Journal of Thermal Analysis, Vol. 6 (1974) 321—333

CHANGES IN THE SURFACE CHARACTERISTICS OF RESIDUES FROM THE THERMAL DECOMPOSITION OF NICKEL OXYSALTS

D. DOLLIMORE and J. PEARCE*

Department of Chemistry and Applied Chemistry, University of Salford;
**The Department of Chemistry, Faculty of Science and Engineering*
Liverpool Polytechnic, U.K.

(Received October 6, 1972; in revised form November 15, 1972)

The changes in surface area and density which occur during the decomposition of eight nickel oxysalts have been reported. Surface area peaks were observed in the temperature range 473 K to 673 K. An equation relating to the number of product particles (*n*) produced from a single particle of original material has been derived. Log *n* was shown to vary linearly with temperature, where *n* is the number of product particles formed from one original reactant particle.

This paper deals with the decomposition of selected nickel(II) oxysalts and the changes in surface area and density during the decomposition. Thermogravimetry has been used to indicate the mode of decomposition and to provide a means of checking the results obtained in the half hour ignition series, from which surface area and density determinations were made. The results also served to check published TG data on nickel(II) oxysalts.

The thermogravimetry of many nickel(II) oxysalts has previously been reported. It should be noted that differences in heating rate often produce slight differences in behaviour but the final product in all the published data has been found to be nickel(II) oxide.

Nickel formate was reported by Duval [1] to be stable up to 423 K when heated at 150 K per hour. Water of crystallisation was lost up to 518 K and the anhydrous form was stable over the temperature range 543 K to 548 K. Nickel(II) oxide was formed at 583 K via the transitory production of metallic nickel.

Nicol [2] reported the decomposition of nickel(II) hydroxide to anhydrous nickel(II) oxide to commence at 498 K.

Duval [1] reported that the TG curve of basic nickel(II) carbonate, $NiCO_3 \cdot NiO$, indicated the salt to be stable from 373 K to 473 K with the formation of the oxide being complete at 1123 K. TG studies on poorly defined carbonates [3] at heating rates of 1.6, 8 and 10 K per minute indicated the transformation from carbonate to oxide to occur between 573 K and 623 K.

Nickel(II) carbonate has also been studied using X-ray techniques [4]. It was shown that the salt lost the majority of its water of crystallisation at 473 K and that carbon dioxide was given off between 533 K and 573 K to give nickel(II) oxide at 573 K. The thermal decomposition of nickel(II) nitrate hexahydrate in air has been studied by Lumme and Peltonen [5]. They found that water of crystallisation was lost without the formation of a stable anhydrous form or any other definite stable solid intermediate. Wendlandt [6] found that nickel(II) nitrate hexahydrate began to lose water of crystallisation at 323 K. After a period of rapid weight loss, a break in the TG curve observed at 478 K corresponded approximately to anhydrous nickel(II) nitrate. Further rapid weight loss was observed to take place above 478 K, resulting in the formation of nickel(II) oxide at 778 K. The heating rate used by Wendlandt was 5.4 K per minute. When the hexahydrate is heated very slowly (10 K or 5 K per day) the intermediate hydrates, tetrahydrate and dihydrate, have been observed [7]. A basic nitrate, $Ni(NO_3)_{0\cdot67}(OH)_{1\cdot33}$ was reported by Weigel et al. [8]. The dehydration of nickel(II) nitrate hexahydrate at 313 K at various low pressures was reported [9] to result in the formation of intermediate tetra- and dihydrates. The formation of a basic nitrate during the dehydration process was not observed.

Nickel(II) sulphate hexahydrate has been reported [5] to lose five of its water molecules on heating up to 569 K with the formation of the anhydrous salt at 806 K. The anhydrous sulphate then decomposed to the oxide at 1143 K. The heating rate was 5.5 K per minute. Thermogravimetry at a heating rate of 0.6 K per minute has indicated the transitory appearance of tetra- and dihydrates of nickel sulphate [10], with the monohydrate being stable over the temperature range 405 K to 604 K and decomposition of the anhydrous form starting at 1003 K.

