JOURNAL OF
THE
INDIAN INSTITUTE OF SCIENCE

VOLUME 43 JULY 1961 NUMBER 3

STUDIES ON THE BASIC CARBONATES OF NICKEL

Part V: Thermogravimetric Behaviour of Basic Nickel Carbonates

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Received on September 16, 1960

Abstract

The thermogravimetric behaviour of basic nickel carbonates was investigated making use of a quartz-fibre spring balance. The basic nickel carbonates showed two distinct stages of decomposition when they were subjected to thermal treatment at a slow rate of heating. The first stage, corresponidng to the expulsion of part of the water, started at 100°C, and was complete at 210°C. The second stage started above 260°C, when the basic carbonate decomposed giving off the rest of the water and the carbondioxide contained in it and this reaction was complete at 420°C. The final product of decomposition was found to be nickel oxide. The results are interpreted in the light of the different natures of the water held by the basic carbonates.

Introduction

In an earlier communication[1] the preparation of basic nickel carbonates and their differential thermal behaviour was reported. In view of the importance of these basic nickel carbonates as intermediates in the preparation of catalytically active nickel a study of their thermal decomposition is essential to throw more light on the nature of the derived catalysts. The amounts of water and carbondioxide present in these compounds varied with their mode of preparation. The mode of thermal decomposition of these basic carbonates could be followed directly using a thermogravimetric balance and the different stages in their composition could be characterised. The thermogravimetric technique[3] enables one to follow the release of water and carbondioxide during the thermal decomposition and a detailed investigation was therefore undertaken.

EXPERIMENTAL

Apparatus: A simple and relatively inexpensive helical quartz fibre spring thermobalance[2] designed and set up in this laboratory was employed. Quartz-fibre springs of approximate sensitivity, 1.5 cm. extension per 100 mg. load were calibrated and used. A small quartz bucket about 150 mg. in weight with a long quartz fibre ending in a hook was suspended from the spring so as to hang freely within the thermobalance tube. A tubular electrical furnace was used to heat the thermobalance section surrounding the bucket and the temperature was measured with a chromel-alumel thermocouple kept close to the bucket. The heating was controlled manually with the help of a variac and kept at a uniform rate. The extension of the spring was measured correct to 0.001 cm. using a sensitive cathetometer.

Procedure: About 150 mg. of the sample of basic nickel carbonate was accurately weighed out into the silica bucket and the extension of the spring measured. The furnace was heated at a uniform rate of 2 to 3°C. per minute up to a temperature of 500°C. The changes in the extension of the spring were followed at intervals of 10°C rise in temperature.

The extension of the spring due to the weight of the sample alone was computed after applying blank corrections. The blank experiment was run in exactly the same manner as above but with an empty bucket. It was found that there was no change in the extension of the spring up to 200°C. At higher temperatures, however, the extension decreased progressively. On cooling the furnace, the curve could be traced backwards showing thereby that the effect was reversible. At each temperature during the thermogravimetric analysis for a particular combination of quartz-spring and bucket, the corresponding blank correction for the change in extension was determined and applied. The vapours evolved during the experiment were allowed to escape through the ventilation provided at different levels and complications due to their condensation within the thermobalance avoided.

The sensitiveness of the above thermogravimetric technique was confirmed by studying the thermogravimetry of the two standard substances $Na_2HPO_4 \cdot 12H_2O$ and $CaC_2O_4 \cdot 2H_2O$. The results were in close agreement with the established thermal behaviour of these samples [2, 3].

RESULTS

The thermogravimetric behaviour of the following samples was investigated and the typical results have been presented graphically as indicated below:

$$\left.\begin{array}{l}(1)\ 2NiO \cdot CO_2 \cdot 5H_2O\\(2)\ 2NiO \cdot CO_2 \cdot 3H_2O\\(3)\ 3NiO \cdot CO_2 \cdot 6H_2O\end{array}\right\}\text{Fig. I}$$

