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The Development of Internal Structure During Thermal Decomposition: Nickel Formate Dihydrate

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The production of highly porous nickel by the dehydration and decomposition reactions of nickel formate dihydrate in vacuum has been studied by a combination of electron microscopic, thermogravimetric and sensitive volumetric techniques. By working with nonagglomerated crystals of uniform size prepared by a droplet evaporation technique which has been described previously, the uncertain effects of size and packing of crystals are eliminated. It is found that the course of the decomposition reaction is dependent in a complex way upon size and this is attributed to the internal defect structure generated during growth of the crystal rather than a surface/volume ratio effect. Details of the kinetics which are masked by thermogravimetric experiments on large samples are demonstrated very clearly by the volumetric technique. Activation energies derived from thermogravimetric studies are for dehydration 25.3 ± 2.0 kcal. mole^{-1} and for decomposition 33.1 ± 3.0 kcal. mole^{-1}. The possibility that the dehydration stage crucially affects the subsequent decomposition behaviour of the formate is discussed.

INTRODUCTION

The preparation of high area metals and metal oxides by the thermal decomposition of a salt of the metal, is now known to be extraordinarily complex. For example, the control of surface area for the production of catalysts, adsorbents and molecular sieves depends upon such factors as the state of subdivision of the starting material, uneven rates of reaction from crystal to crystal, effects due to the ambient atmosphere, and the presence of impurities (promoters). In a practical situation, these factors are often difficult to control since each interacts with the others in a more or less complex way. However, by careful choice of preparative method, the shape and size of crystals, and hence packing of material can be regulated to control the diffusion rate of reaction products and sintering of the residue. Method of preparation can also, in principle, be used to regulate stoichiometry and defect content of the crystals. An extensive discussion of these factors in the preparation and properties of finely divided materials has been given recently (*1*).

In this paper we combine the results of kinetic and microscopic methods of examination to the study of the formation of finely divided nickel by the thermal decomposition of nickel formate dihydrate, as a function of particle size. To overcome the uncertain influences of particle size distribution and degree of packing, we use a previously described method for the preparation of crystals of uniform size which are deposited in a uniform layer with very little agglomeration. A parallel thermogravimetric study on crystal agglomerates allows comparison of the effect of crystal packing on the course of the decomposition reaction.

The thermal decomposition of metal carboxylates for the production of high area solids has recently been reviewed by

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Doremieux (*2*) and a previous study of the dehydration and decomposition reactions of nickel formate closely related to this has been reported by Prettre and Bachelard (*3*).

EXPERIMENTAL METHOD

Materials

The basic starting material was a specially prepared commercial product of high purity (total cation impurity, <400 ppm; Fe, 200 ppm, Na, 30 ppm, Al and Cu, 25 ppm) and narrow size distribution centered around 45 μm diameter. Kinetic measurements were made on groups of particles selected by hand from this preparation. Particles in two smaller size ranges were prepared by the droplet technique described elsewhere (*4*) using solutions prepared from the commercial preparation. The solution concentrations were 0.6% and 0.06% w/v.

Production of Uniformly Sized Crystals

Two of the complicating factors in the study of decomposition reactions in solids, namely the particle size effect and the uncertainty of the influence of agglomeration, are eliminated here by using crystals of uniform size and shape and depositing these on to a substrate in a single layer. An apparatus for doing this has been described by Walker, Gane and Bowden (*4*) and is based upon a method of producing uniformly sized liquid droplets described by Wolf (*5*) and later improved by Harris (*6*).

The question arises as to whether the particles produced by this technique are single crystals. The rapidity with which each particle grows due to the high supersaturation generated by rapid evaporation of the solvent in the solution droplet, implies that at best the structure is one which consists of a microcrystalline mass in which each crystallite is separated by a highly disorganized region. This approximates to a single crystal which is penetrated by subgrain boundaries. Particles of this size are too large for the penetration of a high energy electron beam but in certain favourable cases, electron diffraction patterns could be obtained through the edge of some crystals showing these parts to be single crystal. Electron micrographs also show that the particles are facetted being frequently hexagonal in outline form.

