STUDIES ON THE BASIC CARBONATES OF NICKEL

Part IV: Preparation of Basic Nickel Carbonates and their Differential Thermal Analysis

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ABSTRACT

Several samples of basic nickel carbonates were prepared under different experimental conditions obtained by varying the ratio of reactants, temperature, mode of precipitation and period of ageing Three basic nickel carbonates of composition $2NiO.CO_2 5H_2O$; $3NiO.CO_2.6H_2O$ and $4NiO.CO_2.7H_2O$ were prepared at 25°C by drying precipitates over anhydrous calcium chloride and two others of composition $2NiO.CO_2.3H_2O$ and $4NiO.CO_2.5H_2O$ by drying these samples further in vacuo over phosphorus pentoxide A few samples of basic carbonates obtained at 97°C from boiling solutions had very small carbonate contents. Differential thermal analysis of some of these samples showed that two endothermic reactions take place on heating the samples at a uniform rate up to 600°C.

INTRODUCTION

It has been reported earlier[1] that three basic nickel carbonates of compositions (in the wet conditions) corresponding to $2NiO:CO_2$, $3NiO:CO_2$ and $4NiO:CO_2$ are formed at 25°C when solutions of alkali carbonates and nickel salts are mixed in different proportions. These carbonates are thrown out from solution as very gelatinous precipitates associated with a large amount of water. Since these basic carbonates are intermediates in the preparation of active nickel catalysts it is of considerable interest to characterise the physical and chemical natures of these precipitates and their decomposition products.

Several samples of basic nickel carbonates were prepared at 25°C and at 97°C under varying conditions of precipitation and their compositions determined by analysis. Their thermal behaviour was examined by subjecting some of the samples to differential thermal analysis.

EXPERIMENTAL

Reagent used:—Exactly 0.05 molar solutions of nickel sulphate, chloride and nitrate and decinormal sodium and potassium carbonates were prepared and standardised as described earlier.[2]

Preparation of the Basic Carbonates:—The precipitations at 25°C were conducted in a five litre pyrex beaker kept in a large water thermostat. To one litre of 0.05 molar nickel salt solution taken in the beaker, the requisite amount of decinormal alkali carbonate solution corresponding to a definite molar ratio was added at a fast dropwise rate from a dropping funnel. The solution was stirred mechanically during the addition of the reagent to ensure homogenous dispersion of the reactants. Otherwise it is not possible to get a precipitate of uniform composition under the heterogeneous conditions which prevail.[1] Immediately after the addition of the alkali carbonate was complete, the precipitate was transferred on to a Buchner funnel to drain off the mother liquor under suction. The precipitate was transferred back to the beaker and dispersed into four litres of distilled water by mechanical stirring. The solution was allowed to stand and the supernatant liquid was drained off. The process was repeated six times and the precipitate finally transferred on to a large dish kept in a desiccator through which carbondioxide-free air, dried over anhydrous calcium chloride was passed. The wet precipitate (105 *gms.*) was dried in this manner for nearly six weeks in which time it lost its water gradually to the extent of about 95% of its initial weight (final weight = 5.3 *gms*). The precipitate, which was dark green in colour when dried, was powdered in an agate mortar and transferred to a small petry dish. The process of drying was continued in the same way till constant weight was obtained. The basic nickel carbonate was stored in a weighing bottle and preserved in a desiccator over anhydrous calcium chloride. The powdered basic carbonate of nickel was light green in colour and free flowing.

Some samples of nickel carbonate were precipitated at 97°C. A calculated quantity of alkali carbonate solution was run from a dropping funnel into a boiling solution of 0.05 molar nickel salt solution. The contents were stirred thoroughly during the addition. The temperature of the solution during the addition was found to be $97^\circ \pm 1^\circ$C. Immediately after the addition was complete, the solution was transferred into a Buchner funnel and filtered under suction. The precipitate was freed from ions by washing it with cold distilled water in some cases and in others by washing with hot distilled water. The precipitate was then transferred to a dish and dried in air over anhydrous calcium chloride as in the previous set of experiments. The precipitates were formed as greenish white brittle flakes.