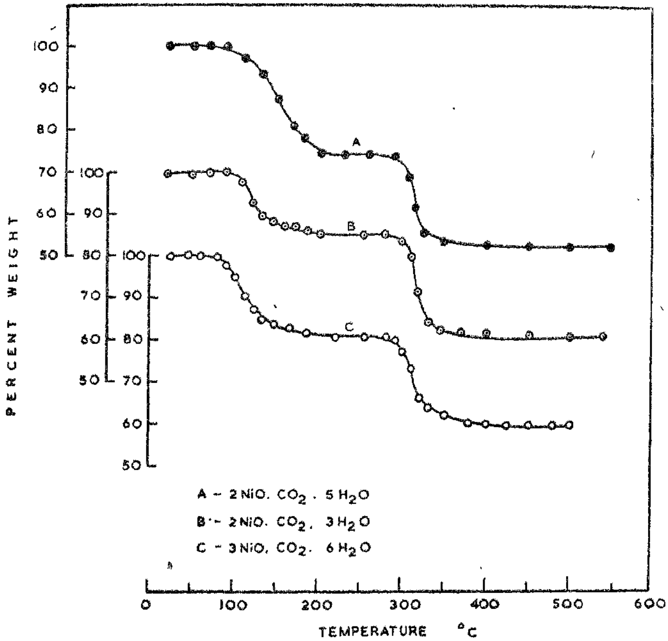

Fig. I

Thermogravimetry of ,basic nickel carbonates

(4) $4NiO \cdot CO_2 \cdot 7H_2O$ } Fig. II
(5) $4NiO \cdot CO_2 \cdot 5H_2O$

(6) $14NiO \cdot CO_2 \cdot 16H_2O$ }
(7) $16NiO \cdot CO_2 \cdot 14H_2O$ } Fig. III
(8) $17NiO \cdot CO_2 \cdot 21H_2O$
(9) $22NiO \cdot CO_2 \cdot 18H_2O$ }

The above samples of basic nickel carbonates were prepared by methods already described in the previous communication[1].

It may be seen from the thermogravimetric curves presented in the figures that in all cases two stages were obtained during the decomposition. The first

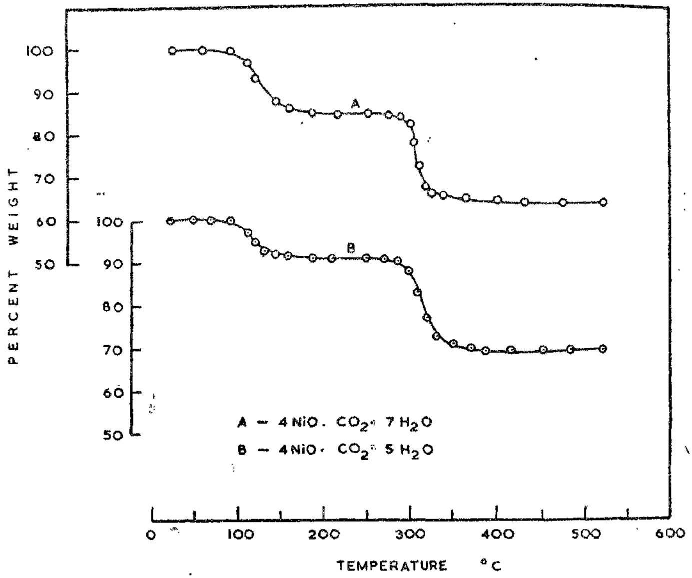

FIG. II

Thermogravimetry of basic nickel carbonates

stage which started at about 90°C was complete at 200°C and the second stage started at 270°C and was over at about 420°C. Analysis showed that the end product was nickel oxide, NiO. The net loss in weight during the pyrolysis corresponded to the loss of the total water and carbondioxide contents of the precipitates. The weight of the residue corresponded to that of nickel oxide and was the same as determined by analysis. After the first stage of decomposition, the intermediate compound is stable between 210°C and 260°C and shows constancy in weight. In order to determine its composition, the various samples of basic nickel carbonates were heated in a furnace at 230°C for one hour and the product analysed as described earlier[1]. The results for the various samples, giving the nickel oxide, carbondioxide and water contents are presented in Table I.

The above thermogravimetric curves indicating two stages of decomposition were obtained only when the samples were heated linearly at 2°C per minute.

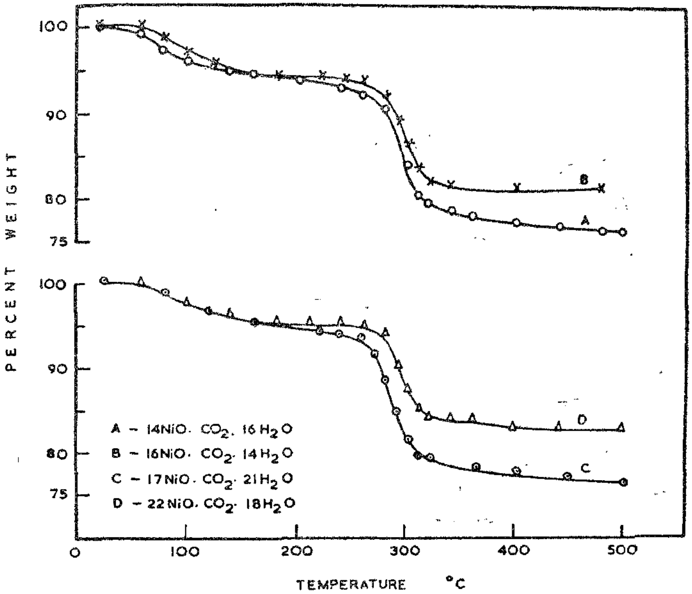

FIG. III

Thermogravimetry of basic nickel carbonates prepared at 97°C

It was found that if the heating rate was slightly faster, namely 4°C per minute, the two stages of decomposition overlapped and only the net decomposition was indicated.

