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A critical examination of a cryochemical method for the preparation of high surface area semiconducting powders

Part 3 *Factors which determine surface area*

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The effect of the nature of precursor salts on the surface area of mixed metal chlorides and mixed metal oxides prepared by freeze-drying was studied in the following systems: $MgCl_2 \cdot 6H_2O$–KCl, acetates and nitrates of lanthanum, strontium and cobalt, nitrates of nickel and cobalt. The intermediates as well as the final products were studied by electron microscopy. X-ray powder diffraction, thermogravimetric analysis and differential scanning calorimetry. If a solid solution of the precursor salts is formed higher ultimate surface areas may be attained. Thus $NiCo_2O_4$ produced via the thermal decomposition of freeze-dried nickel cobalt nitrate had a greater surface area and lower decomposition temperature than $La_{0.5}Sr_{0.5}CoO_3$ prepared from the freeze-dried nitrates, which needed heating above 500° C to decompose $Sr(NO_3)_2$ which fractionates from the mixed nitrates. Arrhenius parameters have been determined for the decomposition of cobalt nitrate, nickel nitrate and freeze-dried nickel cobalt nitrate. The carbon monoxide released on the vacuum thermal decomposition of the mixed acetates resulted in the formation of metallic cobalt. Dehydration of $MgCl_2 \cdot 6H_2O$–KCl occurred with an increase in surface area, but any further effects due to the formation of the perovskite phase were not seen because of sintering.

1. Introduction

This paper is one of a series [1–3] in which aspects of the preparation technique known as freeze-drying have been studied with a view to a proper understanding of the processes involved and consequent improvements in the method.

The preparation of a high surface area mixed oxide powder (the examples in this work are $NiCo_2O_4$ and $La_{0.5}Sr_{0.5}CoO_3$) consists of three parts. First a stoichiometric solution of a precursor salt (e.g. nitrate) is sprayed as an aerosol on to a liquid nitrogen cooled surface, or directly into liquid nitrogen. The solid is warmed in a vacuum causing the solvent to sublime. This step is the slowest in the method and has been studied by Kelly *et al.* [2], while Hibbert and Tseung [3] have studied the use of solvents other than water. When dry the mixture of salts is decomposed, still under vacuum, and the resulting product heated in air to achieve the correct structure and composition. By maintaining mixing on an atomic scale throughout the process the final heating may be carried out at a lower temperature than would otherwise be possible and thus the high surface area is not lost by sintering.

In this paper we have investigated the development of surface area during freeze-drying, the nature of the intermediate freeze-dried salts and the use of different precursor salts.

2. Experimental procedure

2.1. Materials

All chemicals were of Analar grade and recrystallized before use. Solutions were made up in doubly distilled deionised water.

2.2. Apparatus

Solutions were freeze-dried and samples of oxides prepared as given elsewhere [1, 4, 5]. In all experiments water was the solvent and an infrared lamp used to facilitate sublimation [2]. In experiments to characterize the freeze-dried salts, the salts were handled in a dry box during transfer to other apparatus for thermogravimetric analysis (TGA), differential

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thermal analysis (DTA) and X-ray diffraction (XRD). To prepare oxide samples the salts were decomposed *in vacuo* at 300° C.

XRD patterns were recorded or, for moisture-sensitive samples, powder photographs were taken of the sample contained in a sealed tube.

TGA was performed in a vacuum apparatus with a CI Mark II vacuum microbalance (Cambridge Instruments, Cambridge) which had a sensitivity of 1 μg. Temperatures were programmed to $\pm 0.5°$ C and the data collected by a microcomputer. Heating rates were approximately 2° C min^{-1}. The method of analysis used did not require accurate control of the heating rate (see Section 2.3.3). The gases evolved during heating were analysed by a quadrupole spectrometer (VG Micromass II, V.G. Instrument, Crawley) connected to the vacuum line by a variable leak.

DTA and differential scanning calorimetry (DSC) were performed on samples in air or in a flowing nitrogen atmosphere.

The surface area of samples was measured using a single-point BET method on a Micromeritics (London) surface area analyser. The analyser was calibrated with a standard graphite powder and one surface-area determination of a freeze-dried product was done independently on the vacuum microbalance with nitrogen as adsorbate, when the adsorption was plotted according to the BET equation and the monlayer coverage obtained from the slope and intercept [6].

