction analysis (Table I) and the infrared spectra confirmed the presence of ZnO for powders heated at 300 °C for 4 h. The scanning electron micrograph in Figure 5 clearly shows that no change in morphology took place during this calcination procedure and consequent phase transformation.

The weight loss of ~21% was found after heating the described samples, which compares with the theoretical weight loss of 26%, assuming that only ZnO remained.

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(23) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed.; Holden-Day: San Francisco, 1977.

(24) Smykat-Kloss, W. *Beitr. Miner. Petrogr.* **1964**, *9*, 481.

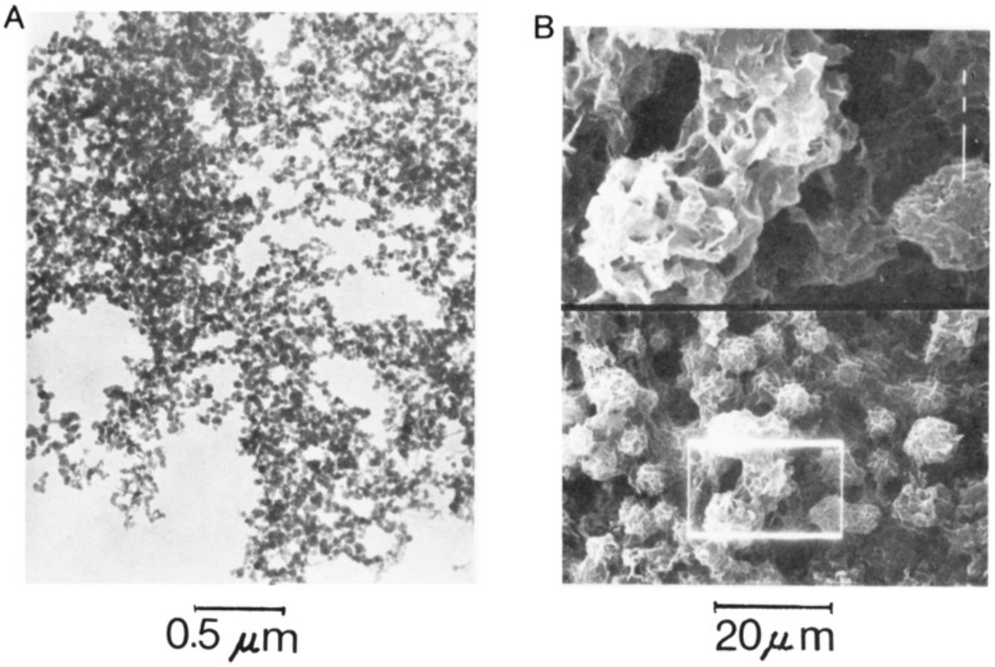

Figure 3. (A) TEM of zinc basic carbonate particles obtained by aging in open tubes at 90 °C for 4 h a solution of 2×10^{-3} mol dm^{-3} $ZnSO_4$, 2.0 mol dm^{-3} urea, and 3×10^{-4} mol dm^{-3} H_2SO_4. (B) SEM of the gellike precipitate formed by aging at 80 °C for 4 h in open tubes a solution of 2×10^{-3} mol dm^{-3} $ZnSO_4$, 2.5 mol dm^{-3} urea, and 3×10^{-4} mol dm^{-3} H_2SO_4.

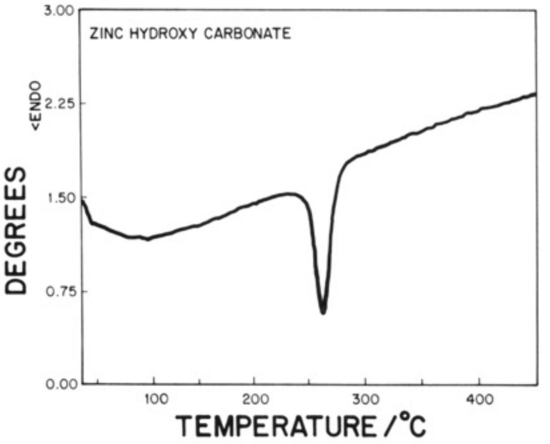

Figure 4. Differential thermal analysis curve for particles of basic zinc carbonate illustrated in Figure 1B.

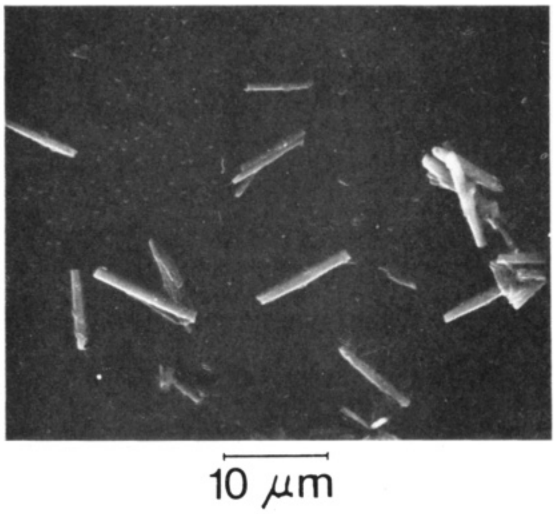

Figure 5. SEM of zinc oxide particles obtained by calcination at 300 °C for 4 h of zinc basic carbonate particles illustrated in Figure 1A.