Basic nickel carbonates of the same composition prepared from different systems of nickel salts and alkali carbonates gave identical thermogravimetric curves. Only typical curves are therefore included in the figures presented.

DISCUSSION

It can be seen from the table that the thermal decompositions of the different samples of basic nickel carbonate $2NiO \cdot CO_2 \cdot 5H_2O$ leads to the formation of an intermediate product of composition $2NiO \cdot CO_2 \cdot H_2O$ above 100°C. This basic carbonate decomposes between 270°C and 420°C to give nickel oxide. The overall reaction is therefore as follows :

TABLE I

Analysis of Basic Nickel Carbonates *Heated* to 230°C for one hour

System from which the Basic Carbonate was precipitated	Wt. of decomposed sample (g)	Found by analysis			Ratio by weight		
		NiO (g)	CO_2 (g)	H_2O (g)	NiO :	CO_2 :	H_2O
I. *Initial Composition*: $2NiO.CO_2.5H_2O$							
(*a*) $NiCl_2 - Na_2CO_3$	0.2476	0.1746	0.0514	0.0210	3.40 :	1.00 :	0.41
(*b*) $NiSO_4 - K_2CO_3$	0.2370	0.1669	0.0491	0.0207	3.40 :	1.00 :	0.42
(*c*) $Ni(NO_3)_2 - NaCO_3$	0.1784	0.1250	0.0369	0.0160	3.39 :	1.00 :	0.43
II. *Initial Composition*: $2NiO.CO_2.3H_2O$							
(*a*) $NiSO_4 - Na_2CO_3$	0.2385	0.1702	0.0486	0.0199	3.50 :	1.00 :	0.41
(*b*) $NiSO_4 - K_2CO_3$	0.1802	0.1264	0.0376	0.0171	3.37 :	1.00 :	0.46
Theoretical Ratio corresponding to $2NiO.CO_2.H_2O$ =					3.39 :	1.00 :	0.41
III. *Initial Composition*: $3NiO.CO_2.6H_2O$							
(*a*) $NiSO_4 - Na_2CO_3$	0.3376	0.2485	0.0486	0.0399	5.11 :	1.00 :	0.82
(*b*) $NiSO_4 - K_2CO_3$	0.3608	0.2654	0.0523	0.0426	5.08 :	1.00 :	0.81
(*c*) $NiCl_2 - Na_2CO_3$	0.2163	0.1591	0.0314	0.0253	5.07 :	1.00 :	0.81
(*d*) $Ni(NO_3)_2 - K_2CO_3$	0.2410	0.1770	0.0349	0.0287	5.07 :	1.00 :	0.82
Theoretical Ratio corresponding to $3NiO.CO_2.2H_2O$ =					5.09 :	1.00 :	0.82
IV. *Initial Composition*: $4NiO.CO_2.7H_2O$							
(*a*) $NiSO_4 - Na_2CO_3$	0.2926	0.2202	0.0324	0.0398	6.80 :	1.00 :	1.23
(*b*) $Ni(NO_3)_2 - K_2CO_3$	0.2596	0.1952	0.0287	0.0351	6.80 :	1.00 :	1.22
(*c*) $NiCl_2 - K_2CO_3$	0.2439	0.130	0.0269	0.0330	6.80 :	1.00 :	1.23