Leicester and Redman [11] reported the thermal decomposition of nickel(II) acetate tetrahydrate in air. The salt started to dehydrate at 343 K and at about 533 K decomposition of the anhydrous salt commenced, resulting in the formation of nickel(II) oxide. It was also found that heating the anhydrous form at temperatures below 723 K resulted in the formation of a black residue corresponding to Ni_2O_3; heating this residue to 1473 K resulted in the formation of green NiO. Nickel(II) ammonium sulphate hexahydrate, $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$, has been observed [12] to lose all of its water of crystallisation in a single step from 403 K to 498 K. The anhydrous form began to decompose slowly at 498 K resulting in the formation of $2NiSO_4(NH_4)_2SO_4$ at 703 K. Further decomposition to the nickel sulphate was complete at 773 K.

During the course of a thermal decomposition, physical changes such as surface area and density are taking place alongside the chemical changes. The production of a surface area maximum on thermal decomposition can occur in two ways [13]: (a) by channels, of molecular dimensions, left by escaping gas in the framework of the solid, as in the dehydration of zeolites [14], or more commonly, (b) by the resulting disperse state of the solid caused by the original material breaking up into smaller particles. This latter mechanism is the subject of this paper. Massive decrease in surface area during heat treatment, particularly when the salt is fully decomposed (i.e. to the oxide in this case), can occur by sintering. Sintering is the process by which particles coalesce on heat treatment. The probable mechanisms involved have been outlined by Gregg [13].

Experimental

Materials

All the salts used in this work were of laboratory reagent grade and supplied by proprietary chemical manufacturers. The specifications were checked by normal analytical techniques and found to be within the quoted limits.

Thermogravimetry

A Stanton Thermobalance (Model TR01) was modified for use with controlled atmospheres in a manner similar to that of Vassallo [15]. 0.10 g samples were decomposed over the temperature range 293 K to 1273 K at a linear heating rate of 4 K per minute.

The experiments were carried out in dry, carbon dioxide-free air with a flow rate of 300 cm^3 per minute. Each TG run was repeated three times for every sample

Table 1

Thermogravimetry of nickel oxysalts in air

Material decomposed	Decomposition reaction	% weight loss		Plateau temperature range (K) product	$\frac{\Delta W}{\Delta T}$ = max (K)
		experimental	theoretical		
Nickel nitrate	$Ni(NO_3)_2 \cdot 5.5H_2O \rightarrow NiO$	73.4	73.5	723–1273	
Ammonium nickel nitrate	$NH_4NO_3Ni(NO_3)_2 \cdot 2H_2O \rightarrow \rightarrow NiO$	75.0	74.7	773–1273	
Nickel carbonate	$NiCO_32Ni(OH)_2 \cdot 4.5H_2O \rightarrow \rightarrow 3NiO$	41.6	41.7	873–1273	
Nickel acetate	$Ni(CH_3COO)_2 \cdot 4H_2O \rightarrow \rightarrow Ni(CH_3COO)_2$	30.0	28.3	403– 493	393
	$Ni(CH_3COO)_2 \rightarrow NiO$	70.0	70.0	623–1273	583
Nickel formate	$Ni(HCOO)_2 \cdot 2H_2O \rightarrow \rightarrow Ni(HCOO)_2$	19.5	19.5	483– 513	453–473
	$Ni(HCOO)_2 \rightarrow Ni$	64.5*	68.5		543
	$Ni(HCOO)_2 \rightarrow NiO$	59.0	59.7	773–1273	543
Nickel hydroxide	$NiO \cdot 1.4H_2O \rightarrow NiO$	25.4	25.4	973–1273	323
Nickel sulphate	$NiSO_4 \cdot 6H_2O \rightarrow NiSO_4$	41.0	41.2	658– 983	363
	$NiSO_4 \rightarrow NiO$	71.0	71.6	1173–1273	1093
Ammonium nickel sulphate	$(NH_4)_2SO_4NiSO_4 \cdot 5H_2O \rightarrow \rightarrow NiSO_4$	59.5	59.6	773–1003	723
	$NiSO_4 \rightarrow NiO$	80.0	80.0	1143–1273	1093–1118

* Maximum weight loss recorded. The metallic nickel produced was immediately oxidized to nickel(II) oxide.

and found to be reproducible to within 1% of the figures quoted. The end product in each experiment was found, by chemical analysis, to correspond to nickel(II) oxide (NiO) and this fact was used in interpreting the TG curves.