Apparently, either some carbonate or hydroxide is still present in the solid phase prepared under the described experimental conditions.

Zinc Phosphate. Adding sodium dihydrogen phosphate to zinc salt solutions in the presence of urea yielded on aging spherical particles, the size distribution of which depended on the concentration of reactants.

The most uniform dispersions were obtained with aqueous solutions containing 1×10^{-3} mol dm^{-3} zinc salts and 3×10^{-4} mol dm^{-3} NaH_2PO_4 with $\sim 10^{-2}$ mol dm^{-3} urea, heated at 90 °C for 3 h in closed tubes. The scanning electron micrograph in Figure 6 illustrates particles so prepared.

Infrared spectra of a polydispersed powder and of a powder of narrow size distribution are shown in Figure 7. The bands at 1000–1100 cm^{-1} are characteristic of ionic P–O stretching (ν_3), while the bands at 650 cm^{-1} indicate O–P–O bending (ν_4).[25,26] The spectrum of powder A (polydispersed) is consistent with parahopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$], while that of the uniform particles (B) is characteristic of a mixed parahopeite and spencerite solid.[22,27,28]

Differential thermal analysis of the zinc phosphate shows a broad external peak in the endothermic part of the curve at 100 °C, which is most likely due to the elimination of water of crystallization. An exothermic peak at 550 °C may indicate phase transformation, caused by sintering of the original powder.

The X-ray diffraction pattern of the solids, as prepared and heated at 450 °C for 3 h, proved these to be amorphous.

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(25) Szymansky, H. A. *Progress in Infrared Spectroscopy*; Plenum Press: New York, 1962; Vol I, p 55.

(26) Pustinger, J. V., Jr.; Cave, W. T.; Nielsen, M. L. *Spectrochim. Acta* **1959**, *11*, 909.

(27) *The Sadtler Infrared Spectra Handbook of Minerals and Clays*; Heyden and Loris: London, 1982; p 430.

(28) Farmer, V. C. *The Infrared Spectra of Minerals*; Mineralogical Society: London, 1974; pp 384–397.

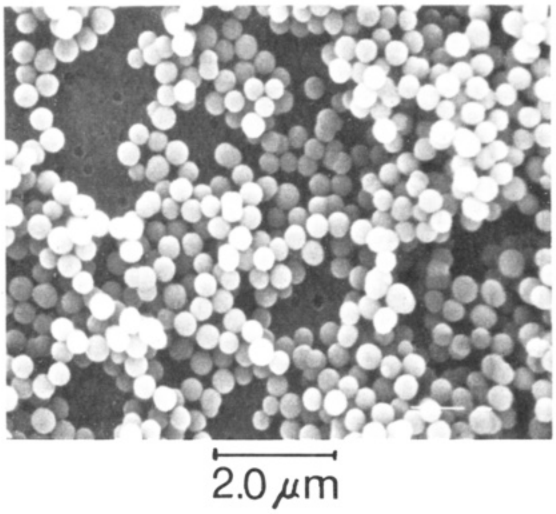

Figure 6. SEM of zinc basic phosphate particles obtained by aging at 90 °C for 3 h a solution of 1×10^{-3} mol dm^{-3} $ZnSO_4$, 0.6 mol dm^{-3} urea, and 3×10^{-4} mol dm^{-3} NaH_2PO_4.

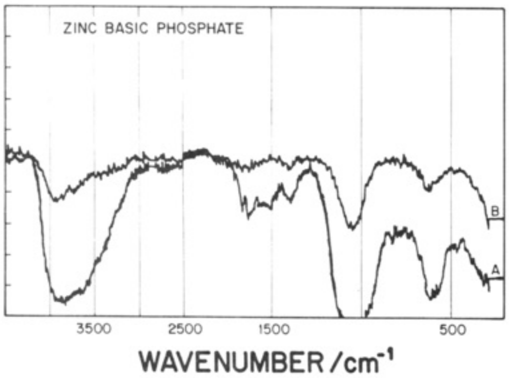

Figure 7. Infrared spectra of zinc basic phosphate: (A) Polydispersed particles obtained by aging at 90 °C for 3 h a solution of 1×10^{-3} mol dm^{-3} $ZnSO_4$, 1×10^{-2} mol dm^{-3} urea, and 3×10^{-4} mol dm^{-3} NaH_2PO_4. (B) Particles illustrated in Figure 6.

