STUDIES ON THE BASIC CARBONATES OF NICKEL

Part VII: Formation and Configurations of Basic Nickel Carbonates

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Abstract

A mechanism for the formation of basic nickel carbonates has been given on the basis of the hydrolysis of $[Ni(H_2O)_6]^{++}$ cation and the olation of the resulting species into aggregates of various polynuclear units. The resulting configurations based on coordination number 4 for nickel, are supported by the nature of the water molecules involved, the coordinated water molecules being lost in the first stage of the decomposition and hydroxyl water and carbondioxide during the second stage. At higher temperatures, the *ol* bridges are partly replaced in the precipitates by *oxo* bridges and also by *carbonato* bridges.

Possible methods whereby the different species of basic nickel carbonates form three-dimensional aggregates have been given and evidence for the same obtained from determination of surface areas of the basic carbonates and their decomposition products.

Introduction

In the earlier communications[1-3] it was shown that the compositions of the precipitated nickel carbonates are governed essentially by the conditions of precipitation such as mode of mixing of reactants, temperature, agitation, ageing and pH of the medium. In general, ageing as well as higher pH of the medium favour the formation of more basic precipitates, the process being sometimes facilitated by agitation, when a dilute solution of alkali carbonate is added at 25°C to a solution containing an equimolar quantity of a nickel salt, the precipitate obtained is found to have the initial composition $2NiO.CO_2.5H_2O$, when dried over anhydrous calcium chloride[4]. If this precipitate is aged for 24 hours with its mother liquor prior to drying it, then the precipitate becomes more basic and the composition is found to be $3NiO.CO_2\ 6H_2O$. This basic carbonate is also obtained by the addition of extra alkali carbonate to nickel salt solution so that the pH of the medium is about 9. If the pH of the medium is increased beyond 9.5 by the addition of more of alkali carbonate, the precipitate suffers further hydrolysis, as a result of which the dried sample has the composition $4NiO.CO_2.7H_2O$. These precipitates are usually highly gelatinous in the wet condition and dark green in colour.

The basic character of these precipitates could be enhanced by carrying out the precipitation at elevated temperatures.[4] At these temperatures their nickel oxide content increases while their carbondioxide content decreases.

These basic carbonates were found to decompose in two stages when subjected to thermal treatment in vacuum or in air, as shown by differential thermal analysis[4], thermogravimetry[5] and vacuum decomposition[6]. In the first stage of the decomposition, around 100°C, only a part of the water is lost. In the second stage, which starts at 270°C, both carbondioxide and the rest of the water content are lost. This clearly indicates that for these basic carbonates a part of the water is differently bound in the solid state.

Considerable differences were observed in the surface properties of several samples of basic carbonates of nickel[6]. The surface areas of these samples at different stages of decomposition were measured and compared.

The several different facts regarding the nature of these basic carbonates of nickel as observed in the present investigations, could be explained on the basis of the hydrolysis and subsequent olation of the hexaaquo nickel ion, which has been shown to exist in aqueous nickel salt solutions.[9].

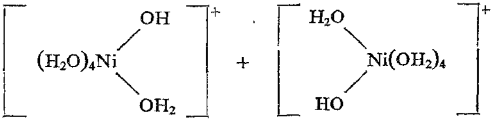
Mechanism for the Formation of Basic Nickel Carbonates: The hydrolysis of the hexa-aquo nickel (I) ion is reported[7,8] to take place through mono-hydroxo (II) and possibly dihydroxo (III) cationic complexes in the following manner:

$$\underset{\text{(I)}}{[\mathrm{Ni(H_2O)_6}]^{++}} \longrightarrow \underset{\text{(II)}}{[\mathrm{Ni(H_2O)_5(OH)}]^{+}} + \mathrm{H}^{+}$$

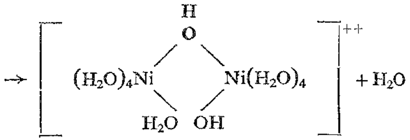
$$\underset{\text{(II)}}{\mathrm{Ni(H_2O)_5(OH)}]^{+}} \longrightarrow \underset{\text{(III)}}{[\mathrm{Ni(H_2O)_4(OH)_2}]} + \mathrm{H}^{+}$$

The formation of these two complexes has been shown to be stepwise and their concentrations depend on the the pH[8]. The higher the pH of the medium, the greater is the tendency towards the formation of the complex (III) which is more basic in character. It was observed during the potentiometric titration of nickel salts with alkali carbonates, that the precipitation of nickel from nickel salt solution takes place initially at constant pH near about the neutral region[3]. In this stage, therefore, the species (II) will be more stable than (III) and the monohydroxo-complex will therefore predominate. This has been found to be the case in the present studies.