There is no set method for establishing from a TG curve the temperature of decomposition of a particular salt; however, a useful method is to plot the derivative curve $\frac{\Delta W}{\Delta T}$ against T (where T is the temperature and W is the weight loss). This method has been used here to obtain the apparent temperature of decomposition by taking the value of T for which $\frac{\Delta W}{\Delta T}$ was a maximum.

The TG data obtained on the samples in general confirm the published data, particularly when heating rates are of the same order. The results are summarised in Table 1.

Ignition series

A half-hour ignition series was carried out on each salt. This consisted of heating about 2.0 g of sample for half an hour at a series of defined temperatures: 373, 473, 573, 673, 773, 873, 973, 1073, 1173 K. The samples were contained in small silica crucibles and after heating were rapidly cooled by part immersion in liquid nitrogen prior to being degassed. After degassing the samples were sealed, whilst still under vacuum, in glass tubes until surface area and density measurements were carried out.

Density measurements

The density of the samples was obtained by displacement of carbon tetrachloride at 298 K. The samples were outgassed at 298 K to a pressure of 0.13 Nm^{-2}. A specific gravity bottle fitted with a B10 socket, attached to a vacuum line, was used for this purpose. The apparatus was so arranged that carbon tetrachloride could be run into the sample whilst it was still under vacuum.

Surface area measurements

The adsorption of nitrogen gas at 77 K was measured volumetrically, and surface areas were calculated from the adsorption data by the B.E.T. method [16]. A value of 16.2 $Å^2$ was used for the cross-sectional area of the nitrogen molecule.

Results and discussion

The results arising from the half-hour ignition series studies on the eight nickel oxysalts are shown in Figs 1, 2, 3 and 4. The percentage weight loss curves agreed with the thermogravimetry data in Table 1. The plots of surface area against temperature for the salts all showed at least one peak. The initial dehydration stage for the salts, nickel(II) sulphate, nickel(II) ammonium sulphate and basic nickel(II) carbonate, was accompanied by an increase in surface area. Nickel(II) ammonium sulphate showed three surface area peaks (Fig. 3b). The first two peaks arise from the dehydration and decomposition of the double salt to nickel sulphate, and the final one is caused by the decomposition of nickel(II) sulphate to nickel(II) oxide. The decrease from maximum surface area values can be attributed to sintering or to a collapse of the lattice structure due to the strain imposed by the decomposition. Nickel(II) sulphate (Fig. 4b) behaved in a similar way, showing a peak in surface area attributable to the dehydration of the salt.

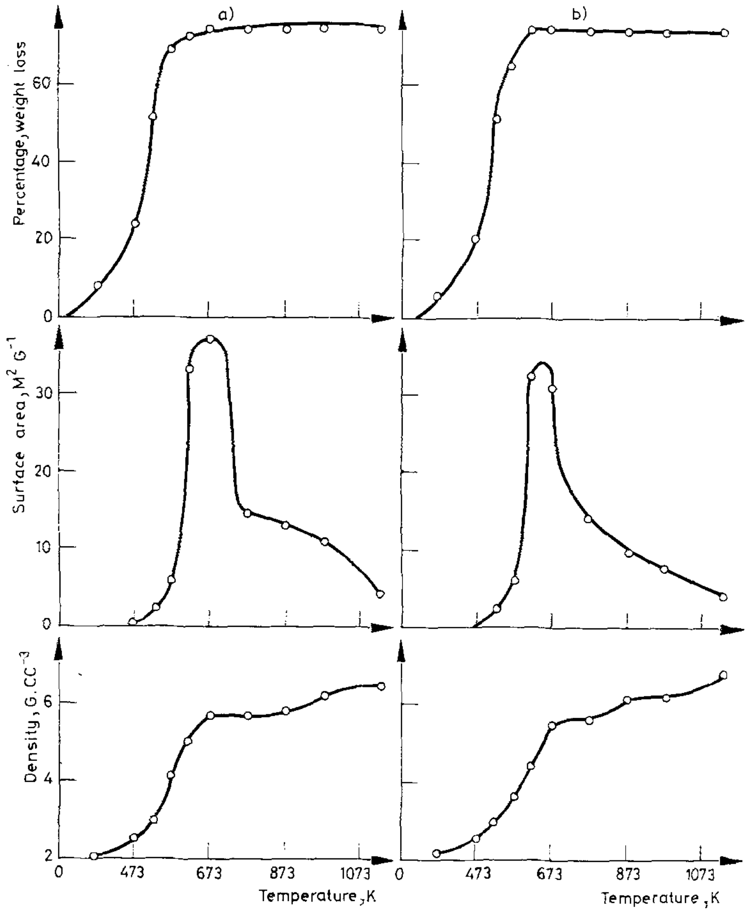

Fig. 1. The variation of the % weight loss, surface area and density for nickel(II) nitrate and nickel(II) ammonium nitrate upon thermal decomposition. a) Nickel(II) nitrate. b) Nickel(II) ammonium nitrate