Conductivities of powdered samples were determined by measurement of the conductance of a ground sample compressed between steel end-pieces in a close-fitting glass tube (3 mm internal diameter, ~2 mm sample thickness) at a constant pressure of 20 kgf (196 N).

Electron micrographs of freeze-dried samples of $NiCo_2O_4$ were taken using a Cambridge Instruments S100 electron microscope.

2.3. Methods

2.3.1. *Choice of salts*

Samples of $La_{0.5}Sr_{0.5}CoO_3$ were prepared separately from the nitrates and acetates of cobalt(II), lanthanum and strontium and from a mixture of cobalt(II) and lanthanum nitrates and strontium acetate. The products were characterized by XRD and surface-area and conductivity measurements.

2.3.2. *Nature of freeze-dried salts*

To determine the extent to which a solid solution of the freeze-dried salts has been formed two systems were studied: cobalt(II) and nickel(II) nitrates and lanthanum, strontium and cobalt(II) nitrates, by XRD, DTA, TGA, and DSC.

2.3.3. *Kinetics of the decomposition of nitrates*

The decomposition of $Co(NO_3)_2$ and $Ni(NO_3)_2$ and their ground and freeze-dried mixtures was followed by TGA. The kinetic parameters A, E_a and n were determined from a numerical analysis of TGA curves fitted to an equation of the form $d\alpha/dt = k(1 - \alpha)^n$, where α is the fractional weight loss and k is an nth-order rate constant given by $k = A \exp(-E_a/RT)$. We have used a different method from that of Mu and Perlemutter [7, 8], who plotted $\log[(d\alpha/dt)/(1 - \alpha)^n]$ against $1/T$ for different values of n. Our method uses a simplex optimization of the parameters A, E_a and n by minimizing the objective function $\Sigma_{\text{data}}(\alpha_{\text{calc}} - a_{\text{exptl}})^2$. The values of α_{calc} are obtained by a numerical integration of the rate equation using interpolated values for the temperature at any time. The method has the advanatge of giving values for n directly from the analysis with no *a priori* assumptions. An additional advantage is that the temperature need not be ramped linearly, only measured with some accuracy. The numerical solution requires a set of temperature values taken throughout the experiment that may be interpolated to provide values for the solution of the differential rate equations.

2.3.4. *Surface area changes during freeze-drying*

In order to study the effects on surface area of loss of water of crystallization, samples of $MgCl_2 \cdot 6H_2O$, KCl and equimolar mixtures were freeze-dried and heated in air. The change in surface area of $MgCl_2$ accompanying the loss of $5H_2O$ and then the final water of crystallization was measured, and effects due to the formation of the perovskite $KMgCl_3$ were sought.

Surface area and conductivity changes during the preparation of $La_{0.5}Sr_{0.5}CoO_3$ and $NiCo_2O_4$ were followed, particularly as the nitrates decomposed and during the subsequent heating in air.

3. Results and discussion

3.1. Choice of salt

Early work [1] has suggested that salts with a large number of redundant atoms may lead ultimately to higher surface areas. When preparing mixed metal oxides an efficient mixing of the precursor salts in the freeze-dried product should encourage the formation of a solid solution. The solid solution may then decompose at a single temperature to give a product which would require a minimum of heating in air to attain the final structure. The metal ions should therefore have similar charge and ionic radius. Cobalt(II) and nickel(II) fulfill these conditions ($r_{Co^{2+}} = 82$ pm, $r_{Ni^{2+}} = 78$ pm) and evidence for the formation of a solid solution is given in Section 3.2. With the nitrates of lanthanum, strontium and cobalt(II) we found that the product after vacuum decomposition had an X-ray pattern which had sharp lines of $Sr(NO_3)_2$ [9] superimposed on a broad uninterpreted background. The undecomposed nitrate was leached into distilled water and the strontium determined gravimetrically as sulphate. The remaining solid was fired in air for one hour at 1000° C. The XRD pattern, now sharp, was of Co_3O_4 [10] and $LaCoO_3$ [11]. The product of vacuum decomposition was $(LaCoO_3)(Co_3O_4)_{0.33}Sr(NO_3)_2$. The cubic perovskite structure of $La_{0.5}Sr_{0.5}CoO_3$ is only attained after firing in air at a higher temperature. As $LaCoO_3$ has

