Preparation and Properties of Uniform Coated Inorganic Colloidal Particles. 11. Nickel and Its Compounds on Manganese Compounds[†]

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Uniform cubic manganese carbonate, $MnCO_3$, particles of two modal sizes (~0.8 and 8 μm) were produced by homogeneous precipitation from aqueous solutions of manganese sulfate and urea at elevated temperatures under limited experimental conditions. The larger particles were converted into Mn_2O_3 and MnO on calcination at 700 °C either in the flow of air and or in nitrogen. The $MnCO_3$ particles were also coated with $NiCO_3.Ni(OH)_2{\cdot}H_2O$ by aging dispersions of the cores in aqueous solutions of nickel sulfate and urea at 80 °C, yielding a molar ratio [Ni]/[Mn] = 0.45 in the final solid. On calcination at 700 °C in air, the shell and core materials of the coated particles transformed independently into NiO and Mn_2O_3, which on further heating at 350 °C in hydrogen were reduced to Ni and Mn, respectively. The coating solutions aged at the same temperature in the absence of cores resulted in nearly spherical of $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$ particles of narrow size distribution. The latter solids transformed into NiO on calcination at 700 °C and to Ni on reduction with H_2 at 350 °C without a significant change in their morphology.

1. Introduction

Science and technology of uniform fine particles of different chemical compositions and properties are gaining in interest, due to their importance in ceramics,[1] catalysis,[2] medicine,[3] pigments,[4] water treatment,[5] and others. In recent years, much success was achieved in the synthesis of "monodispersed" particles of metals, metal (hydrous) oxides, metal sulfides, and other compounds in a variety of morphologies. Several review articles[6−9] describe these results and challenges associated with the production of such dispersions.

An important area of colloid dispersions deals with coating of fine particles with compounds of different chemical composition. In doing so, one can modify surface properties of original dispersed solids. The method is also useful in the preparation of particles of a given morphology, which cannot be achieved directly, by using cores of the desired shape and coating them with the material of interest.

The shells are commonly produced by direct precipitation of the coating material on the cores dispersed in liquids (usually aqueous solutions), yielding homogeneous layers.[10−21] Alternatively, the second component is precipitated in the form of tiny particles, which are then deposited on the cores.[10,11,17,22−25] Obviously, in the latter case the outer layer is physically inhomogeneous.

In previous studies the cores and shells consisted, as a rule, of different compounds, such as oxides of two metals. The purpose of this work was to produce metal particles with a coating of another metal. Since, it is difficult, if not impossible, to obtain such dispersions directly by precipitation in homogeneous solutions, in

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the adopted approach coated particles of two compounds are prepared first, and subsequently reduced to pure metals. Specifically, uniform cubic particles of manganese carbonate were coated with a composite nickel compound, then transformed in stages to pure manganese cores and nickel shells.

2. Experimental Section

A. Materials. Reagent grade manganese(II) sulfate, nickel(II) sulfate, urea, sodium borohydride, hydroxylamine hydrochloride, and hydrazine were used without further purification. All stock solutions were made with doubly distilled water and were filtered through 0.2 μm pore size membranes before use.

B. Preparation of Cores. Hamada et al. described a procedure which yielded uniform spherical (~5.3 μm) and cubic (~2.8 μm) particles of manganese(II) carbonate using solutions of $MnSO_4$ and NH_4HCO_3.[26] In the present study colloidal particles of manganese compounds were prepared by aging aqueous solutions containing 0.01−0.3 mol dm^{-3} manganese(II) sulfate and 0.2−1.0 mol dm^{-3} urea, in Teflon-coated capped 50 cm^3 Pyrex glass tubes, for different periods of time (15−200 min) and temperatures (80−90 °C) in a preheated thermostated water bath. The resulting dispersions were quenched to room temperature and then the solids were separated by centrifugation, washed extensively with doubly distilled water, and finally kept in a desiccator for drying. In some cases, the mother liquor separated from these solids was reheated under the above-mentioned conditions, which also yielded additional dispersions of fine particles.

C. Coating of Particles. A known amount (50−300 mg) of uniform powders of manganese compounds was introduced into 250 cm^3 of aqueous solutions containing 0.01−0.1 mol dm^{-3} nickel(II) sulfate and 0.1−1 mol dm^{-3} urea and stirred for 3 h at 25 °C. These dispersions were transferred into preheated glass stoppered 400 cm^3 double-walled Pyrex vessels and aged from 30 to 240 min at temperatures of 80−90 °C with constant stirring. The resulting solids were washed several times with doubly distilled water and kept in a desiccator for drying before characterization. In some cases, the coating solutions were also aged in the absence of core particles and treated as described above.