A smaller peak at 1123 K was due to decomposition of the anhydrous salt to the oxide. The small size of this peak is the result of the high temperature at which the reaction occurs.

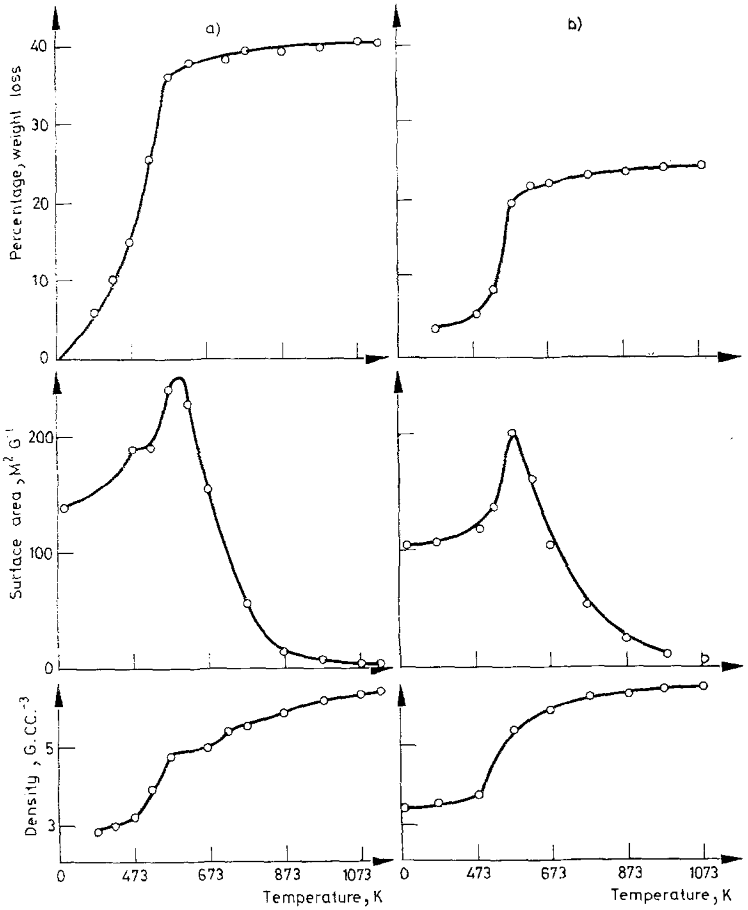

Fig. 2. The variation of the % weight loss, surface area and density for basic nickel(II) carbonate and nickel(II) hydroxide upon thermal decomposition. a) Basic nickel(II) carbonate. b) Nickel(II) hydroxide

Basic nickel(II) carbonate was a fine powder with a surface area of 140 m^2 g^{-1}. The initial dehydration and decomposition of this salt resulted in an increase of surface area to a value of 240 m^2 g^{-1} at 573 K. The recorded percentage weight loss at this surface area maximum was 36%. Further decomposition was accompanied by a rapid decrease of surface area, so that at 973 K the recorded percentage weight loss was 40.5% (41.7% for NiO) and the surface area was 8 m^2 g^{-1}.

The rapid decrease in surface area between the temperature 573 K and 973 K could be attributed to lattice collapse followed by sintering of the product particles at the higher temperatures.