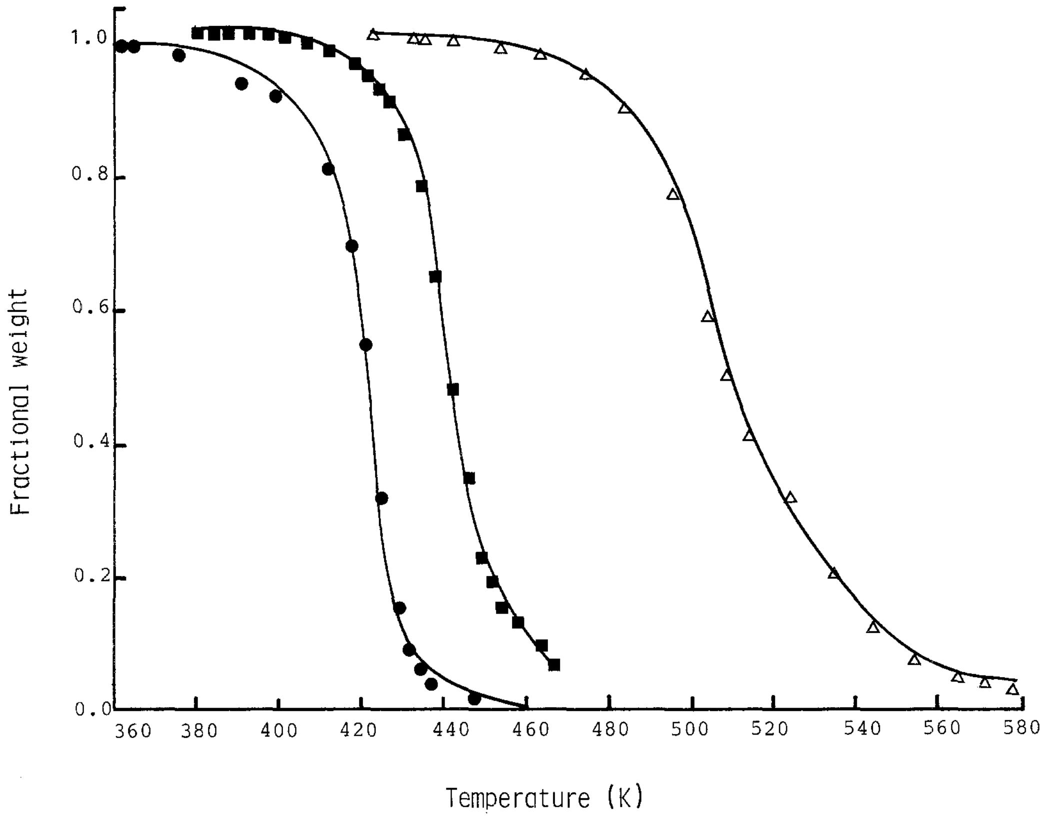

Figure 1 TGA of (●) anhydrous freeze-dried $Co(NO_3)_2$, (△) $Ni(NO_3)_2$ and (■) a freeze-dried solid solution $NiCo_2(NO_3)_6$. Continuous lines are fitted by the rate parameters given in Table I.

a rhombohedral structure that is only slightly distorted from the cubic perovskite [11] the introduction of strontium into $LaCoO_3$ must still occur readily at the relatively low temperatures at which it is eventually formed (500 to 550° C [4]), even though the atomic mixing which is required in freeze-drying is evidently not maintained throughout the process. It may be noted that strontium nitrate decomposes rapidly only above 600° C [12] in air, which is above the published melting point of 570° C [13].

In an attempt to find salts of lanthanum, strontium and cobalt that decompose in a narrower temperature range, and to study the use of salts that decompose giving a reducing environment, mixtures of the acetates were freeze-dried from aqueous solutions. During vacuum sublimation the solid was more prone to melting than were frozen nitrate solutions, indicating a lower-melting eutectic [3]. During vacuum decomposition a purple sublimate appeared on the cooler parts of the apparatus and the mixture of acetates always melted. In a separate experiment the sublimate was identified as cobalt(II) acetate. After prolonged heating an insulating black oxide was formed and a mirror of cobalt metal covered the base of the flask. Mu and Perlemutter [7] have shown that in a nitrogen atmosphere cobalt acetate ($\cdot 2H_2O$) first loses water of crystallization then is converted to Co_3O_4 via $Co(CH_3CO)_2$. The oxalate gives metallic cobalt, although Mehandjiev and Nikolova-Zhecheva [14] report that CoO is formed.