Kinetics of Decomposition

The temperature dependence of the decomposition rate was studied by the pressure-time method. However, because of the small amounts of material available from the droplet technique, rather sensitive methods of detecting decomposition products were necessary. This was achieved in a very high vacuum system in which the background pressure was reduced to the 10^{-9} Torr range. The composition of the decomposition products was continuously followed by repeatedly monitoring the mass spectrum of the gas phase with a partial pressure gauge of the mass filter type (Varian Associates R. G. A.).

Experiments were performed by inserting the sample into a tube furnace at a known temperature. The time required for thermal equilibrium was reduced to a minimum (~2 min) by making the specimen support of conveniently small size and by ensuring good thermal insulation between support and insertion mechanism. This is particularly important for specimens of such small mass and thermal capacity.

Independent thermogravimetric experiments (Combustion Instruments Microforce Balance) were carried out in a vacuum (background pressures 5×10^{-6} Torr) on relatively large samples (10 mg) of the 45 μm preparation, as an independent check on the course of both dehydration and decomposition reactions and as an indication of the effect of sample size on the decomposition kinetics. The effect of particle aggregation in samples of this size was also checked mass spectrometrically.

Morphological Studies

Changes in gross morphology during dehydration and decomposition were followed in the transmission electron microscope and in the scanning electron microscope both fitted with heating stages. Scanning microscopy proved to be the more useful technique because the thickness of the particles allows only studies of the change in their profile to be made in the transmission microscope.

RESULTS AND DISCUSSION

General Features

Thermogravimetric experiments carried out on the 45 μm diameter particles show that decomposition takes place in two simple steps corresponding firstly to dehydration and then to break up of the formate ion. Moreover, the percentage decomposition, 68.2% corresponds to the formation of nickel (theoretical, 68.2%). The weight loss on dehydration amounts to 21.0% compared with that corresponding to the loss of two molecules of water of 19.5%. Examination of the gas phase during dehydration showed that CO was present representing some decomposition of the formate molecule, the rate of which reached a maximum at about the maximum rate of dehydration, i.e., ~70°C and which stopped when dehydration was complete. The activation energies for dehydration and decomposition derived from isothermal weight loss experiments are 25.3 ± 2.0 kcal mole^{-1} and 33.1 ± 3.0 kcal mole^{-1}, respectively, which are to be compared with the values of 15 kcal mole^{-1} and 42 kcal mole^{-1} given by Prettre and Bachelard (*3*).

Figure 1 shows a typical thermogram plotted as weight change against temperature and this is compared on the same figure with the change in linear dimensions accompanying dehydration and decomposition. There is an obvious qualitative similarity between the two curves, the differences lying in their detailed shape. For instance from the size change curve, dehydration appears to take place as soon as the specimen is viewed in the microscope and this may be attributed to heating of the particles in the electron beam. The thermogravimetric experiments showed that at room temperature, the dihydrate was stable indefinitely under vacuum and that loss of weight could first be detected at temperatures above ~40°C. The size change which occurs on decomposition is more gradual and takes place over a larger temperature range. The reduction in size with increasing temperature is largely attributable to the collapse of internal porous structure generated by the dehydration process. The dehydration and decomposition of the large particle is, however, significantly different from that just described for the smaller particles. On dehydration, regular cracks appear along crystallographic planes and this is accompanied by an appreciably smaller size reduction than in the previous case. Moreover, the subsequent decomposition of the formate does not produce such a catastrophic collapse of the internal structure of the porous particle produced. The development of these effects can be followed in the series of photographs shown in Figs. 2(a) and (b).

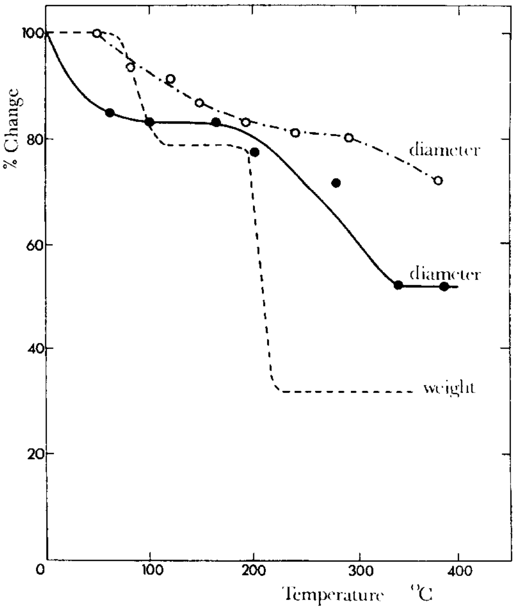

FIG. 1. Comparison of the linear size change with weight loss during dehydration and decomposition of nickel formate showing much larger collapse of the structure for smaller particles — 3 μm diam. particles, —·— 45 μm diam. particles, — — weight loss.