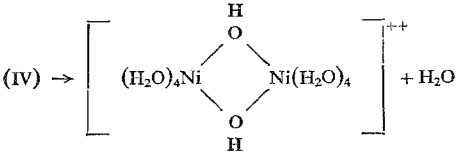
The presence of alkali in the medium favours the process of olation of the species present in solution[10]. The hydroxo units conglomerate *via* bridging *ol* groups into larger units as shown below.



(II) (II)



(IV)

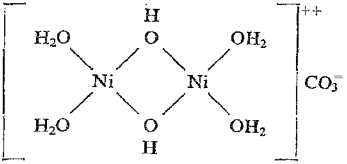


(V)

The nickel atoms in the polynuclear olated complexes may be bridged *via* one *ol* group as in (IV) or through two *ol* bridges as in (V). These aggregates tend to become less soluble as the olation proceeds and therefore precipitate out. Such units will be heavily hydrated and if the process of aggregation involves the formation of two or three dimensional cross-linked networks, they will incorporate a large amount of water within the network and the precipitate will therefore be gelatinous.

The hydroxo-cationic complexes (IV) and (V) are doubly charged and may be associated with different anions to form basic salts. In the present case the anion is the carbonate. The neutralization of carbonic acid formed by hydrolysis of carbonates has tremendous buffering capacity[3] and therefore the carbonate ions present in solution exert a marked influence on the process of precipitation.

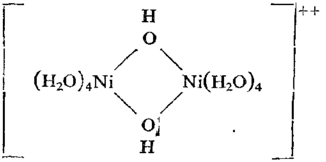
The corresponding carbonates obtained from (IV) and (V) would have the compositions $2NiO\ CO_2.10H_2O$ and $2NiO.CO_2.9H_2O$ respectively. In these complexes, nickel is presumed to have a coordination number six. In several solid compounds nickel is known to exhibit a coordination number four. If, in the basic carbonate formed from the complex (V), nickel were to exhibit a coordination number of four, then each nickel atom in complex (V) may be expected to lose two molecules of water. The resulting carbonate will therefore have the configuration (VI). This corresponds to the composition $2NiO.CO_2.5H_2O$. A basic nickel carbonate of this composition has been prepared in the present work by precipitation from equimolar amounts of nickel salts and alkali carbonates[4].



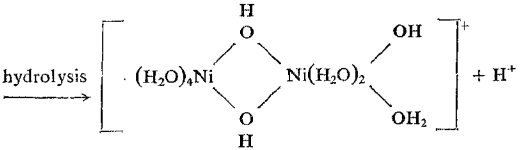
(VI)

The basic nickel carbonate with the composition and configuration (VI) will have four molecules of water coordinated to two nickel atoms. The other molecule of water is in the form of two bridging hydroxyl groups, forming a part of the skeleton of the unit. It is to be expected, therefore, that these two bridging OH groups or the water molecule forming them, would be more firmly bound to the metal atoms than the other four water molecules bound by coordination through weaker ion-dipole interactions. This is clearly seen from the results of thermogravimetric[5] and differential thermal analysis[4]. On heating the basic nickel carbonate $2NiO.CO_2.5H_2O$, four molecules of water are lost easily in the first stage of the decomposition around 100°C. At higher temperatures around 290°C, when the last molecule of water is lost, the species becomes unstable and carbondioxide is also expelled along with the water and nickel oxide is left behind[6].