A mixture of cobalt and lanthanum nitrates and strontium acetate gave unreacted strontium nitrate after vacuum sublimation and vacuum decomposition. It may be inferred that the system is under thermodynamic control and the most stable salt, strontium nitrate, is formed.

3.2. Nature of freeze-dried salts

The results reported above show clearly that a solid solution is not formed between the nitrates of lanthanum, strontium and cobalt. That a solid solution is formed between cobalt(II) and nickel(II) nitrates is confirmed by the TGA of the nitrates separately and of a freeze-dried mixture (Fig. 1). It is clearly seen that the anhydrous freeze-dried mixture decomposes as a single compound at a temperature between that of each separate nitrate. The loss of water of crystallization from each nitrate was consistent with the transitions $Co(NO_3)_2 \cdot 4H_2O \rightarrow Co(NO_3)_2 \cdot 2H_2O$ (fraction of initial weight: calculated 0.86, found 0.86) $\rightarrow Co(NO_3)_2$ (calculated 0.72, found 0.75) $\rightarrow Co_3O_4$ (calculated 0.32, found 0.32) and $Ni(NO_3)_2 \cdot 4H_2O \rightarrow Ni(NO_3)_2 \cdot 1H_2O$ (calculated 0.79, found 0.78) $\rightarrow Ni(NO_3)_2$ (calculated 0.72, found 0.73) $\rightarrow$ NiO (calculated 0.29, found 0.31. The freeze-dried mixture of molar ratio 2 Co : 1 Ni lost water in the

TABLE I Kinetic parameters for the vacuum decomposition of cobalt and nickel nitrates

Compound	log *A*	E_a (kJ mol^{-1})	*n*	*S**
Freeze-dried $Co(NO_3)_2$	10.48	91.23	0.84	0.023
Ground $Ni(NO_3)_2$	17.00	165.5	2.5	0.016
Freeze-dried $2Co(NO_3)_2 \cdot Ni(NO_3)_2$	18.85	162.8	1.6	0.013

*Standard deviation $S = [F/(N - 1)]^{1/2}$, where F is the objective function defined in Section 2.3.3. and N is the number of data points.

initial stages of heating. This demonstrates the existence of water of crystallization which survives vacuum drying, although the amount was dependent on the length of time and duration of heating in this step. The TGA of freeze-dried cobalt and nickel nitrates was consistent with the transition $2Co(NO_3)_2 \cdot Ni(NO_3)_2 \cdot 9H_2O \rightarrow 2Co(NO_3)_2 \cdot Ni(NO_3)_2 \cdot 7.5H_2O$ (calculated 0.96, found 0.96) $\rightarrow 2Co(NO_3)_2 \cdot Ni(NO_3)_2$ (calculated 0.77, found 0.77) $\rightarrow 2CoO_{1.33} \cdot NiO$ (i.e. a stoichiometric amount of Co_3O_4 and NiO) (calculated 0.33, found 0.33). Within the limits of experimental error the final stoichiometry could have been $2CoO_{1.5} \cdot NiO$, that is $NiCo_2O_4$ (calculated 0.34). In another experiment the starting material after vacuum drying had the formula $2Co(NO_3)_2 \cdot Ni(NO_3)_2 \cdot 6H_2O$ which lost all of its water of crystallization (calculated 0.84, found 0.82) and then decomposed to the mixture of oxides as above (calculated 0.36, found 0.37). A mixture of ground nitrates that were not freeze-dried gave a TGA that indicated a loss of water of crystallization from $2Co(NO_3)_2 \cdot Ni(NO_3)_2 \cdot 12H_2O$ (calculated 0.72, found 0.74) and successive decompositions of $Co(NO_3)_2$ (calculated 0.44, found 0.46) and then $Ni(NO_3)_2$ (calculated 0.31, found 0.30).

DTA gave similar results. A mixture of cobalt and nickel nitrates showed two distinct peaks as first cobalt nitrate and then nickel nitrate decomposed. The freeze-dried mixture gave a single broad peak covering the range of decomposition temperatures. Some fine structure was observed but this has not been attributed to any particular transition. The decomposition at atmospheric pressure as measured by DTA may be by a different mechanism than that under vacuum.