An earlier study[27] indicated that a nickel compound [$NiCO_3.Ni(OH)_2 \cdot H_2O$] of nearly spherical particles was precipitated in $NiSO_4$/urea solutions under optimum experimental conditions.

D. Calcination. The calcination of powders was carried out in a tube furnace (Nabertherm, M7/11, with a program controller) at 700 °C for 1 h at the heating rate of 5 °C min^{-1} in air or nitrogen.

E. Reduction. The reduction of solids containing nickel compounds (either directly precipitated or as shells) was attempted using two methods. In the first procedure, 0.05−0.2 g of the powder was transferred into a glass microreactor, attached with a Deji-sense temperature controller through a thermocouple. The sample was heated for 3−7 h in a stream of hydrogen at different flow rates (20−80 cm^3 min^{-1}) and at different temperatures (200−370 °C). At the end of this treatment the solid was recovered from the reactor, weighed, and stored in a desiccator. In the second method, the same amount of solid was dispersed in 100 cm^3 of an aqueous solution containing 0.1−3 mol dm^{-3} of a reducing agent (sodium borohydride, hydroxylamine hydrochloride, or hydrazine) and allowed to react for 1−24 h at 50 to 90 °C.

F. Characterization. Solids were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD), and thermogravimetric (TGA) and differential thermal (DTA) analyses. Electrophoretic mobilities of some dispersions were determined as a function of the pH at a constant ionic strength of 1 × 10^{-3} mol dm^{-3} with the PenKem 3000 instrument.

The coated samples were assayed for nickel and manganese content by atomic absorption spectrometry. For this purpose, known amounts (220−500 mg) of coated samples were dissolved in aqua regia and their solution was diluted to 100 cm^3 with doubly distilled water before analysis.

3. Results

A. Particles Formed in $MnSO_4$/Urea Solutions. To synthesize particles uniform in size and shape by precipitaton in homeogeneous solutions, it is in general necessary to systematically alter experimental parameters in order to establish the optimum conditions; otherwise, irregular or agglomerated solids are usually generated.[6,8] Specifically, in the studied system dispersions of small nearly cubic particles (~0.8 μm) of narrow size distribution were obtained by aging aqueous solutions of 0.08−0.2 mol dm^{-3} in manganese(II) sulfate and 0.2−0.6 mol dm^{-3} in urea, for different intervals of time (15−25 min) at temperatures of 85−90 °C. On continued aging for longer than 25 min and up to 150 min, larger sized cubic particles (~8 μm) started to appear, resulting in dispersions of bimodal size distributions. The determination of the solid contents in these dispersions during the aging indicated that the precipitation started after 15 min and was completed in 150 min. The pH of the aging mixtures changed from ~2.5 to ~6.9 in the first 15 min and then increased by less than 1 unit during the rest of the reaction.

Dispersions of only large cubic particles (~8 μm) were obtained when the mother liquor, separated from the small cubic particles, obtained in the above-described solutions during the initial reaction time (15−25 min), was aged for an additional 10−120 min at temperature of 85−90 °C.

Furthermore, both kinds of particles precipitated in a test experiment when the reactant mixture, described in Figure 1A was first adjusted to pH ~6.9 and then heated at 85 °C for 90 min.

Scanning electron micrographs in Figure 1A,B illustrate typical small and large cubic particles prepared under the conditions given in the legend. It was observed that in both cases the concentrations of reactants and aging times, specified in section 2B, had a negligible influence on the particle size and shape, while the yield was affected significantly. For example, the content of solid shown in Figure 1A increased from 0.07 to 0.31 g dm^{-3} when the same reactant mixture was heated at 85 °C from 15 to 25 min. Similarly, the amount of large particles [Figure 1B] ranged from 0.1 to 0.44 g dm^{-3} when the mother liquor was aged from 10 to 120 min at the same temperature. It was further observed that the ratio of weights of small to large cubic particles was generally 0.7, irrespective of the composition of the aged reactant mixtures.

It is noteworthy that the procedure developed by Hamada et al. yielded dispersions of uniform spherical and monoclinic manganese carbonate.[26]

The X-ray pattern of larger cubic particles is displayed in Figure 2A, which is characteristic of crystalline $MnCO_3$ (rhodochrosite). The same result was obtained with the small cubes.