Discussion

It has been shown in several examples that the decomposition of urea in aqueous solutions at elevated temperatures can be utilized to produce colloidal dispersions consisting of uniform particles. The products of these thermolysis processes depend on the pH. Thus, in acidic media the reactions can be written as

$$CO(NH_2)_2 \rightleftharpoons NH_3 + HNCO \rightleftharpoons NH_4^+ + OCN^-$$

$$OCN^- + 2H^+ + H_2O \rightarrow NH_4^+ + CO_2$$

while in neutral or basic media urea decomposes according to

$$CO(NH_2)_2 + OH^- + H_2O \rightarrow CO_3^{2-} + NH_3 + NH_4^+$$

In the presence of metal ions the chemical composition of the particles precipitated on heating aqueous solutions of urea depends on several parameters, i.e., the hydrolyzability of the cations, the kind of anions present, pH, and the temperature of aging. Thus, readily hydrolyzable ions will precipitate at lower pH values as metal (hydrous) oxides, such as in the case with solutions of zirconium salts.[29] Lanthanides (e.g., Y^{3+}, Gd^{3+}, etc.) on the other hand, require higher pH values and, accordingly, the spherical particles consist of basic carbonates[30,31] when aging is carried out at reasonably low temperatures (~90 °C). At somewhat higher temperatures (115 °C) and longer reaction times rodlike yttrium amide carbonate is formed.[32] In some other cases anions other than carbonate are incorporated in the solids. For example, aging of ferric sulfate solutions at 98 °C in the presence of urea yielded, at convenient concentrations of reactants, colloidal crystals of ammoniojarosite, $NH_4Fe_3(SO_4)_2(OH)_6$.[33] Finally, by properly manipulating urea solutions, pure finely dispersed cadmium carbonate, having X-ray characteristics of mineral otavite, was generated.[34]

Since zinc ion is less strongly hydrolyzed than most trivalent transition metals, higher pH is needed to initiate precipitation. As a result, basic carbonate is preferentially formed in the presence of urea. In zinc nitrate or chloride solutions, uniform colloidal crystals are generated of rodlike morphology that show X-ray patterns of hydrozincite.

Several zinc basic carbonates have been reported in the literature, of which the best characterized is $Zn_5(OH)_6(CO_3)_2$, of the same composition as the naturally occurring hydrozincite. Structurally, this compound contains zinc in coordination numbers of 4 and 6 and it can appear in stacking ordered or disordered phases.

Different zinc basic carbonates have been prepared by various techniques, such as from ZnO, $Zn(OH)_2$, and CO_2, but in no case have uniform particles of different morphologies been reported. Spherical particles of zincite of narrow size distribution were prepared, however, by controlled hydrolysis of ethylzinc *tert*-butoxide.[35]

The nature of the generated solids is drastically affected by the presence of the sulfate ion. It has been amply documented that this ion plays a special role in the homogeneous precipitation of metal (hydrous) oxides. In most cases sulfate anion promotes the formation of spheres, as, for example, in forced hydrolysis of chromium,[36] aluminum,[37] and cerium(IV) ions.[38] It was shown in this work that in the homogeneous precipitation of zinc compounds sulfate ion exhibits a strong effect on particle morphology. This anion affects not only the shape but also the structure of the solids; hence, the spherical particles are amorphous.

One characteristic of (basic) carbonates is that they are readily converted to the corresponding metal oxides without losing their shape.[30,34] The zinc basic carbonate behaved in the same manner, yielding uniform either rodlike or spherical zinc oxide particles.

Recently colloidal spherical cobalt phosphate particles were prepared from solutions of $CoSO_4$ and NaH_2PO_4. An anionic surfactant (sodium dodecyl sulfate) had to be added[39] to achieve dispersions of uniform size distribution. It is shown here that exceedingly uniform zinc (hydrous) phosphate can be obtained in the absence of the surface active agent, but urea was added to promote the reaction.

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(29) Aiken, B.; Hsu, W. P.; Matijević, E. *J. Mater. Sci.*, in press.

(30) Matijević, E.; Hsu, W. P. *J. Colloid Interface Sci.* **1987**, *118*, 506.

(31) Akinc, M.; Sordelet, D. *Adv. Ceram. Mater.* **1987**, *2*, 232.

(32) Aiken, B.; Hsu, W. P.; Matijević, E. *J. Am. Ceram. Soc.* **1988**, *71*, 845.

(33) Matijević, E.; Sapieszko, R. S.; Melville, J. B. *J. Colloid Interface Sci.* **1975**, *50*, 567.

(34) Janeković, A.; Matijević, E. *J. Colloid Interface Sci.* **1985**, *103*, 436.

(35) Heistand, R. H., II; Chia, Y.-H. *Mater. Res. Symp. Proc.* **1986**, *73*, 93.

(36) Demchak, R.; Matijević, E. *J. Colloid Interface Sci.* **1969**, *31*, 257.

(37) Brace, R.; Matijević, E. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3691.

(38) Hsu, W. P.; Rönnquist, L.; Matijević, E. *Langmuir* **1988**, *4*, 31.

(39) Ishikawa, T.; Matijević, E. *Langmuir* **1988**, *4*, 26.