Analysis of the XRD patterns of each nitrate separately freeze-dried confirmed the presence of the tetrahydrate, dihydrate and anhydrous forms. The latter became more prominent as the nitrates were heated in a vacuum. The lines with $h\,k\,l$ 3 1 1 and 2 2 2 are sufficiently intense and may be unambiguously assigned and used to identify the phases present and to calculate the unit cell length a_0. Anhydrous cobalt(II) nitrate and nickel(II) nitrate each crystallize in similar cubic habits [15] with $a_0 = 741.0$ pm and 730.2 pm, respectively. In our studies of the freeze-dried nitrates we find for $Co(NO_3)_2$ $a_0 = 738.8$ pm and $Ni(NO_3)_2$ $a_0 = 732.8$ pm. We see only one phase in freeze-dried mixtures and for Co : Ni = 2 : 1 the value of a_0 linearly interpolates the pure compounds (736.3 pm).

3.3. Kinetics of the vacuum decomposition of nitrates

Kinetic parameters for the vacuum decomposition of anhydrous freeze-dried cobalt(II) nitrate, anhydrous, recrystallized nickel(II) nitrate and a 2 : 1 Co : Ni freeze-dried mixture are given in Table I. They were calculated from TGA data as described in Section 2.3.3. and the calculated TGA curves are plotted in Fig. 1. It is seen that a single set of parameters adequately describes the decomposition of the freeze-dried mixture. It is not possible to compare the values of the kinetic parameters with those of Mu and Perlemutter [7] which were determined under different conditions.

3.4. Surface area changes during freeze drying

3.4.1. *$KMgCl_3$*

The loss of $5H_2O$ (118° C) then $1H_2O$ (160° C) from freeze-dried $MgCl_2 \cdot 6H_2O$ results in an increase of specific surface area (s.s.a.) from 9.0 to 20.9 $m^2\,g^{-1}$ and then to 43.5 $m^2\,g^{-1}$, showing that loss of water of crystallization can be an important factor in producing surface area. It was not possible to detect any effect of the formation of the mixed compound $KMgCl_3$ which has a well-known distorted perovskite structure [16]. The DSC of an equimolar mixture gave an endothermic peak at 412° C (685 K) as the perovskite was formed. However, 658 K is above the Tamman temperature ($= 0.5T_{\mathrm{melting}}$) [17] of either KCl (m.p. 1049 K) or $MgCl_2$ (m.p. 981 K) and so when the surface area was measured at 400° C the material sintered too quickly to observe effects specifically due to compound formation.

3.4.2. *$La_{0.5}Sr_{0.5}CoO_3$*

Ground mixtures of the nitrates of lanthanum, strontium and cobalt(II) had immeasureably small surface areas which in terms of the method used indicates that the s.s.a. was less than 0.1 $m^2\,g^{-1}$. Two freeze-dried mixtures had s.s.a. values of 0.8 and 1.0 $m^2\,g^{-1}$. It is possible that some water of crystallization had already been driven off which could account for the small increase in s.s.a. The greatest increase in area occurred on the initial decomposition under vacuum. After 1 to 3 h at 300° C samples of freeze-dried nitrates had s.s.a values of between 40 and 55 $m^2\,g^{-1}$, with some evidence for loss of surface area after heating for the longer periods. On heating in air at higher temperatures (500 to 550° C) the samples lost surface area to values of s.s.a. of 20 to 30 $m^2\,g^{-1}$. A comparison was made between a freeze-dried sample of nitrates and one in which recrystallized nitrates were ground together. After heating *in vacuo* to 300° C for 1 h the s.s.a. values of the samples were 55 and 36 $m^2\,g^{-1}$, respectively. After 40 min in air at 550° C they had both fallen to similar low values, 28 and 23 $m^{-2}\,g^{-1}$. However, the resistivity of each sample ($\varrho = 0.91$ and 12.5 Ω m) indicated that the freeze-dried sample was further advanced towards the conducting perovskite structure (ca. 0.1 Ω m). Sintering in the intermediate range in which surface diffusion is important may be modelled by an equation of the form $\mathrm{d}A/\mathrm{d}t = -k(A - A_\mathrm{f})$ where A is the surface area and A_f the final sintered surface area [18]. This expression has been used to determine the activation energy for the sintering of nickel oxide [19]. A plot of log $(A - A_\mathrm{f})$ against t for the freeze-dried and ground nitrates is given in Fig. 2. The resistivities of the samples are also plotted. The Nicholson equation is followed after an initial period in which the surface area falls at a steeper rate. To what extent the formation of the perovskite phase affects the rate of sintering is not known, although the fall in resistivity occurs largely in this initial period. Gregg [20] has discussed the