Analysis of the dry precipitates:—The various samples of dry basic nickel carbonates were analysed for their water, carbondioxide and nickel oxide contents gravimetrically. A weighed amount of the sample contained in a porcelain boat was kept in a horizontal hard glass combustion tube and heated to 500°C at a slow rate in a tubular electric furnace. The gases evolved were swept by a current of pure and dry (freed from carbondioxide and water by bubbling through caustic potash and concentrated sulphuric acid) nitrogen into a series of three clean, weighed U-tubes. The first contained anhydrous magnesium perchlorate to absorb water and the second ascarite for absorption of carbondioxide. The third U-tube again contained anhydrous magnesium perchlorate to absorb any water given off by ascarite.[3] The gas was then passed through a guard U-tube containing anhydrous calcium chloride and through a bubbler containing barium hydroxide solution. This served to indicate that the absorption of carbondioxide was complete. When the sample had been heated up to 500°C, the furnace was switched off and the current of nitrogen was continued for half an hour more. The assembly was then disconnected. The porcelain boat and the U-tubes were transferred to a desiccator and weighed. The increase in weight of the first U-tube gives the amount of water absorbed and that of the second and third U-tubes the net amount of carbondioxide absorbed. The necessary blank corrections were made and a special method of weighing the U-tubes was employed as described below. The residue in the boat was nickel oxide and its nickel content was confirmed by dissolving the residue in dilute (1 : 1) hydrochloric acid and determining the nickel content gravimetrically by the dimethylglyoxine method. The results were expressed to give the composition of the precipitates in terms of the nickel oxide, carbon dioxide and water contents.

Procedure adopted for weighing the U-tubes :—Considerable difficulty was experienced initially in the determination of the exact weights of the U-tubes with contentents. Depending upon the atmospheric conditions and the interval of time for which the U-tubes were exposed to laboratory conditions, differences in the weights of the U-tubes were recorded even when counterpoised suitably. These differences could not be adequately accounted for by applying corrections for the temperature changes and buoyancy effects. After a number of attempts to standardise the weighing process, it was concluded that the difference observed was chiefly due to the different weights of the film of water adsorbed at the glass surface. It was therefore necessary to subject the U-tubes to the same uniform treatment prior to each weighing. Such a a treatment was given in a satisfactory manner as follows. A piece of muslin was washed with water and then squeezed to remove all droplets of water from it. Before weighing the U-tube each time, it was first wiped with this moist muslin and then immediately with a dry piece of muslin. The U-tube was then suspended in the balance pan for exactly 15 minutes and then weighed. In this manner the weighings could be reproduced to ± 0.0001 *g*.

Blank correction :—In order to apply corrections for the moisture and carbon dioxide adsorbed within the apparatus and which are liberated during the experiments, blank experiments were run in exactly the same manner as described above, but with an empty porcelain boat. There were slight increases in the weights of the first and second U-tubes but none in the third. The mean amounts of water and carbondioxide absorbed in the U-tubes during any determination were 1.9 *mg*. and 0.1 *mg*. respectively. The corresponding corrections were therefore applied to each experimental result.

The procedure described above was applied to the determination of water and/or carbondioxide in standards like sodium bicarbonate, magnesium sulphate heptahydrate and magnesium carbonate. When the necessary blank corrections were applied, the results were in close agreement (within 0.4 per cent) with the theoretical values.

RESULTS

The analysis of the various samples of basic nickel carbonates prepared at molar ratios of reactants alkali carbonate/nickel salt = 1.0, 1.5 and 3.0 under different conditions at 25°C and 97°C are presented in Tables I and II respectively.