Dehydration

It is well to consider what influence dehydration may have on the form of the porous nickel produced by decomposition since it is well-known that water vapour has a profound effect on the final state of

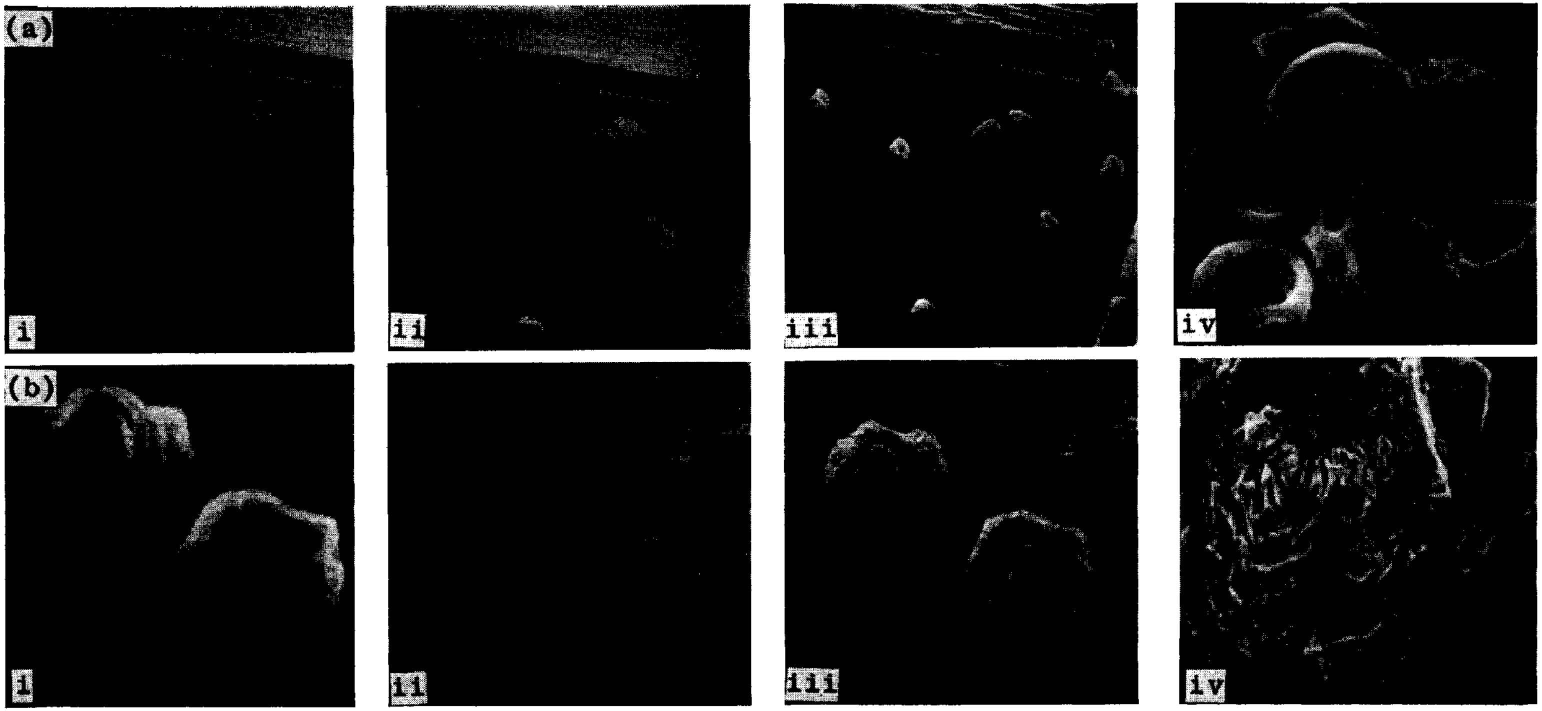

FIG. 2. (a) Decomposition of 3.5 μm particles, (i) before heating, (ii) after dehydration, (iii) after decomposition, (iv) detail of particles showing internal collapse of porous structure after decomposition.