The TGA [Figure 3a] of particles illustrated in Figure 1B indicates the decomposition of the manganese carbonate at ~500 °C, in agreement with the corresponding

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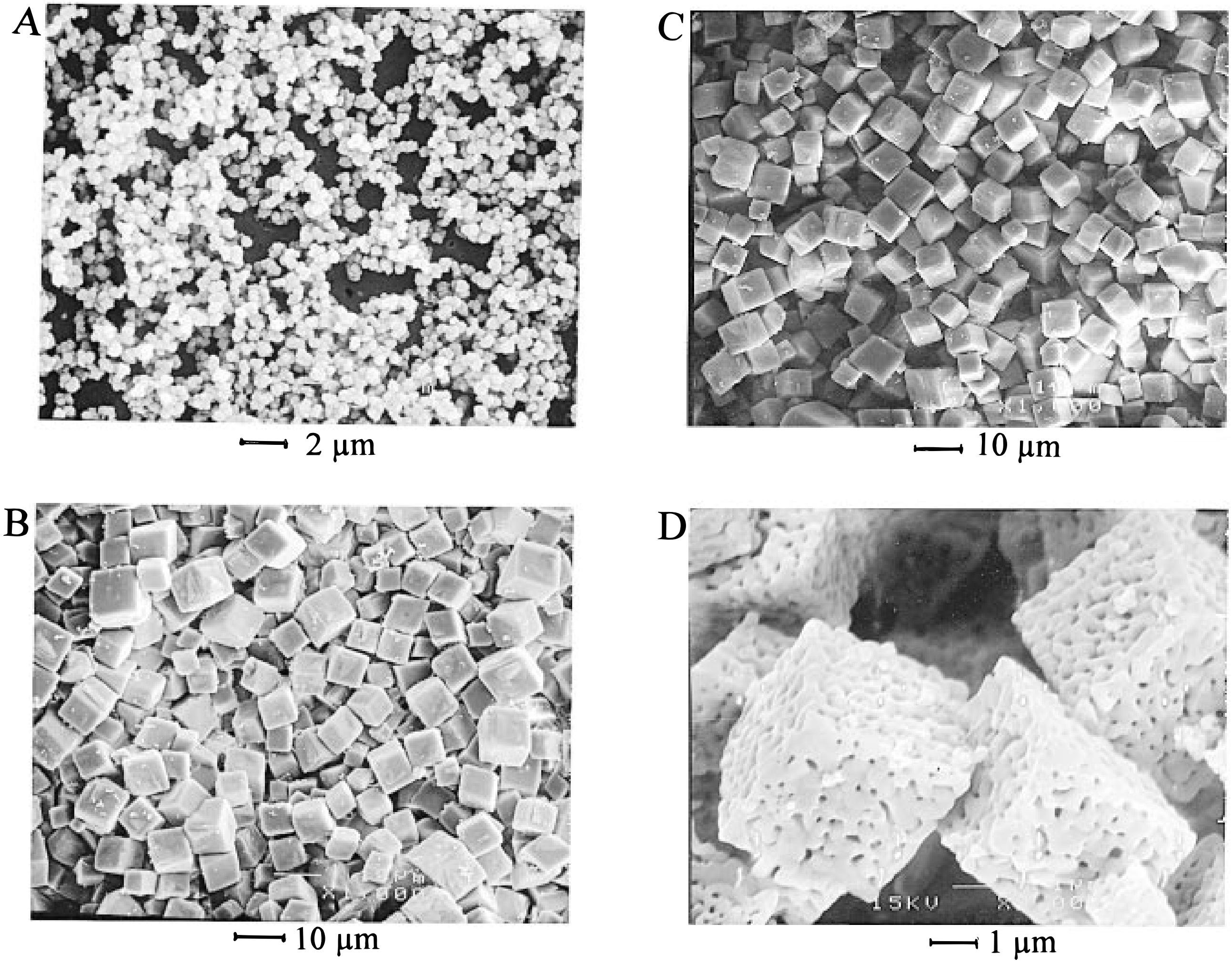

Figure 1. Scanning electron micrographs (SEM) of particles obtained, when (A) an aqueous solution, 0.16 mol dm^{-3} in $MnSO_4$ and 0.4 mol dm^{-3} in urea was aged for 25 min at 85 °C; (B) mother liquor of (A) was separated and aged for additional 90 min at 85 °C; (C) particles shown in (B) were calcined at 700 °C for 1 h in air; (D) particles shown in (B) were calcined at 700 °C in nitrogen.

