STUDIES ON THE BASIC CARBONATES OF NICKEL

Part VI: Thermal Decomposition of Basic Nickel Carbonates in Vacuum and the nature of the surfaces

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ABSTRACT

Various samples of basic nickel carbonates were subjected to thermal decomposition in vacuum at different temperatures. These carbonates were found to decompose when heated beyond 250°C. The amount of carbondioxide liberated at each temperature was measured. The results obtained were correlated with those obtained from other thermal studies and analysis.

The surface areas of the various basic nickel carbonates and of their products of decomposition were measured by following the adsorption of nitrogen and argon on them at $-191°C$ and applying the B. E. T. equation as well as the method of Harkins and Jura. A marked increase in the surface area was observed when the precipitate was allowed to age in contact with the mother liquor prior to drying it.

INTRODUCTION

In earlier communications[1,2] it was shown by thermogravimetric and differential thermal analytical studies that the thermal decomposition of the several basic nickel carbonates in air takes place in two stages. Since these compounds release water and carbondioxide on heating, the decomposition stages of the compounds had to be characterized by analysis of the residues. It was of interest to study the decomposition of basic nickel carbonates under vacuum conditions and also to follow the changes in surface areas associated with the decomposition processes.

By employing a volumetric gas adsorption cum decomposition unit the gases evolved during decomposition have been collected and measured at various temperatures. The structural changes accompanying these transformations would alter the surface area of the solid. The changes in surface area have been followed by measuring the adsorption of nitrogen and argon at $-191°C$ and applying the B.E.T. equation and the Harkins and Jura method. The surface areas of several samples of basic nickel carbonates prepared under different experimental conditions as specified earlier[1], have been measured in the present investigation.

EXPERIMENTAL

Apparatus: The experimental set up consists of the following components: the decomposition tube, manometric section, gas measuring burette, Topler

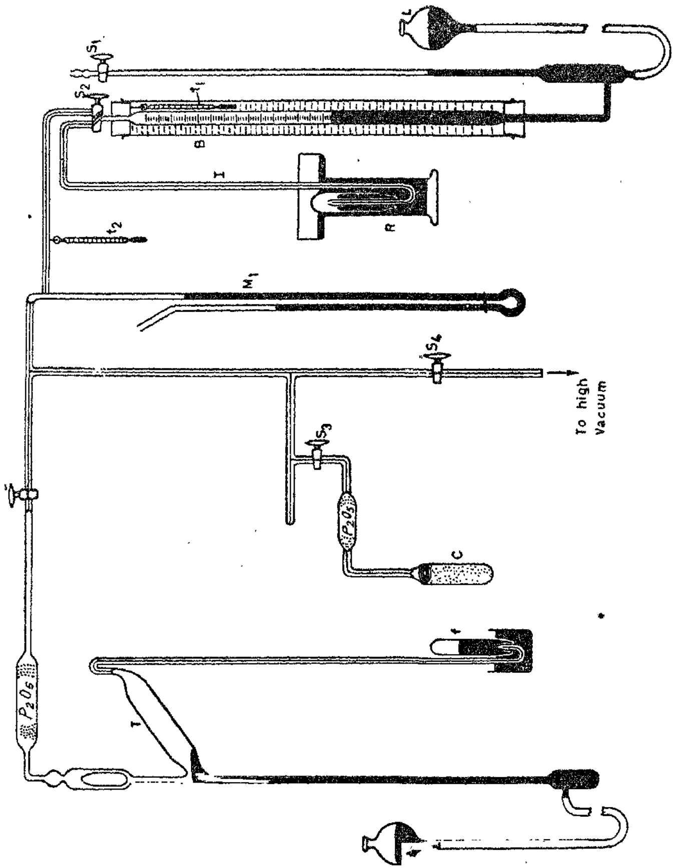

FIG. I

Apparatus for studies on thermal decompositions in vacuum pump and an evacuation unit. A diagrammatic sketch of the apparatus is shown in Fig. 1.