V.	*Initial Composition* : $4NiO.CO_2.5H_2O$							
	$NiSO_4 - Na_2CO_3$ ……	0.2610	0.1964	0.0290	0.0359	6.77 :	1.00 :	1.24
	Theoretical Ratio corresponding to $4NiO.CO_2.3H_2O$ =					6.78 :	1.00 :	1.23
VI.	*Initial Composition* : $14NiO.CO_2.16H_2O$							
	(*a*) $NiSO_4 - Na_2CO_3$ ……	0.1310	0.1050	0.0051	0.0204	20.60 :	1.00 :	3.99
	(*b*) $NiCl_2 - Na_2CO_3$ ……	0.1964	0.1568	0.0079	0.0298	19.85 :	1.00 :	3.77
	Theoretical Ratio corresponding to $14NiO.CO_2.11H_2O$ =					23.75 :	1.00 :	4.50
VII.	*Initial Composition* : $16NiO.CO_2.14H_2O$							
	$NiSO_4 - Na_2CO_3$ ……	0.2100	0.1791	0.0068	0.0241	26.34 :	1.00 :	3.55
	Theoretical Ratio corresponding to $16NiO.CO_2.9H_2O$ =					27.14 ;	1.00 :	3.68
VIII.	*Initial Composition* : $17NiO.CO_2.21H_2O$							
	$NiSO_4 - Na_2CO_3$ ……	0.1608	0.1278	0.0045	0.0273	28.40 :	1.00 :	6.06
	Theoretical Ratio corresponding to $17NiO.CO_2.15H_2O$ =					28.84 :	1.00 :	6.14
IX.	*Initial Composition* : $22NiO.CO_2 18H_2O$							
	$NiSO_4 - K_2CO_3$ ……	0.2710	0.2471	0.0065	0.0022	38.02 :	1.00 :	4.96
	Theoretical Ratio corresponding to $22NiO : CO_2 : 12H_2O$ =					37.33 :	1.00 :	4.91

$$2NiO{\cdot}CO_2{\cdot}5H_2O \xrightarrow[100-200^\circ C]{-4H_2O} 2NiO{\cdot}CO_2{\cdot}H_2O \xrightarrow[270-420^\circ C]{-(H_2O+CO_2)} 2NiO$$

The corresponding losses in weight should be 25.42 per cent of the initial weight at the completion of the first stage of decomposition and 47.21 per cent at the end of the second stage. The thermogravimetric curve [Fig. I Curve A] shows that the first plateaux corresponds to a loss in weight of 25.5 per cent and the total loss in weight at 450°C is 47.5 per cent. The thermogravimetric results therefore agree with the analytical results at each stage.

The basic carbonates containing higher percentage of water could be dried over phosphorus pentoxide in vacuum. The samples obtained by these methods approach a definite composition containing less of water. Thus, the basic carbonate, $2NiO{\cdot}CO_2{\cdot}5H_2O$ loses 2 molecules of water on drying in this manner and approaches the composition $2NiO.CO_2\text{-}3H_2O$. The thermogravimetry of this compound [Fig. I, Curve B] indicates two stages of decomposition corresponding to the loss of 14.7 per cent and 39.75 per cent of the initial weight respectively. Analysis of the intermediate product shows it to be the same compound as obtained earlier, *viz.*, $2NiO.CO_2.H_2O$. The thermal decomposition should therefore take place as follows:

$$2NiO.CO_2.3H_2O \xrightarrow[100-200^\circ C]{-2H_2O} 2NiO.CO_2.H_2O \xrightarrow[270-420^\circ C]{-(CO_2+H_2O)} 2NiO$$

The corresponding losses in weight being 14.56 per cent and 39.63 per cent respectively of the initial weight in close agreement with the experimental results.

From the thermal decomposition of other basic nickel carbonates other intermediate compounds could be similarly characterised. Thus analysis shows that the pyrolysis of the basic nickel carbonate $3NiO.CO_2.6H_2O$ is as follows:

$$3NiO.CO_2.6H_2O \xrightarrow[(80-200^\circ C)]{-4H_2O} 3NiO.CO_2.2H_2O \xrightarrow[(270-380^\circ C)]{-(CO_2+2H_2O)} 3NiO$$

The corresponding losses in weight should be 19.15 per cent and 40.43 per cent of the initial weight respectively. From thermogravimetry [Fig. 1, Curve C] the losses in weight obtained for the first and second stages of decomposition are 19 per cent and 39 per cent respectively in agreement with the expected values.

The basic nickel carbonate, $4NiO.CO_2.7H_2O$, decomposes on heating and from the analysis of the intermediate and final products of decomposition, the process should be as follows:

$$4NiO.CO_2.7H_2O \xrightarrow[(90^\circ-200^\circ C)]{-4H_2O} 4NiO.CO_2.3H_2O \xrightarrow[(260-400^\circ C)]{-(CO_2+3H_2O)} 4NiO$$

The corresponding losses in weight should be 15.37 and 36.29 per cent of the initial weight respectively. From the thermogravimetric curves [Fig. II, Curve A] the losses in weight obtained were 15 and 36 per cent of the original weight respectively. For the sample dried over phosphorus pentoxide in vacuum the thermal decomposition is similar and gives rise to the same intermediate basic carbonate as follows:

$$4NiO.CO_2.5H_2O \xrightarrow[(90-200^\circ C)]{-2H_2O} 4NiO.CO_33H_2O \xrightarrow[(260^\circ-400^\circ C)]{-(CO_2+3H_2O)} 4NiO$$

The corresponding losses in weight are theoretically 8.32 per cent and 30.97 per cent of the initial weight. The actual losses in weight obtained were 9 per cent and 31.5 per cent respectively as determined from the pyrolysis curve [Fig. II, Curve B].