TABLE I

Analysis of Basic Nickel carbonates obtained at 25°C

System	Amt. of ppt. taken (*g*)	Amount Found (*g*)			Ratio by weight
		NiO	CO_2	H_2O	$NiO : CO_2 : H_2O$
A. Reagent Ratio M_2CO_3/Ni salt = 1.0					
[I] Unaged Ppt. Dried over anhydrous $CaCl_2$					
(*a*) $NiSO_4 - Na_2CO_3$	0.1678	0.0884	0.0261	0.0532	3.39 : 1.00 : 2.04
(*b*) $Ni(NO_3)_2 - Na_2CO_3$	0.1594	0.0840	0.0247	0.0505	3.40 : 1.00 : 2.04
(*c*) $NiCl_2 - Na_2CO_3$	0.0610	0.0320	0.0094	0.0192	3 41 : 1.00 : 2.03
(*d*) $NiSO_4 - K_2CO_3$	0.0956	0.0508	0.0147	0.0302	3.43 : 1.00 : 2.06
	Compn. $2NiO \cdot CO_2 \cdot 5H_2O$ corresponds to				3.394 : 1 00 : 2.046
[II] Unaged ppt. dried in vacuo over P_2O_5					
(*a*) $NiSO_4 - Na_2CO_3$	0.0888	0.0526	0.0161	0.0199	3.41 : 1.00 : 1.23
(*b*) $NiSO_4 - K_2CO_3$	0.0734	0.0439	0.0132	0.0162	3.40 : 1.00 : 1.22
	The composition $2NiO \cdot CO_2 \cdot 3H_2O$ corresponds to				3.394 : 1.00 : 1.228
[III] Precipitate aged for 4 hours with agitation dried over anhydrous $CaCl_2$					
(*a*) $NiSO_4 - Na_2CO_3$	0.8075	0.0640	0.0126	0.0309	5.08 : 1.00 : 2.45
(*b*) $NiCl_2 - Na_2CO_3$	0.1258	0.0748	0.0147	0.0361	5.09 : 1.00 : 2.46
(*c*) $Ni(SO_4)_2 - K_2CO_3$	0.1685	0.0998	0.0196	0.0486	5.09 : 1.00 : 2.48
B. Reagent ratio M_2CO_3/Ni Salt = 1.50 (1 hour's agitation) ppt. dried over anhydrous $CaCl_2$					
(*a*) $NiSO_4 - Na_2CO_3$	0.1018	0.0601	0.0118	0.0291	5.09 : 1.00 : 2.47
(*b*) $NiCl_2 - Na_2CO_3$	0.1066	0.0634	0.0124	0.0305	5.19 : 1.00 : 2.46
(*c*) $Ni(NO_3)_2 - K_2CO_3$	0.1420	0.0925	0.0144	0.0350	5.10 : 1.00 : 2.43
	The composition $3NiO \cdot CO_2 \cdot 6H_2O$ corresponds to				5.091 : 1.00 : 2.456

Table I—(*Contd.*)