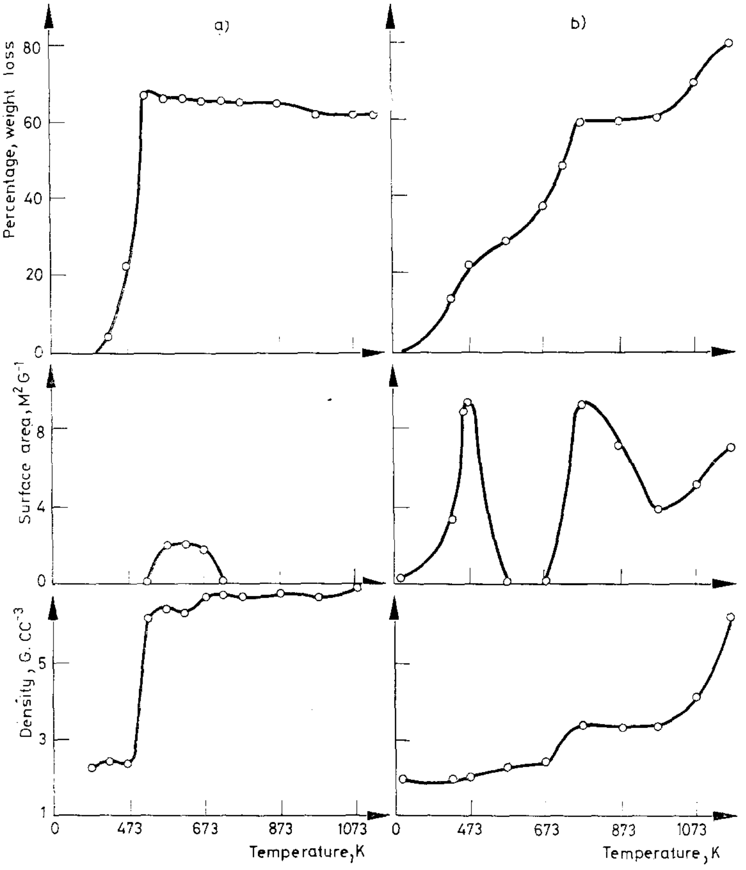

Fig. 3. The variation of the % weight loss, surface area and density for nickel(II) formate and nickel(II) ammonium sulphate upon thermal decomposition. a) Nickel(II) formate. b) Nickel(II) ammonium sulphate

The dehydration of nickel(II) hydroxide was accompanied by a surface area increase from 103 m^2 g^{-1} to 201 m^2 g^{-1}, but the last traces of water, which were lost slowly between 573 K and 1073 K, resulted in a surface area decreased to 5 m^2 g^{-1} at 1073 K. In contrast to the salts just discussed, the remaining salts: the acetate, formate, nitrate and ammonium nitrate double salts, showed no surface area increase during the initial dehydration stage of decomposition, but, surface area increases were observed during the decomposition to the oxide. The subsequent sintering of the oxide was evidenced by a rapid decrease in surface area for these latter salts.

The density of nickel(II) oxide is greater than the density of any of the salts which were studied [17]. This fact was evident from the variation in density of the salts during decomposition. An initial increase in density corresponded to the conversion of the hydrated salt to the oxide. Further increase in density of the product oxide was attributed to the sintering of the oxide particles. Sintering can be considered the reverse of activation, both being evident in changes of the physical and chemical properties of a powdered material [18].