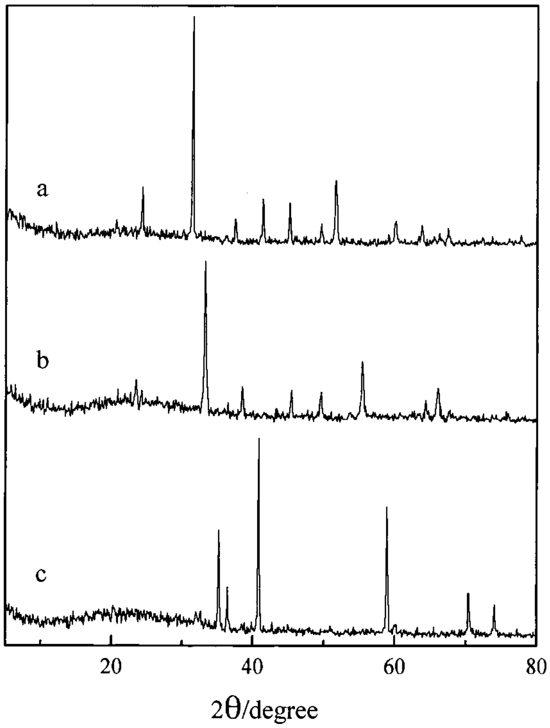

Figure 2. X-ray diffraction (XRD) patterns of the particles shown in Figure 1B (a), Figure 1C (b), and Figure 1D (c).

DTA curve [Figure 3c], which shows a prominent endothermic peak at the same temperature, caused by the phase transformation. On calcination at 700 °C for 1 h in air and nitrogen, these particles transformed into Mn_2O_3 (bixbyite) [XRD, Figure 2b] and MnO (manganosite) [XRD, Figure 2c], respectively. Scanning electron micrographs [Figure 1C, and D] illustrate such calcined particles.

To determine electrophoretic mobilities as a function of the pH, either 1×10^{-3} mol dm^{-3} NaOH or 1×10^{-3} mol dm^{-3} HCl solution was added as needed. Both kinds of particles illustrated in Figure 1A,B, gave the isoelectric point (iep) at pH $\sim$ 5.8 (Figure 4), in agreement with the value obtained earlier[22] with spherical colloidal $MnCO_3$.

B. Coated Particles. The cubes shown in Figure 1B were used as cores in the coating experiments. Uniform shells of variable thickness were formed when dispersions containing 0.4–0.8 g dm^{-3} $MnCO_3$ particles, 0.03–0.08 mol dm^{-3} $NiSO_4$, and 0.3–0.8 mol dm^{-3} urea, were aged from 50 to 150 min at temperatures of 80–85 °C. In most other cases, either mixtures of coated and core particles or agglomerated solids were obtained.

It was observed that at a given concentration of $NiSO_4$ and urea, the amount of coating decreased proportionally with the increased amount of cores. Furthermore,

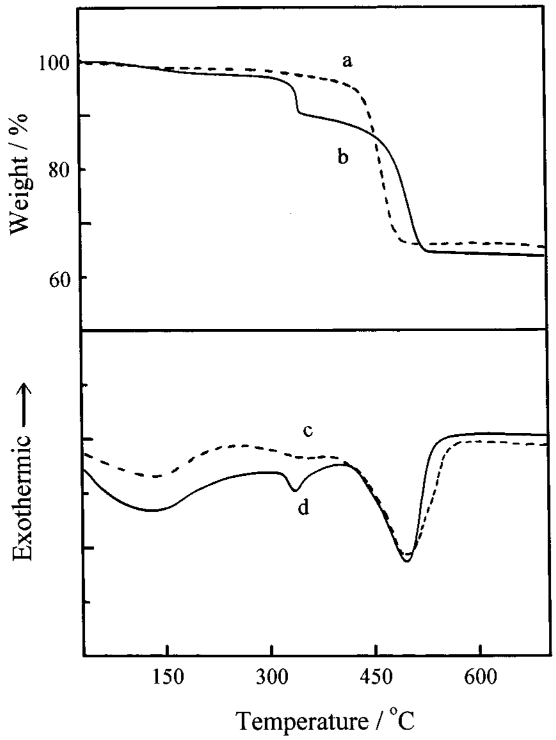

Figure 3. Thermogravimetric (TGA) (a, b) and differential thermal (DTA) analyses (c, d) obtained with particles shown in Figure 1B (---) and Figure 5A (—), at the heating rate of 10 °C min^{-1}.