System	Amt. of ppt. taken (g)	Amount Found (g)			Ratio by Weight
		NiO	CO_2	H_2O	NiO : CO_2 : H_2O
C. Reagent ratio M_2CO_3/Nt salt = 3.0					
[I] Unaged ppt. dried over $CaCl_2$					
(*a*) $NiSO_4 - Na_2CO_3$	0.1364	0.0869	0.0128	0.0365	6.79 : 1.00 : 2.85
(*b*) $Ni(NO_3)_2 - Na_2CO_3$	0.1664	0.1251	0.0184	0.0528	6.81 : 1.00 : 2.87
(*c*) $NiCl_2 - Na_2CO_3$	0.1173	0.0748	0.0110	0.0315	6.80 : 1.00 : 2.85
(*d*) $NiSO_4 - K_2CO_3$	0.1834	0.1169	0.0172	0.0492	6.79 : 1.00 : 2.86
(*e*) $Ni(NO_3)_2 - K_2CO_3$	0.1321	0.0835	0.0123	0.0353	6.79 : 1.00 : 2.87
(*f*) $NiCl_2 - K_2CO_3$	0.1710	0.1096	0.0161	0.0461	6.81 : 1.00 : 2.87
[II] Precipitate aged for 10 days dried over $CaCl_2$					
(*a*) $NiSO_4$-Na_2CO_3	0.1216	0.0773	0.0114	0.0327	6.78 : 1.00 : 2.87
(*b*) $NiCl_2$-Na_2CO_3	0.1090	0.0694	0.0102	0.0291	6.80 : 1.00 : 2.85
The composition $4NiO.CO_2.7H_2O$ corresponds to					6.787 : 1.00 : 2.865
[III] Precipitate dried in Vacuum over P_2O_5					
(*a*) $NiSO_4$-Na_2CO_3	0.1264	0.0872	0.0129	0.0262	6.76 : 1.00 : 2.03
(*b*) $NiCl_2$-Na_2CO_3	0.1048	0.0723	0.0107	0.0217	6.76 : 1.00 : 2.03
The composition $4NiO\cdot CO_2\cdot 5H_2O$ corresponds to					6.787 : 1.00 : 2.046

The precipitate obtained when a nickel salt solution is treated with an equivalent amount of alkali carbonate solution at 25°C has a composition $2NiO.CO_2.5H_2O$ when dried in air over anhydrous calcium chloride. It is immaterial whether a chloride, nitrate or sulphate salt of nickel is used for the purpose of precipitation. If this same precipitate is subjected to further desiccation in vacuum over phosphorus pentoxide it loses some of its water content and approaches slowly the composition $2NiO.CO_2.3H_2O$· If the wet precipitate is allowed to remain with the mother liquor for a longer interval (about 4 hours with agitation) the final composition of the aged precipitate, when dried over anhydrous calcium chloride, corresponds to $3NiO\cdot CO_2\cdot 6H_2O$. A precipitate with the same composition can also be obtained if the alkali carbonate added is 1.5 times the molar content of the nickel salt taken. Ageing has no perceptible effect on the composition of this precipitate which is consequently a more stable composition. If the alkali carbonate added is three times the amount

TBALE II

Analysis of basic nickel carbonates prepared at 97°C

System	Amt. of ppt. taken (g)	Amount Found (g)			Ratio by Weight
		NiO	CO_2	H_2O	NiO : CO_2 : H_2O
A. Reagent Ratio M_2CO_3/Ni salt = 1.0					
[I] Precipitate washed with cold water					
(*a*) $NiSO_4$-Na_2CO_3	0.1074	0.0810	0.0034	0.0225	23.82 : 1.00 : 6.62
(*b*) $NiCl_2$-Na_2CO_3	0.1756	0.1331	0.0055	0.0367	24.19 : 1.00 : 6.67
[II] Precipitate washed with hot water					
(*a*) $NiSO_4$-Na_2CO_3	0.1257	0.1005	0.0037	0.0212	27.16 : 1.00 ; 5.73
(*b*) $NiSO_4$-K_2CO_3	0.1384	0.1106	0.0041	0.0236	26.98 : 1.00 : 5.75
B. Reagent Ratio M_2CO_3/Ni salt = 3.0					
[I] Precipitate washed with cold water					
(*a*) $NiSO_4$-Na_2CO_3	0.1458	0.1099	0.0038	0.0321	28.93 : 1.00 : 8.45
(*b*) $NiCl_2$-Na_2CO_3	0.1677	0.1253	0.0042	0.0371	29.84 : 1.00 : 8.84
(*c*) $NiSO_4$-K_2CO_3	0.1193	0.0865	0.0031	0.0243	27.90 : 1.00 ; 7.84
[II] Precipitate washed with hot water					
(*a*) $NiSO_4$-Na_2CO_3	0.0915	0.0748	0.0021	0.0146	35.62 : 1.00 : 6.95
(*b*) $NiSO_4$-K_2CO_3	0.1526	0.1244	0.0034	0.0242	36.60 : 1.00 : 7.12

of nickel salt taken, the composition of the precipitate after drying over anhydrous calcium chloride is found to be $4NiO \cdot CO_2 \cdot 7H_2O$. Ageing and stirring have no influence on the composition of this precipitate. The same composition of the precipitate is obtained at this molar ratio of reactants irrespective of the nickel salt used.