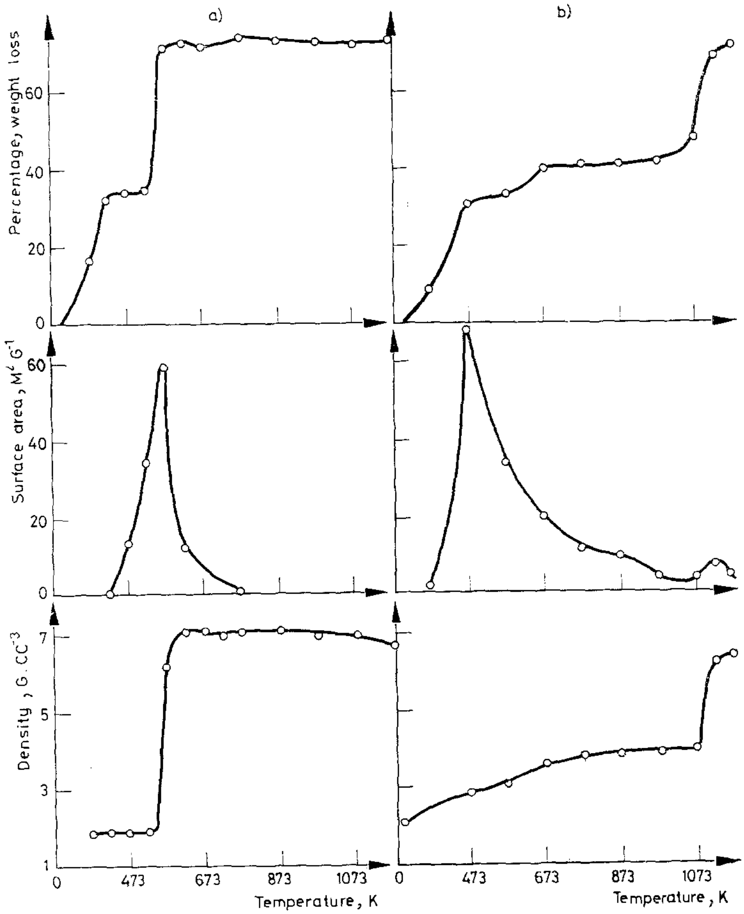

Fig. 4. The variation of the % weight loss, surface area and density for nickel(II) acetate and nickel(II) sulphate upon thermal decomposition. a) Nickel(II) acetate. b) Nickel(II) sulphate

The extent of sintering is a function both of the temperature and the time of heating, with different mechanisms of sintering being temperature dependent. As the temperature is raised the sintering mechanisms in order of appearance are as follows: (a) adhesion between particles, leading to the formation of seized joints at points of contact; (b) surface diffusion, in which coalescence of particles is accelerated by movement of particles along the surface, and (c) bulk diffusion. At higher temperatures viscous and plastic flow of material take place.

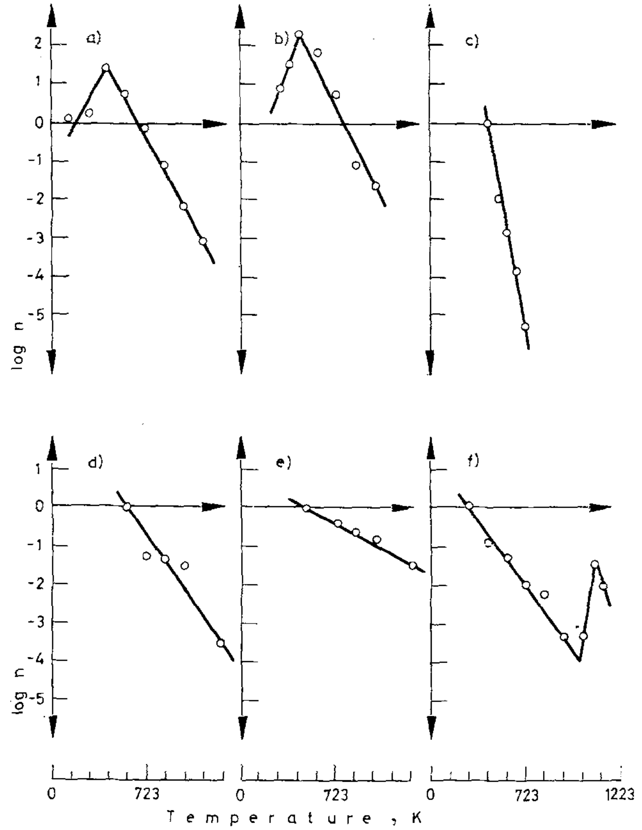

Fig. 5. Plots of log n against temperature for various nickel(II) oxysalts. a) Nickel(II) hydroxide. b) Basic nickel(II) carbonate. c) Nickel(II) acetate. d) Nickel(II) nitrate. e) Nickel(II) ammonium nitrate. f) Nickel(II) sulphate

Sufficient evidence exists to suggest that the various mechanisms become operative at defined temperatures, often expressed as a fraction of the melting point

(T_m). Surface diffusion is considered to be important above 0.30 T_m and bulk diffusion processes are thought not to be operative until the temperature is half that of the melting point of nickel oxide, 0.50 T_m [13, 19]. Table 2 gives the values of the ratio of the temperature at which the maximum surface area occurred, to the melting point of the nickel oxide (T/T_m). The nickel(II) oxide product formed during the thermal decomposition of nickel(II) nitrate and nickel(II) ammonium nitrate is subject to sintering by a surface diffusion process, whereas nickel(II) oxide produced during the thermal decomposition of nickel(II) sulphate and nickel(II) ammonium sulphate is subject to sintering by a bulk diffusion process.