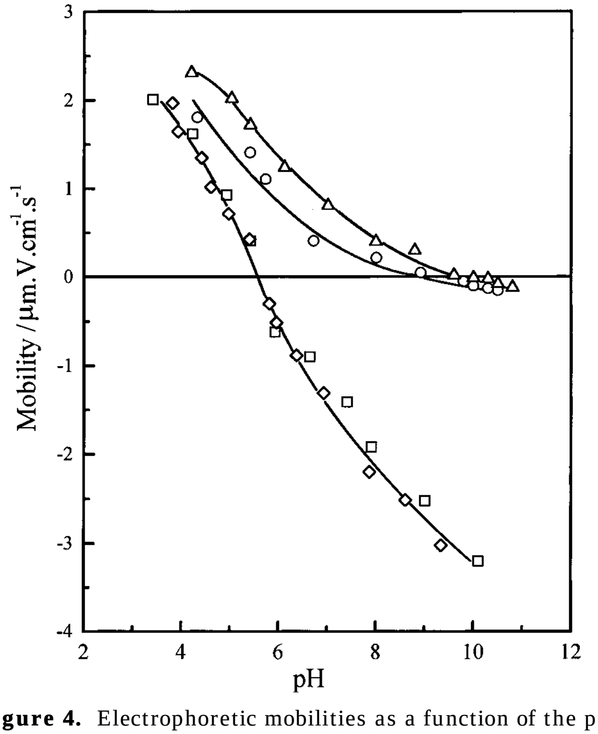

Figure 4. Electrophoretic mobilities as a function of the pH of manganese carbonate particles shown in Figure 1A [◇], Figure 1B [□], as well as of the coated nickel basic carbonate on manganese carbonate particles shown in Figure 5A [○], and of the coating precursor nickel basic carbonate particles shown in Figure 6A [Δ].

it was established that on heating a dispersion containing 0.4 g dm^{-3} cores, 0.26 mol dm^{-3} $NiSO_4$, and 0.4 mol dm^{-3} urea at 80 °C for 50 to 150 min, the fraction of the coating increased from 16 to 46%, as estimated from the gain in weight.

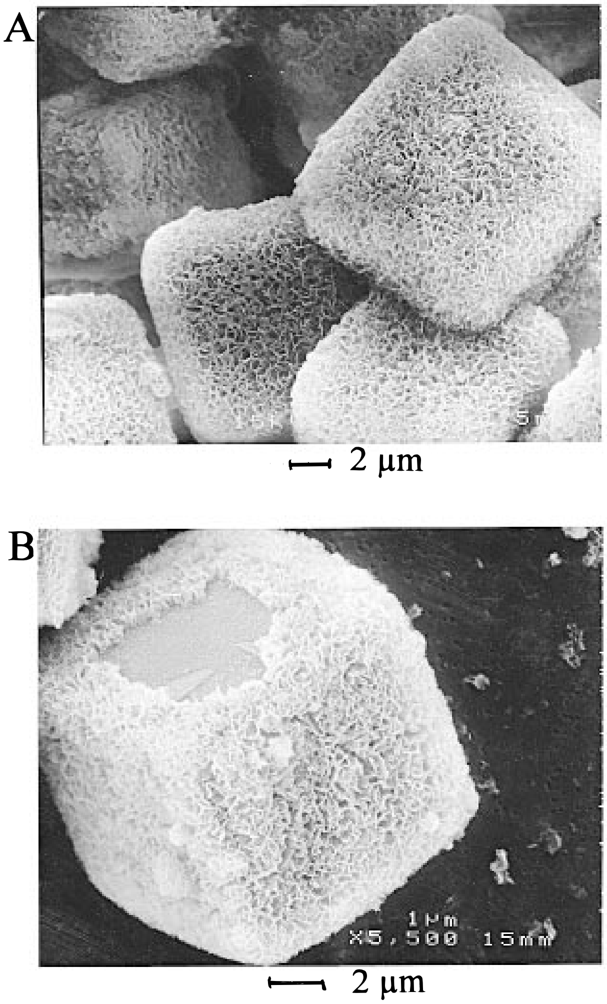

Figure 5. SEM of particles obtained, when (A) an aqueous dispersion containing 0.4 g dm^{-3} of manganese carbonate cores (Figure 1B), 0.26 mol dm^{-3} $NiSO_4$, and 0.4 mol dm^{-3} urea was aged for 2 h at 85 °C; (B) the dispersion of freshly prepared particles shown in (A) was stirred for 5 h with a magnetic stirrer.

Figure 5A exemplifies coated particles, for which the EDX analysis [Figure 8] indicated qualitatively the presence of manganese and nickel, while the atomic absorption spectrometry yielded the molar ratio [Ni]/[Mn] = 0.45. The XRD analysis [Figure 9 (upper)] of these particles indicated the shell and core to consist of independent phases, i.e., $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$ and $MnCO_3$, respectively. When the freshly prepared coated particles were redispersed in doubly distilled water and mechanically stirred for 5 h at a relatively high speed, the shell was separated from the core, which made the thickness of the coating clearly visible [Figure 5B].