If the precipitation is carried out at 97°C and the reactants are used in equimolar proportions, the carbonate content of the precipitate is very much decreased. The composition of the precipitate when washed with cold water and dried over anhydrous calcium chloride is nearly $14\ NiO.CO_2.16H_2O$. When the precipitate is washed with hot water there is a further decrease in the water and carbondioxide contents of the precipitate. The composition of the precipitate is around $16NiO.CO_2.15H_2O$. Similar observations are made when excess of alkali carbonate is used for precipitation. Considerable variation is observed in the results depending on the manner and extent of washing.

The precipitates obtained from boiling solutions are pale, whitish-green, crystals, which when dried are easily powdered by pressing with a spatula. On the other hand, the precipitates obtained at 25°C are dark green and gelatinous and contract to a hard mass on drying. This can be powdered only in an agate mortar. The precipitates obtained at 97°C settle down very easily and are also easy to wash. However, on washing with cold water, the supernatant layer becomes slightly turbid indicating that the precipitate is broken up into particles of collodial dimensions. This peculiar behaviour exhibited by these basic salts may be explained on the mode of precipitation and its mechanism which are discussed at a later stage in this series.[4] Such an effect, was notobserved when hot water was used for washing.

Differential thermal analysis of the basic nickel carbonate:—The heavy metalic carbonates are relatively unstable at higher temperatures where the corresponding carbonates of the alkali metals are stable. Most of the normal metallic carbonates decompose giving rise to the corresponding oxide and carbon dioxide. The nature of the oxide left behind is of interest since it plays a role in such properties of the oxides as its influence on the course of reactions when it functions as a catalyst. The thermal decomposition of basic nickel carbonates is of great interest since several important nickel catalysts are prepared by decomposition of these basic carbonates and the subsequent reduction of the product. The differential thermal analysis of representative samples of basic nickel carbonate was therefore undertaken.[6, 7]

Apparatus:—The apparatus for differential thermal analysis comprised of a tubular furnace constructed by winding SWG 24 nichrome wire on a silica (or alundum) tube (2.3″ diameter) and lagged with magnesia-asbestos powder. The furnace was mounted vertically. A cylindrical nickel block with two symmetrical parallel holes was used as the specimen holder and mounted suitably on a vertical, movable, refractary support. Two chromel-alumel thermocouples, connected in opposition to each other were fixed, each at the centre of one hole and the terminals were maintained at O°C in a bath of melting ice. The temperature of the furnace was measured by means of a Leeds and Northrup potentiometric unit (No. 248224) standardised against the standard Weston Cadmium Cell. The differential temperature was noted by means of a high-sensitive, D'Arsonval moving coil galvanometer (Leeds and Northrup, sensitivity = 0 0003 $\mu c/mm$) with a lamp and scale arrangement. The furnace was heated at a uniform rate manually with the help of a ' variac '.

Procedure;—One of the holes of the sample block was packed tightly with freshly ignited alumina which served as the inert reference material. The powdered sample of basic nickel carbonate was similarly packed into the other hole. The furnace was heated uniformly at a rate of 12°C per minute and at various intervals the differential shift and the temperature at which it occurs were noted.

Results:—The differential thermal analyses of several samples of basic nickel carbonates of composition $2NiO{\cdot}CO_2{\cdot}5H_2O$ and $4NiO{\cdot}CO_2{\cdot}7H_2O$ prepared as described earlier in this paper, was conducted. The results with some representative samples are shown in Figures I and II.