The composition of the precipitated basic carbonate obtained at 97°C from an equimolar mixture is $14NiO.CO_2.16H_2O$ when washed with cold water and $16NiO.CO_2.14H_2O$ when washed with hot water. When, at 97°C the amount of alkali carbonate added is thrice that of the nickel salt, the precipitate obtained has the composition $17NiO.CO_2.21H_2O$ when washed with cold water and $22NiO.CO_2.18H_2O$ when washed with hot water. In all cases, there are two stages of decomposition as shown in Fig. III. In the first stage of decomposition, only water is lost between 90°C and 180°C. In the second stage of the decomposition, between 260°C and 420°C the rest of the unit breaks down to nickel oxide. The reactions as determined by the analysis of the products at the end of the first and second stages of decomposition are given below. The corresponding theoretical and experimental weights are also indicated in terms of the percentage of the initial weight. As mentioned earlier[1] these compositions are not strictly exact:

Curve (A)	$14NiO.CO_2.16H_2O \longrightarrow$	$14NiO.CO_2.11H_2O \longrightarrow$	$14NiO$
	Theoretical weight 100%	93.48%	75.93%
	From thermogravimetry 100%	93.5 %	76%
Curve (C)	$17NiO.CO_2.21H_2O \longrightarrow$	$17NiO.CO_2.15H_2O \longrightarrow$	$17NiO$
	Theoretical weight 100%	93.63%	75.06%
	From thermogravimetry 100%	93.8%	76%
Curve (B)	$16NiO.CO_2.14H_2O \longrightarrow$	$16NiO.CO_2.9H_2O \longrightarrow$	$16NiO$
	Theoretical weight 100%	93.96%	80.13%
	From thermogravimetry 100%	94%	81%
Curve (D)	$22NiO.CO_218H_2O \longrightarrow$	$22NiO.CO_2.12H_2O \longrightarrow$	$22NiO$
	Theoretical weight 100%	94.64%	81.70%
	From thermogravimetry 100%	95%	82.5 %

The results indicate clearly that in all these compounds water is bound in two different ways and that part of the water and all the carbon dioxide are constituents of the skeleton of the units which form the basic nickel carbonates.

In recent studies conducted by Francois-Rossetti and co-workers[4, 5, 6] several basic nickel carbonates have been distinguished by X-ray methods and studied employing thermogravimetry and differential thermal analysis. The compounds $Ni(OH)_2.NiCO_3$ and $2Ni(OH)_2.NiCO_3$ mentioned by them are shown in the present work to be the products of decomposition of $2NiO.CO_2.5H_2O$ and $3NiO.CO_2.6H_2O$, respectively. In the present work the basic nickel carbonate $4NiO{\cdot}CO_2.7H_2O$ and its dehydration products $4NiO.CO_2.3H_2O$ have also been characterised.

The results are explained in greater detail in a later paper[7] and a mechanism for the formation of the basic nickel carbonates has been put forward on the basis of the configurations and thermal behaviour of these compounds.

ACKNOWLEDGMENT

The authors are grateful to Prof. K. R. Krishnaswami and to Prof. M. R. A. Rao for their keen interest in the present work.

REFERENCES

1. Mallya, R. M. and Vasudeva Murthy, A. R. *J. Indian Inst. Sci.*, 1961, **43**, 87.
2. Vasudeva Murthy, A. R., Bharadwaj, D. S. and Mallya, R. M. *Chem. and Ind.* 1956, **16**, 300.
3. Duval, C. "Inorganic Thermogravimetric Analysis", (Amsterdam : Elsevier Publishing Co.). 1953, 13-30, 31-43.
4. Francois-Rossetti, J. and Imelik, B. *J. Chim. Phys.*, 1954, **51**, 451-60.
5. ———— *Bull. Soc. Chim. France*, 1957, 1115.
6. Francois-Rossetti, J., Charton, M. T. and Imelik, B. *Ibid*, 1957, 614-15.
7. Mallya, R. M. and Vasudeva Murthy, A. R. *J. Indian Inst. Sci.* 1961, **43**, 148.