(b) Decomposition of 45 μm particles, (i) before heating, (ii) after dehydration, (iii) after decomposition, (iv) detail of a single particle showing the development of porosity with little collapse of the original particle. ×2800.

subdivision in many decomposition reactions (see, for example, the paper and discussion by Anderson *et al.* (*7*) and (*8*)). Figure 1 shows that the size change on dehydration is much greater for the smaller than for the larger particles and this implies a greater collapse of the internal structure in the former case and would result in a material of smaller surface area. This initial collapse is followed by a similarly larger collapse for the smaller particles on subsequent decomposition.

Whether the dehydration stage is crucial to the course of the subsequent decomposition reaction is problematic. Bachelard (*9*) has shown that the dehydration conditions affect the degree of subdivision of the anhydrous salt and later (*3*) that the amount of fragmentation is dependent on the dehydration temperature and the particle size of the starting material. In the present experiments we have shown that dehydration is also accompanied by decomposition which must be a structural rather than a thermal effect, i.e., the rupture of bonds produced by change in crystal structure on a molecular scale brought about by the loss of water from the lattice. It is tempting, therefore, to relate this and the greater collapse of the droplet particles to dehydration which takes place at a larger number of sites which may be grown-in lattice imperfections whose number is dependent upon the method of preparation of the particle. Observations on the effect of lattice imperfections on a dehydration reaction were first made by Faraday (*10*) for the dehydration of sodium carbonate.

Decomposition

Effects which may be attributed to the defect structure of individual crystals varying in reactivity from one to another have recently been described for the preparation of finely divided zirconium oxide (*11*) and the reduction of nickel oxide (*12*).

In these experiments we have carefully controlled the method of formation of the starting material and so by implication effects due to widely varying defect concentrations have been reduced to a minimum. Thus while the internal structure on which decomposition takes place may well depend upon the initial dehydration step, the final porous network of nickel will depend upon the way in which nickel atoms coalesce. In the case of the smaller particles this sintering process seems to be rather effective, producing a much larger collapse of the structure than for the larger particles. The collapse of internal structure has been demonstrated by Prettre and Bachelard who showed that the surface area resulting from the decomposition of pure nickel formate was much lower than that produced in formate containing calcium or magnesium oxides as impurities. This can be attributed to the possibility that subsequent sintering of the otherwise high area pure nickel specimen is prevented by the presence of impurities which are said to act as promoters. The fact that the sintering occurs at such a low temperature (compared with the conventional temperature of half the melting temperature in °K) can be attributed to the very small size of the sintering particles (single atoms in the limit) and this will be assisted by the heat evolved in the decomposition reaction.

Reaction Kinetics

The rate of formation and relative amounts of gaseous reaction products are an indication of the detailed mechanism of the decomposition reaction. In the present experiments we have eliminated such complicating factors as degree of compaction of individual particles limiting the rate of release of reaction products as described previously for nickel formate (*3*, *13*). Nevertheless, a detailed examination of the mechanism of the decomposition reaction shows that under the present experimental conditions, this is much more complex than has hitherto been described in the literature (*3*, *13–17*), being sensitively dependent upon particle size.

For all particles studied, decomposition was accompanied by an initial rapid rise in CO_2 pressure which subsequently decayed to a constant value. This was also accompanied by the evolution of CO and it is in the relative rates and the size of the partial pressure maxima of these two species that the difference in decomposition behaviour as a function of particle size lies. Broadly speaking, three reproducible and temperature independent types of behaviour have been observed and these are illustrated in Fig. 3. That corresponding to the largest and the smallest particles (Figs. 3 (a) and (c), respectively) differ only in the initial rates of CO_2 evolution and for both, the final CO pressure is much larger than the maximum CO_2 pressure attained. The decomposition of particles in the intermediate size range is characterized by a very rapid rise in CO_2 pressure which reaches a value close to the ultimate CO pressure, before decaying (Fig. 3b).