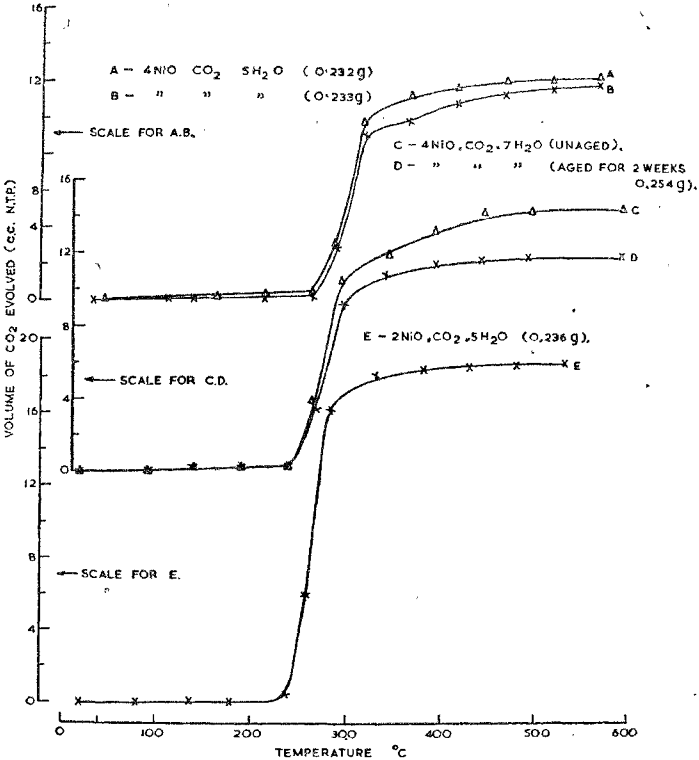

FIG. II

Thermal decomposition of basic nickel carbonates in vacuum

Theoretical CO_2 content

A	12.00 (Gas toplered out)
B	12.06 (Gas measured monometrically)
C	14.72
D	12.13
E	18.65

The decomposition tube, C containing a known weight of the sample was connected to the assembly *via.* a phosphorus pentoxide tube and stop-cock, S_3. The manometric space was evacuated through S_4 by means of a mercury diffusion pump connected to a cenco hyvac pump. The sample was decomposed by surrounding C with a tubular electrical furnace maintained at the required temperature within $\pm 1^\circ$C. The gas evolved and dried over phosphorus pentoxide was removed through S_5 by means of the Topler pump and collected in a thumb tube. The gas was transferred into the burette *B*, through the intake tube I. The burette being surrounded by the water jacket is always at a constant temperature measured by the thermometer t_1. When the gas had attained the temperature of the burette and enclosure, the mercury levels were equalised and the volume of the gas measured accurately to 0.005 c.c. by employing a travelling microscope with a scale micrometer eye piece.

The thermal decomposition of the substance could be followed either manometrically or volumetrically employing the Topler pump and analysing the gas suitably. The same apparatus could also be adopted for measuring the surface area[3].

The dead space of the different parts of the apparatus were determined at laboratory temperature and the volume of the gas evolved or absorbed could be obtained directly.

RESULTS

Vacuum Decomposition Studies: The following samples were subjected to decomposition at several temperatures upto 550°C and the results are presented graphically.

(1) $4NiO.CO_2.5H_2O$	(A) & (B)
(2) $4NiO.CO_2.7H_2O$	(C) unaged
(3) $4NiO.CO_2.7H_2O$	(D) aged for 2 weeks.
(4) $2NiO.CO_2.5H_2O$	(E) unaged

The volume of carbondioxide evolved at different temperatures have been plotted in the graphs as shown in Fig 2. The different stages of decomposition were followed by maintaining the sample at different temperatures till there was no further evolution of gas at that temperature. After collecting the gas by means of the Topler pump and measuring its volume, the sample was raised to the next higher temperature.

It is seen from curve A, Fig. 2 that the results obtained by collecting the gas using the Topler pump and by the manometric method are very close. However in the latter, the volume of carbon dioxide measured was slightly less (Curve B) when the gas was measured manometrically, the sample portion C had to be cooled back to laboratory temperature prior to taking measurements. It is generally known that metallic carbonates decompose at higher temperatures to give carbondioxide and the metal oxides, which take up the gas on cooling to slightly lower temperatures to reform the carbonate. It is therefore likely that the carbondioxide liberated reacts with the solid to form the carbonate again. The results with the unaged and aged samples of $4NiO.CO_2.7H_2O$ (Curve C and D) and the unaged sample $2NiO.CO_2.5H_2O$ (Curve E) are similar as seen from the corresponding decomposition curves.