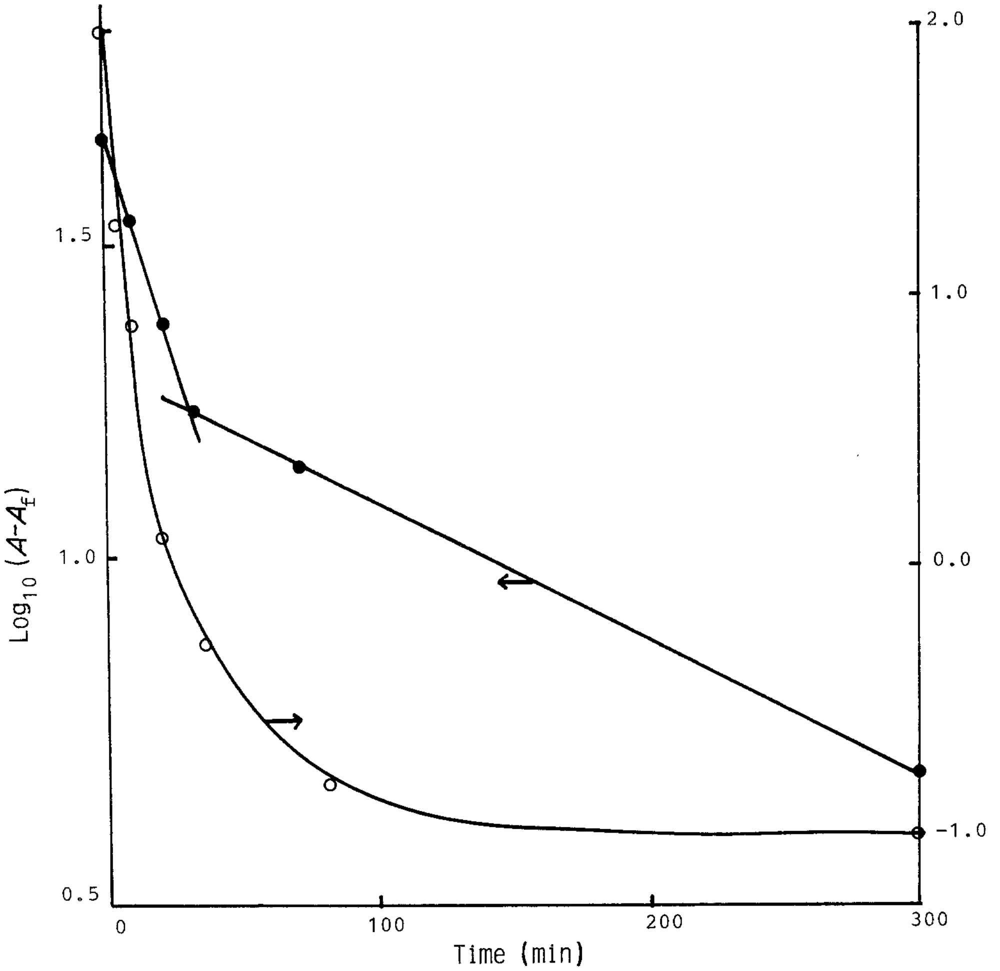

Figure 2 (○) Loss of surface area and (●) change of resistivity with time of a freeze-dried sample of $La_{0.5}Sr_{0.5}CoO_3$ heated at 500° C. A_f is the final surface area attained.