Aging the coating solution described in Figure 5A under the same experimental conditions, but in the absence of cores, resulted in particles illustrated in Figure 6A. These solids were identified by XRD also to be $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$, which on calcination at 700 °C converted into NiO, without a change in their shape and size [Figure 6B]. Dispersions comprised of solids of the same chemical compositions and morphological features have been reported in an earlier study,[27] which were produced under rather different experimental conditions.

The TGA and DTA [Figure 3] of the same particles indicated significant weight loss regions and endother-

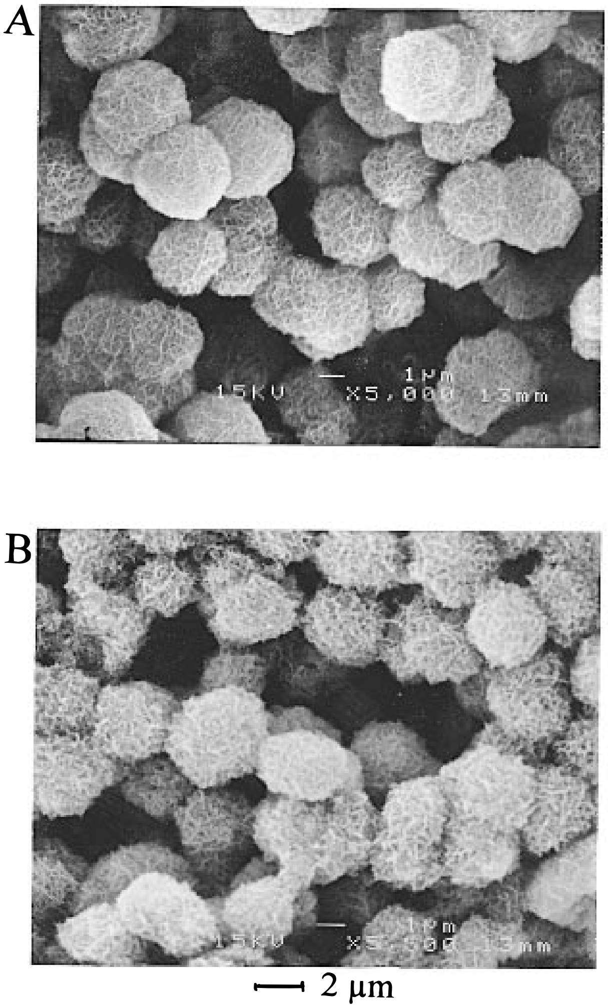

Figure 6. SEM of particles obtained when (A) the solution mixture given in Figure 5A was heated under the same conditions, but in the absence of cores; (B) the particles shown in (A) were calcined at 700 °C for 1 h in air.

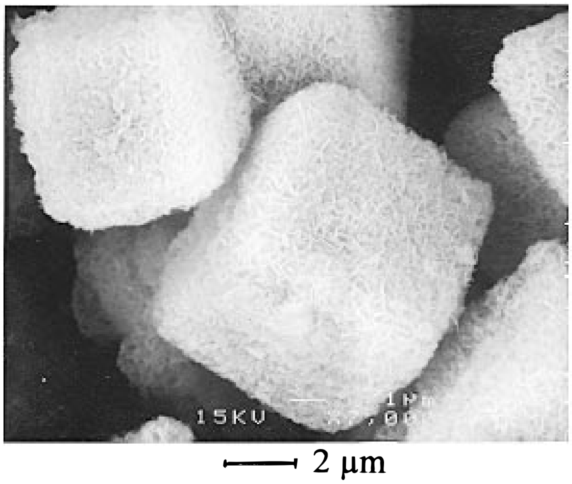

Figure 7. SEM of particles displayed in Figure 5A, calcined at 700 °C for 1 h in air.

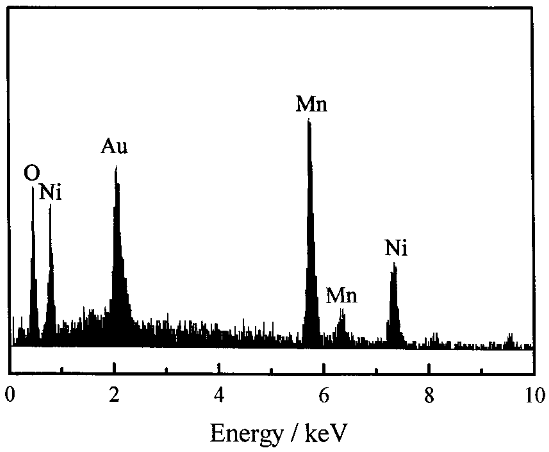

Figure 8. Energy-dispersive X-ray (EDX) analysis pattern of particles shown in Figure 5A.