It is seen that in all the cases the evolution of gas is negligibly small below 200°C. At 250°C, however, there is slight evolution of gas corresponding to about 1% of the theoretical carbondioxide content. There is rapid evolution of carbondioxide between 275° and 300°C. At 300°C, nearly 85 to 90 per cent of the carbondioxide content of the solid has been evolved. At 400°C, only 2 per cent of the carbonate still remains undecomposed. The carbondioxide evolved between 500° to 550°C corresponds to the theoretical carbondioxide contents of the basic carbonates. The residue, when analysed was found to be nickel oxide, NiO, in all the cases.

Even though the various basic carbonates differ in their carbondioxide and water contents yet their mode of decomposition seems to be practically the same. Only water is evolved at temperatures below 250°C and there is hardly any perceptible decomposition of the carbonate. This is in agreement with analytical results, that the first stage of decomposition noticed from differential thermal analysis and thermogravimetric studies correspond to the loss of part of the water content of the precipitates. The major portion of the carbondioxide is given off between 275 and 300°C and the last portions of carbondioxide are eliminated only at higher temperatures. These results are also in agreement with the conclusious drawn from differential thermal analysis[1] and thermogravimetry[2] corresponding to the second stage of decomposition.

Surface Areas of basic Carbonates: Even though the chemical composition of these basic carbonates differ, their modes of decomposition are more or less similar as seen earlier. However, it has been shown already that the physical properties of the wet precipitates such as surface area are not identical as is evident from the different amounts of dye adsorbed on these solids[4]. Similar measurements of surface areas by gas adsorption on the different samples revealed that there is considerable difference in the surface areas of the samples prepared under different experimental conditions.

Known volumes of pure and dry argon and nitrogen were introduced into the adsorption unit and the amount of gas adsorbed by the sample cooled to the temperature of boiling liquid air or liquid oxygen was measured. From these values the B.E.T. plots and the Harkins and Jura plots corresponding to different samples were drawn. From the slopes of these plots, the monolayer volumes and hence the surface areas of the solids were calculated by standard methods. The Table I gives the results obtained.

It is seen that 1 g. of the unaged basic nickel carbonate $4NiO.CO_2.7H_2O$ has a surface area of 39.8 m^2. After decomposition at 250°C the solid product, *viz.* $4NiO.CO_2.3H_2O$ has a surface area of 104.0 m^2 which is nearly two and a half

TABLE I

Changes in Surface Area on Decomposing One Gram of Basic Nickel Carbonate.

Sample	Surface area in Square metres		
	Initial	At the end of 1st stage of Decompn. (250°C)	At the end of 2nd stage of decompn. (500°C)
1. $4NiO.CO_2.7H_2O$ (unaged)	39.8	104.0	38.8
2. $4NiO.CO_2.7H_2O$ (aged for 2 Weeks)	152.3	116.4	60.7
3. $4NiO.CO_2.7H_2O$ (prepared from dil. soln.)	1.71	......	......
4. $17NiO.CO_2.21H_2O$	65.5	75.0	84.9

times greater. The nickel oxide obtained from this sample by decomposition at 500°C has a surface area of 38.8 m^2, which is nearly that of the original sample. When the same basic nickel carbonate of composition $4NiO.CO_2.7H_2O$ had been prepared after ageing it with the mother liquor for two weeks prior to drying, the surface area of the sample increases four-fold. Thus 1 g. of this sample has a surface area of 152.3 m^2. At the end of the first stage of decomposition the surface area of the sample changed to 116.4 m^2 and at the end of the second stage it was 60.7 m^2. When the same basic carbonate was prepared from very dilute solutions *viz.*, 0.025N solutions, the surface area was reduced considerably to 1.71 m^2/g.

When the samples of basic nickel carbonates prepared at 97°C were studied relatively small changes in surface area were noticed. Thus 1 g. of the basic carbonate of composition $17NiO.CO_2.21H_2O$ had a surface area of 65.5 m^2. On decomposition at 250°C, this changed to 75.0 m^2. When the sample was decomposed further at 500°C to nickel oxide, the surface area increased to 84.9 m^2. Large surface areas of basic nickel carbonates have been noticed also by Francois-Rossetti and coworkers[5,6,7].

The changes in surface areas accompanying the processes of ageing and of decomposition of the basic nickel carbonates are to be explained on the basis of the structural changes associated with such processes. The very large surface areas of these samples of basic carbonates imply the formation of a complex network incorporating a large number of crevices and capillaries in the samples and their decomposition products. The results are discussed in the following paper[8].

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