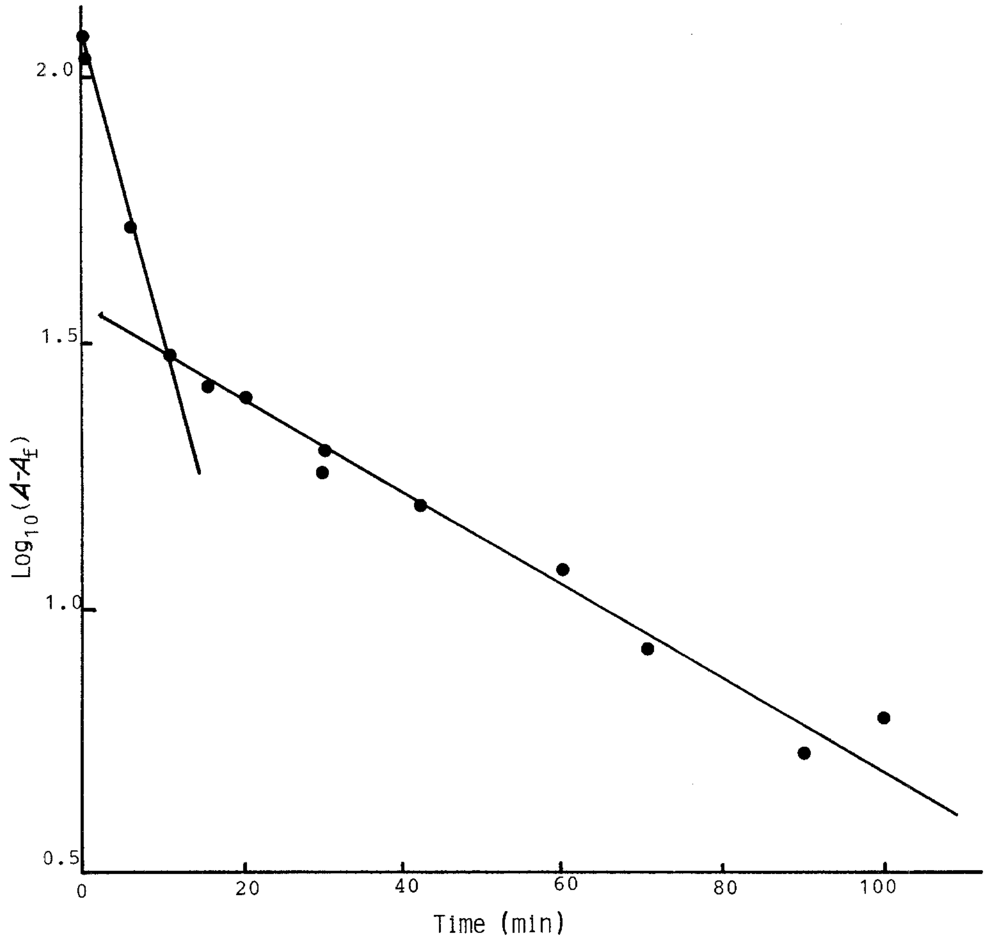

Figure 3 Loss of surface area with time of a sample of freeze-dried $NiCo_2O_4$ heated at 380° C.