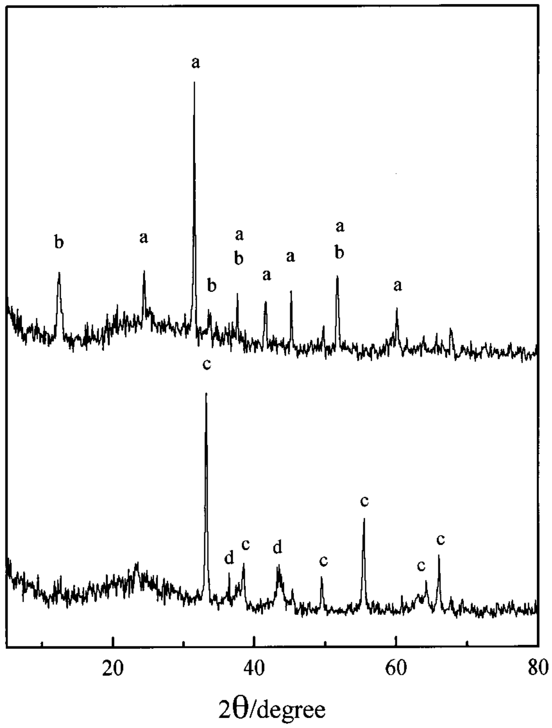

Figure 9. X-ray diffraction (XRD) patterns of particles shown in Figure 5A (upper) and Figure 7 (lower). Symbols: a, $MnCO_3$; b, $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$; c, Mn_2O_3; d, NiO.

mic peaks around 340 and 500 °C, which were attributed to the phase transformation of the shell and core materials, respectively.

On calcination the coated particles transformed into NiO and Mn_2O_3 [XRD, Figure 9 (lower)] without any observable change in the size and shape [Figure 7]. Furthermore, no sintering resulted by the heat treatment, since the calcined particles were readily dispersible in water.

Mobility measurements [Figure 4] indicated that the iep of coated particles approached that of the shell material as precipitated separately [Figure 6A], which pointed to the same chemical composition of the coating.

C. Reduction. Attempts to directly reduce some of the powders [e.g., shown in Figures 6A and 7], dispersed in aqueous solutions of several reducing agents (i.e., sodium borohydride, hydroxylamine hydrochloride, and hydrazine), proved unsuccessful. However, the same particles were reduced to metals by heating the powders for 6 h at 350 °C in a stream of hydrogen at a flow rate of 50 cm^3 min^{-1} [Figure 10A,B]. The experimentally determined weight losses of 22.1% and 28.6%, following the reduction, corresponded well with the calculated ones of 21.4% and 27.7% for the particles shown in Figures 6A and 7, respectively. An inspection of Figure 10 also demonstrated that both the cores and the coated

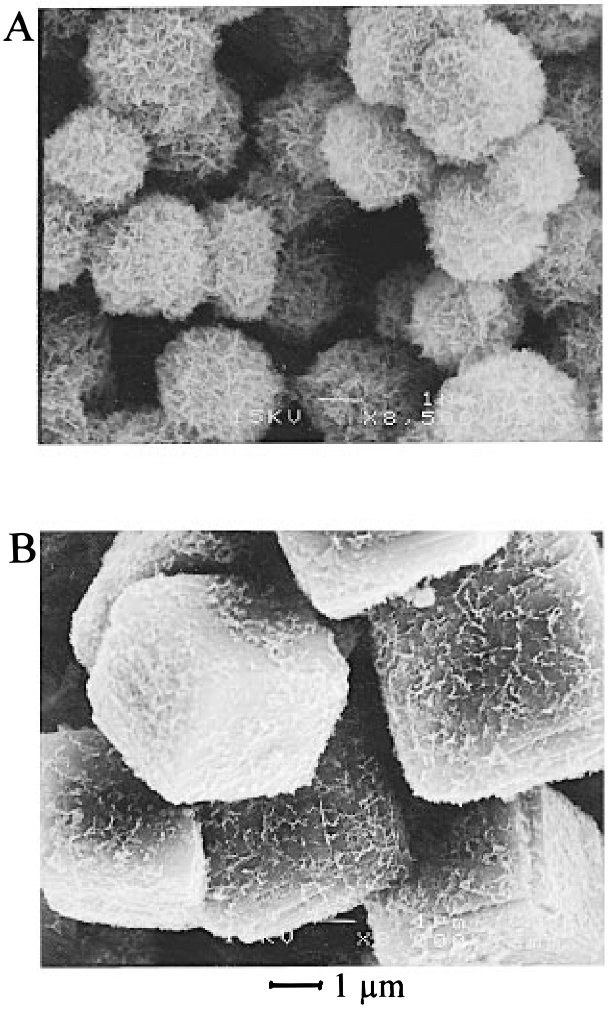

Figure 10. SEM of particles obtained when powders shown in Figure 6B (A) and Figure 7 (B) were reduced at 350 °C in a flow of hydrogen for 6 h at the flow rate of 50 cm^3 min^{-1}.