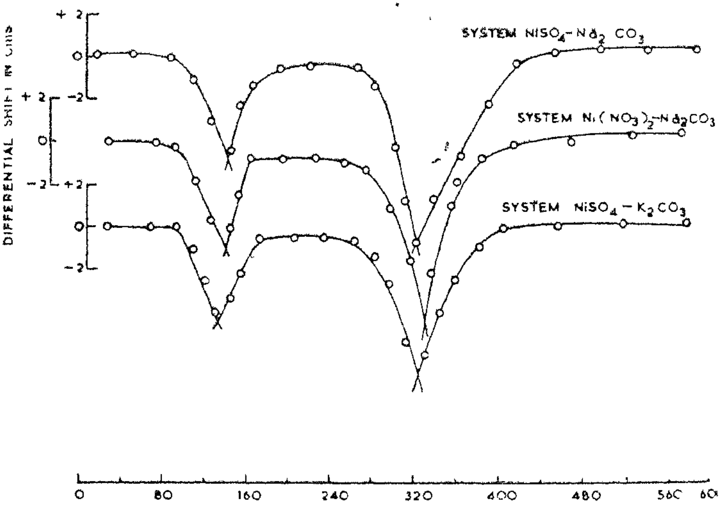

FIG. I

Differential thermal analysis of basic nickel carbonate $2NiO.CO_2.5H_2O$

The results show that the decomposition consists of a two stage process. In the decomposition of both the carbonates, the minima obtained in the differential thermal curves indicate that both the reactions occurring are accompanied by the absorption of energy. The first peak is less endothermic than the second. The peak temperature corresponding to the first decomposition is about 130°C and that of the second is about 320°C. The first endothermic peak corresponds to the expulsion of part of the water and the second to that

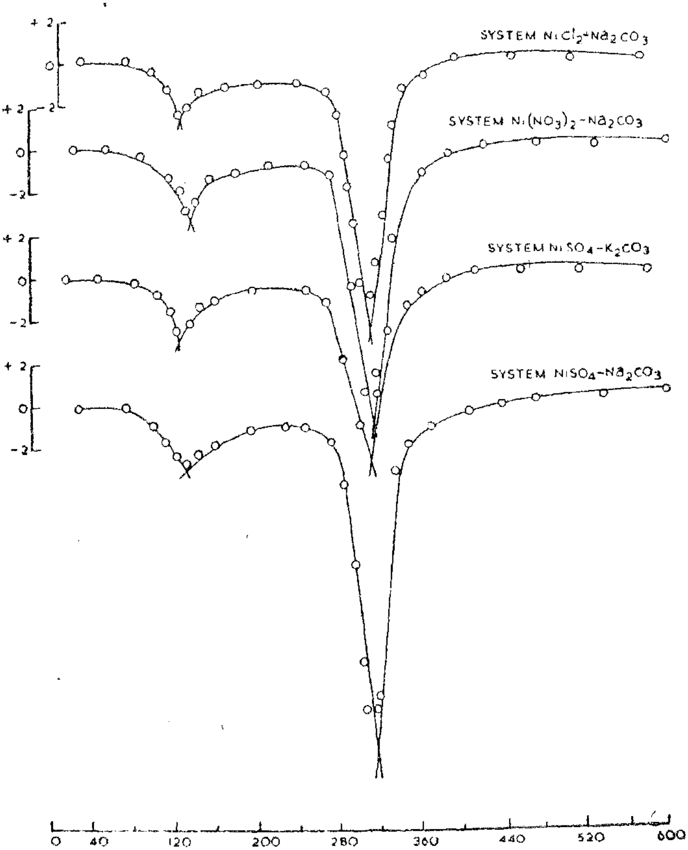

FIG. II

Differential thermal analysis of basic nickel carbonate $4NiO.CO_2.7H_2O$

of the rest of the water content and also of carbondioxide. These observations are supported fully by the results of thermogravimetry and analysis of the products of decomposition at the corresponding stages.[4, 5]

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