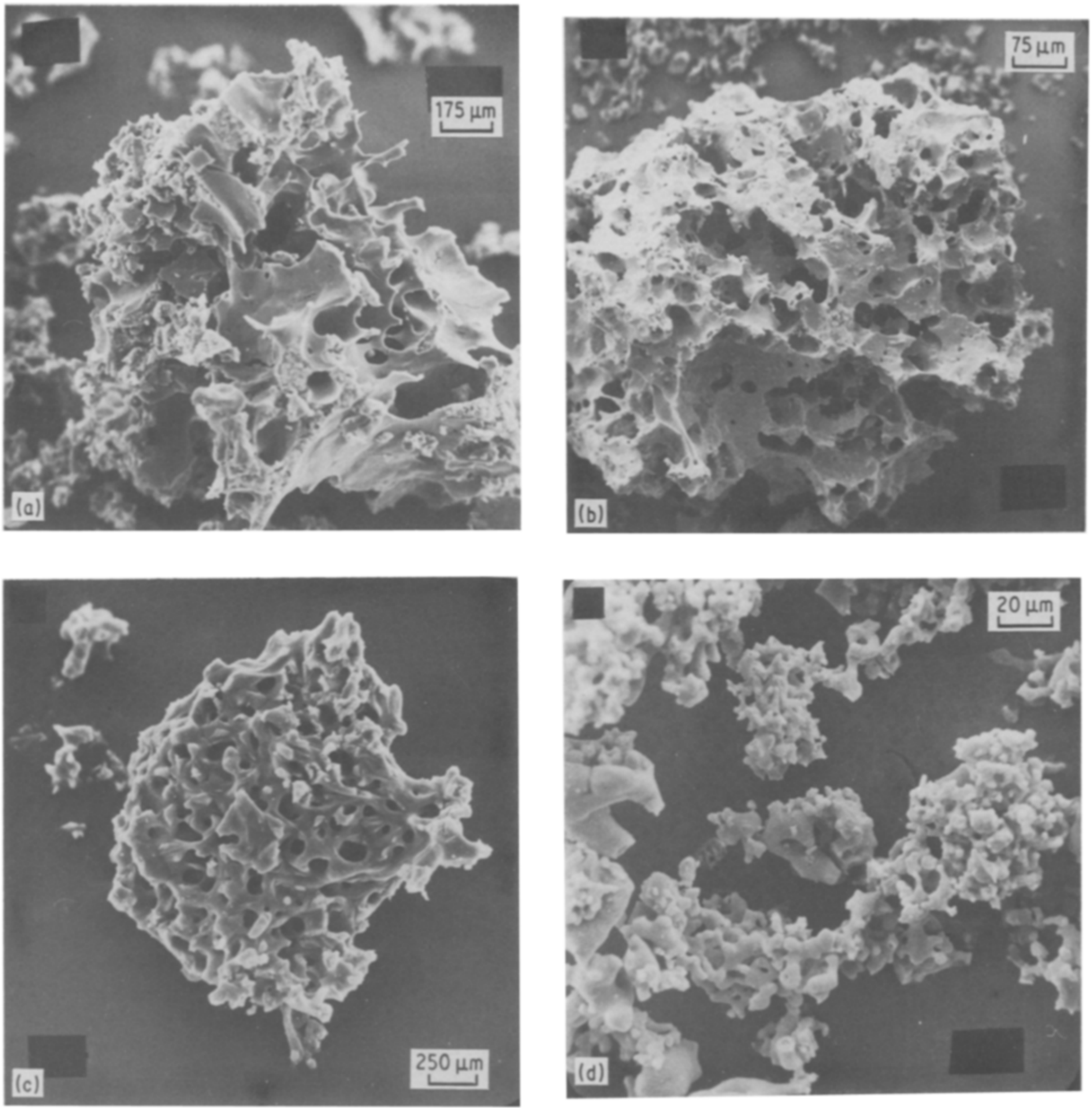

Figure 4 Electron micrographs of particles of freeze-dried $NiCo_2O_4$ after heating at 400° C for (a) 60 min, (b) 150 min and (c) 360 min; (d) heated at 600° C for 1350 min.

decomposition of salts with gas evolution. He proposes a mechanism in which the reactant decomposes, leaving a product atom still on the lattice sites of the reactant. The product must then rearrange to the correct structure. If the system is above the Tammann temperature the latter process may be accompanied by sintering. Thus in our case a high surface area is formed by the decomposition of the nitrates but the product is not the desired conducting structure. This forms later with a loss of surface area.

3.4.3. $NiCo_2O_4$

In the case of $NiCo_2O_4$ a solid solution is formed (see Section 3.2) which on vacuum decomposition gave a product of high surface area, typically $150\,m^2\,g^{-1}$. This sintered rapidly at temperatures as low as 380° C (Fig. 3), following kinetics similar to that of $La_{0.5}\,Sr_{0.5}CoO_3$. At higher temperatures a transition occurs to a non-conducting cubic form. The progress of a sample as it sinters is shown in Fig. 4. Large macroporous particles give way to smaller but non-porous particles. This appears to involve a more complex mechanism than that of simply filling pores as proposed by German [21] and others [22].

4. Conclusions

4.1. The formation of high surface area oxides by freeze-drying

From the results of experiments described above the following conclusions may be drawn concerning the preparation of high surface area mixed oxides.

1. The salts should form as near as possible solid solutions. The choice of solvent will determine the eutectic of the solution and thus the time required to complete the vacuum sublimation [2]. It is seen from the initial surface area after vacuum decomposition that cobalt and nickel nitrates, which do form solid solutions, give much greater s.s.a. values

(ca. 150 $m^2 g^{-1}$) than the nitrates of lanthanum, strontium and cobalt (ca. 50 $m^2 g^{-1}$). It may be noted here that in an earlier paper [3] it was not possible to predict that the frozen solution always reaches the eutectic during vacuum drying irrespective of the starting composition. However a consideration of the temperatures of the frozen solutions show that they are all considerably above the Tammann temperature of the solution, which leads to the conclusion that solid-state diffusion and thus the observed behaviour should occur.

2. Salts that evolve reducing gases during decomposition give low oxides or metals, and thus may not be suitable choices as precursors.

3. The surface area of the freeze-dried product is developed entirely during vacuum decomposition. Water of crystallization is evolved and then the anhydrous salts decompose.

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