Table 2 also gives the surface area at 673 K (0.3 T_m). It can be seen that in general a loss in surface area has occurred, due to sintering of the oxide at temperatures less than 673 K.

Table 2

T/T_m values at the max. surface area of the oxide formed from the decomposition of nickel oxysalts

Salt	Surface area max. m^2 g^{-1}	Surface area at 673 K	Temp. at maximum surface area, K	T/T_m*
Nickel nitrate	37	37	673	0.302–0.297
Ammonium nickel nitrate	33	31.0	618–673	0.277–0.273 0.302–0.297
Nickel carbonate	240	153	573–623	0.258–0.254 0.279–0.275
Nickel hydroxide	201	105	573	0.257–0.253
Nickel acetate	59	7	573	0.257–0.253
Nickel sulphate	7.0	–	1123	0.504–0.496
Ammonium nickel sulphate	7.0	–	1173	0.526–0.518
Nickel formate	2.0	2.0	573–673	0.257–0.253 0.302–0.297

* NiO, T_m K in literature is given in range 2230–2263 K.

Inspection of the surface area variations given in Figs 1, 2, 3 and 4 show that dehydration or decomposition results in increase of surface area (activation) while sintering forces cause a decrease in surface area. The increase–decrease in surface area with temperature is almost symmetrical for some of the salts. If the production of surface area maximum is due to the original material breaking up [13] into smaller particles, and surface area minimum due to the smaller particles coalescing then one equation might describe both the mechanisms of activation and sintering. Consider the original material to be in particulate form, consisting of n_1 particles mol^{-1} with a molar volume and molar surface area of V_1 and S_1 respectively.

The molar volume of the original untreated material can be expressed by:

$$V_1 = \frac{M_1}{\rho_1} = \frac{4}{3}\pi n_1 r_1^3 \tag{1}$$

where M_1 = gramme molecular weight, ρ_1 = density, r_1 = the average radius of the particles.

The molar surface area of the original unreacted material can be expressed by:

$$S_1 = s_1 M_1 = 4\,\pi n_1 r_1^2 \tag{2}$$

where s_1 = the experimental surface area in $m^2\,g^{-1}$.

From (1) and (2)

$$r_1 = \frac{3\,V_1}{S_1} \tag{3}$$

and rearranging (2)

$$r_1 = \left(\frac{S_1}{4\,\pi n_1}\right)^{1/2} \tag{4}$$

Suppose that during the decomposition process the nickel salt produces n_2 particles mol^{-1} with a molar volume and molar surface area of V_2 and S_2 respectively. Then:

$$V_2 = \frac{M_2}{\rho_2} = \frac{4}{3}\pi n_2 r_2^3 \tag{5}$$

and

$$S_2 = s_2 M_2 = 4\,\pi n_2 r_2^2 \tag{6}$$

where M_2 = the "effective" molecular weight of the partially decomposed reacted material; see Eqs (13) and (14); s_2 = the experimental surface area in $m^2\,g^{-1}$, ρ_2 = density, r_2 = average radius of particles.

From (5) and (6)

$$r_2 = \frac{3\,V_2}{S_2} \tag{7}$$

and rearranging (6)

$$r_2 = \left(\frac{S_2}{4\,\pi n_2}\right)^{1/2} \tag{8}$$

from equations (3) and (7)

$$\frac{r_1}{r_2} = \frac{V_1 S_2}{V_2 S_1} \tag{9}$$

from equations (4) and (8)

$$\frac{r_1}{r_2} = \left(\frac{S_1 n_2}{S_2 n_1}\right)^{1/2} \tag{10}$$

equating (9) and (10)

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2} \left(\frac{n_2}{n_1}\right)^{1/2} \tag{11}$$

If we put $n_1 = 1$ and $n_2 = n$, equation (11) becomes

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2} n^{1/2} \tag{12}$$

which describes a process where n is the number of product particles formed from a single reactant particle.

The molecular weight of the original reactant material (M_1) is known, as is the molecular weight of the final product oxide (say M_3). The effective molecular weight of the partially reacted material (M_2) must be estimated. It is suggested that M_2 might be given by

$$M_2 = (1 - \alpha)M_1 + \alpha M_3 \tag{13}$$

where α = fraction decomposed.