particles retained their shapes, but their sizes decreased significantly. The latter must be due to the loss of material during the reduction processes, although the porosity may have also changed.

4. Discussion

The precipitation of particles in the described reactants mixtures was caused by thermal decomposition of urea, which liberated carbonate ions and increased the pH of the medium. The resulting solids consisted of cubes of two distinct sizes, having the same chemical composition and the identical iep (at pH ~5.8).

As described elsewhere, [28,29] the urea solution decomposes on heating according to the following reactions in acidic media:

$$CON_2H_4 \rightarrow NH_4^+ + NCO^- \qquad (1)$$

$$NCO^- + H_2O + 2H^+ \rightarrow NH_4^+ + CO_2 \qquad (2)$$

and according to

$$CON_2H_4 + 2OH^- \rightarrow CO_3^{2-} + 2NH_3 \qquad (3)$$

in neutral and basic media.

The appearance of particles in two sizes can be attributed to the variation in the composition of the reactant mixture, resulting from the thermal decomposition of urea. Small particles of $MnCO_3$ were produced during the initial time period of 15–25 min, when the pH reached nearly the neutral value. The subsequently essentially constant pH may be due to the buffering effect of carbonate species in solutions generated by the decomposition of urea. When the aging continued for more than 25 min, large particles appeared in the resulting dispersion. It would seem that during the first aging period a high critical supersaturation is needed for the initial nucleation to take place, yielding a large number of small particles, which are strongly negatively charged, due to the large excess of carbonate ions. The formation of the solid phase brings about a release of the supersaturation, causing fewer secondary nuclei and slower growth to larger size of less strongly charged particles.

This mechanism explains the finding that a freshly prepared solution of the same composition as the mother liquor on heating yields a mixture of small and large particles. The reaction in this case starts at room temperature and the concentration of carbonate ions must be built up on heating to reach the necessary supersaturation at which time the small particles will precipitate first.

The iep of dispersions of small and large particles was the same, which can be explained by the fact, that the electrokinetic measurements were carried out with thoroughly washed solids.

The transformation of cubic particles of $MnCO_3$ [Figure 1B] to Mn_2O_3 [Figure 1C] can be explained by the following reaction, i.e.

$$2MnCO_3 \xrightarrow[700\ °C/air]{31.3\%} Mn_2O_3 + CO + CO_2 \qquad (4)$$

since the calculated weight loss correlates well with the experimental value of 32.5%. These particles retained their shape after heat treatment, although the oxidation state of manganese increased from +2 to +3 due to the presence of oxygen during calcination.

Conversion of the same particles [Figure 1A] in nitrogen atmosphere to MnO can be described by

$$MnCO_3 \xrightarrow[700\ °C/N_2]{38.3\%} MnO + CO_2 \qquad (5)$$

in agreement with the experimentally determined weight loss of 39.2%. The roughening of MnO particles [Figure 1D] should be due to the significant loss of the material during the phase transformation.

The large cubic particles of $MnCO_3$ were also employed for the coating with the nickel compound. Shells of these composite particles were composed of $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$, which is the same as the coating material obtained in the absence of cores. This result showed that the presence of cores in the coating medium had no effect on the chemical composition of the precipitated solid from $NiSO_4$/urea solutions. The XRD analysis of the coated particles also proved cores and shells to be independent phases. Furthermore, stripping the outer

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layer from the cores by mechanical stirring suggested the absence of any strong chemical bonds between the shell and core materials. When heated at 700 °C, transformations into Mn_2O_3 and NiO indicated that the cores did not interfere with the phase change of the coatings. Though obvious loss in material occurred during the controlled reduction process, these particles retained most of their morphological features.

The absence of chemical interaction between cores and shells was observed earlier[14] with $Cu_2(OH)_2\,CO_3$ particles with titania, which on calcination converted into CuO and TiO_2. It was also found that the reduction of calcined coated particles was only possible by heating them in the flow of hydrogen.

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