It is interesting to note that under these experimental conditions, the reaction shows no marked induction period although in experiments carried out on larger samples in which the particles are agglomerated, an accelerating reaction is observed after the initial rise of CO_2 has subsided.

These observations, although qualitative, are reproducible from one sample to another within a given size range. However, attempts to derive activation energies from the rates of evolution of CO_2 and CO were unsuccessful. Moreover, no simple relationship exists between reaction rates and nominal surface area or sample weight.

The decomposition of nickel formate has been described by several authors (*3*, *13*, *15*) in terms of the simultaneous evolution of CO and CO_2 according to the following scheme

$$\mathrm{Ni(HCO_2)_2} \rightarrow \mathrm{Ni + H_2 + 2CO_2} \qquad \text{(a)}$$

$$\mathrm{Ni(HCO_2)_2} \rightarrow \mathrm{Ni + H_2O + CO + CO_2} \qquad \text{(b)}$$

although the relative importance of each reaction seems to be in doubt. Thus Balandin *et al.* consider that both take place simultaneously up to about 50% decomposition when only reaction (a) becomes important. However, Bircumshaw and Edwards consider that both reactions are of equal importance. The present results show that both CO and CO_2 are produced but the relative rates and amounts are dependent upon particle size which in turn is dependent upon the mechanism of formation of the crystals in each specimen. In all cases the pressure of CO_2 after an initial rise falls to a value which is constant and low compared with that of CO (the possibility that the evolution of either gas is catalysed by the substrate on which the crystals rest is precluded by the fact that the same behaviour has been reproduced with tantalum, stainless steel and glass substrates). The disappearance of CO_2 is probably due to its catalysed reaction with hydrogen on the nickel formed to give CO and water since the partial pressure of water in the gas phase is seen to increase at this stage in the reaction.

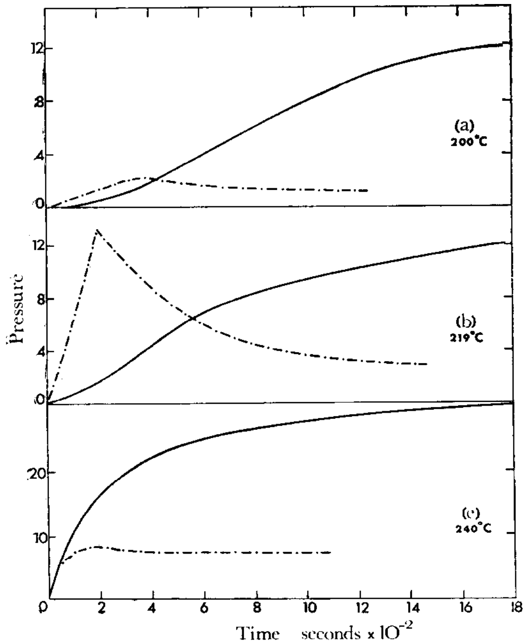

Fig. 3. Pressure-time curves for particles of different sizes, (a) 45 μm, (b) representative of the size range 1–10 μm, (c) representative of the size range <1 μm. — CO, —·—·—CO_2. Because of the very small scatter in the data, individual points are not shown.

CONCLUSIONS

Two significant results emerge from this study, viz., that the development of the internal structure during the formation of highly porous nickel by thermal decomposition is very dependent upon the method of preparation of the starting material. In addition, for the type of decomposition reaction studied here, which is preceded by a dehydration stage, the loss of water may affect the subsequent structure produced by decomposition.

The effect of method of preparation is undoubtedly related to the defect structure of the material formed and it is this (and the influence of impurities (*3*)) which controls the collapse of the porous structure formed on decomposition. These effects are mirrored in a complex way by the kinetics of decomposition which depend sensitively on the particle size, although with existing techniques it seems unlikely that one could relate structure to the mode of decomposition in any detatil. (A close study of the relationship between kinetics of decomposition and the dislocation systems in large single crystals of calcite has recently been described (*18*)).

However, it is evident that for the type of reaction studied here, the most effective method of producing high area solids lies in the prevention (with the aid of promoters) of the structural collapse of the porous mass produced by decomposition rather than in attempts to generate high areas by suitably tailoring the defect structure of the starting material. The additional problems of the effect of particle size and the difference in decomposition behaviour between individual particles on the overall kinetics of decomposition are still largely unresolved.

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