Thus the molar surface area of partially reacted material will be given by:

$$S_2 = s_2\{(1 - \alpha)M_1 + \alpha M_3\} \tag{14}$$

The value of n in equation (12) has been calculated over the activation and sintering temperature ranges for basic nickel(II) carbonate, nickel(II) sulphate and nickel(II) hydroxide. Equation (12) has also been applied to the sintering of the oxide product resulting from the thermal decomposition nickel(II) acetate, nickel(II) ammonium nitrate and nickel(II) nitrate.

Fig. 5 shows that sintering obeys a log law of the form:

$$\log n = KT + C \tag{15}$$

where K and C = constants, T = temperature of treatment.

This law also appears to hold for the activation process although this was not conclusive. The fact that the materials decompose at different temperatures and at different rates, producing varying degrees of strain on the crystal lattices, introduces many parameters additional to those studied here. In general the results do confirm previous observations on oxalate materials [20, 21] and show that observations of density and surface areas provide direct evidence regarding thermal decomposition which can be placed alongside TG or DTA.

References

1. C. Duval, Inorganic Thermogravimetric Analysis, 2nd (revised) Ed. Elsevier, Amsterdam, 1963.
2. A. Nicol, Compt. Rend., 222 (1946) 1034.

3. J. FRANÇOIS-ROSSETI, M. T. CHARTON and B. IMELIK, Bull. Soc. Chim. France (1957) 614.
4. J. FRANÇOIS, Compt. Rend., 230 (1950) 2813.
5. P. LUMME and J. PELTONEN, Suomen Kemistilehti B., 37 (1964) 162.
6. W. W. WENDLANDT, Texas, J. Sci., 10 (1958) 392.
7. D. WEIGEL, Thesis, Paris, 1960.
8. D. WEIGEL, B. IMELIK and P. LAFFITTE, Bull. Soc. Chim. France (1962) 345.
9. R. C. WHEELER and G. B. FROST, Can. J. Chem., 257 (1955) 546.
10. R. FRUCHART and A. MICHEL, Compt. Rend., 245 (1957) 1544.
11. J. LEICESTER and M. J. REDMAN, J. Appl. Chem. London, 12 (1962) 357.
12. M. CAPESTAN, Ann. Chim. Paris, 5 (1960) 225.
13. S. J. GREGG, J. Chem. Soc. (1953) 3940.
14. R. M. BARRER, Proc. Roy. Soc. London, Ser. A, 167 (1938) 392, 406.
15. D. A. VASSALLO, Anal. Chem., 33 (1961) 1823.
16. S. BRUNAUER, P. M. EMMETT and E. TELLER, J. Am. Chem. Soc., 60 (1938) 309.
17. Handbook of Chemistry and Physics, 42nd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 614.
18. H. G. CRONE and J. H. MCKEE, Bcura Bull., 14 (1950) 329.
19. G. F. HUTTIG, Kolloid-Z., 98 (1942) 263; 99 (1942) 262.
20. D. DOLLIMORE and D. NICHOLSON, J. Chem. Soc. (1962) 960.
21. N. ARMSTRONG, P. CAMPION, J. L. DAWSON, D. DOLLIMORE and C. E. WOOD, J. Chem. Soc. (1963) 2556.

RÉSUMÉ — Etude des changements de surface spécifique et de densité pendant la décomposition de huits oxysels du nickel entre 473 K à 673 K. En désignant par n le nombre de particules issues d'une particule unique du matériau initial, on montre que log n varie linéairement avec la température.

ZUSAMMENFASSUNG — Es wird über die Veränderungen der Oberfläche und Dichte berichtet, welche bei der Zersetzung von acht Nickeloxysalzen auftreten. Oberflächenpeaks wurden im Temperaturbereich von 473 K bis 673 K beobachtet. Eine Gleichung wurde abgeleitet, welche sich auf die Zahl (n) der sich aus einem einzigen Partikel der Ausgangssubstanz bildenden Produktpartikel bezieht. Es wurde bewiesen, daß sich log n linear zur Temperatur ändert, wobei n die Zahl der sich aus einem reagierenden Ausgangspartikel bildenden Produktpartikel ist.

Резюме — Описаны изменения в поверхности и плотности 8 окси-солей никеля, происходящие при их разложении. Пики, соответствующие изменениям поверхности, наблюдаются в области температуры 473—673 K. Выведено уравнение, описывающее число частиц продукта (n), образовавшихся из единственной частицы исходного материала. Установлено что log n линейно изменяется с температурой.