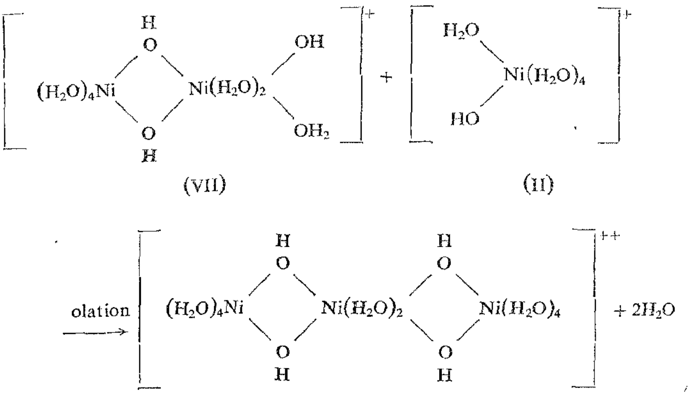
With the progressive addition of alkali carbonate to the medium, the processes of hydrolysis and olation may proceed further than complex (V) to form other polynuclear hydroxo-complexes. The formation of these polynuclear complexes may be pictured as follows:



(V)



(VII)

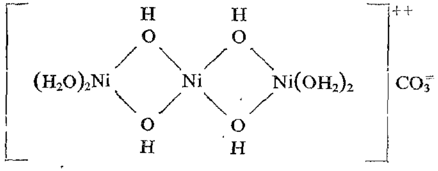


(VII) (II)

olation

(VIII)

In the above complexes, nickel has a coordination number of six. If in the complex (VIII), nickel were to have a coordination number four, the composition of the corresponding carbonate salt would be $3NiO.CO_2,6H_2O$. The configuration of the resulting unit would be as in (IX) with four molecules of water coordinated to the two nickel atoms at the ends. The other two molecules of water form four bridging OH groups between the adjacent metal atoms. These two, differently held, water molecules are lost at a later stage than the other four water molecules when the basic carbonate is subjected to thermal treatment.

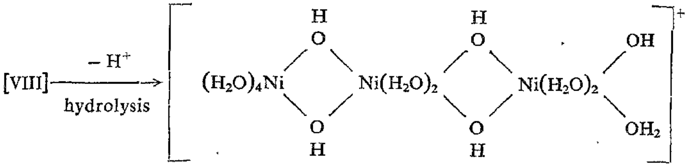


(IX)

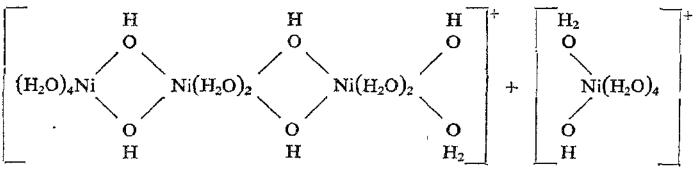
These expectations have been experimentally confirmed by results of thermogravimetric[5] and differential thermal analysis[4] of the basic carbonate of nickel of composition $3NiO.CO_2{\cdot}6H_2O$ which was prepared by suitable reaction between alkali carbonate and nickel salt, taken in the molar ratios 1.5 : 1.

As has already been pointed out, when the amount of alkali carbonate added is nearly three times the molar concentration of the nickel salt, the precipitate tends to be more basic. The composition of the precipitate obtained at pH 9.8, corresponding to these conditions, was $4NiO.CO_2.7H_2O$ when dried over anhydrous calcium chloride. Such a salt can be expected to be formed in either of two possible ways described below.

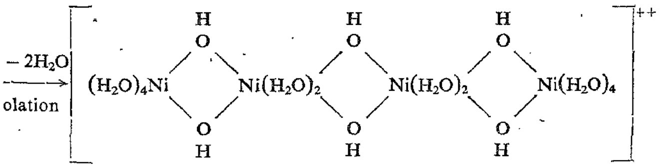
The trinuclear complex (VIII) can hydrolyse to give (X) which olates with the monohydroxo-species (II) to form the tetranuclear linear nickel complex (XI) as follows :



(X)

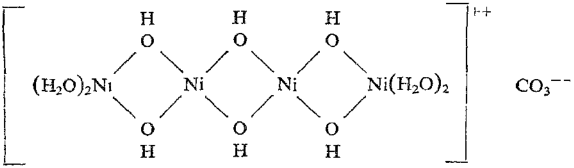


(X) (II)



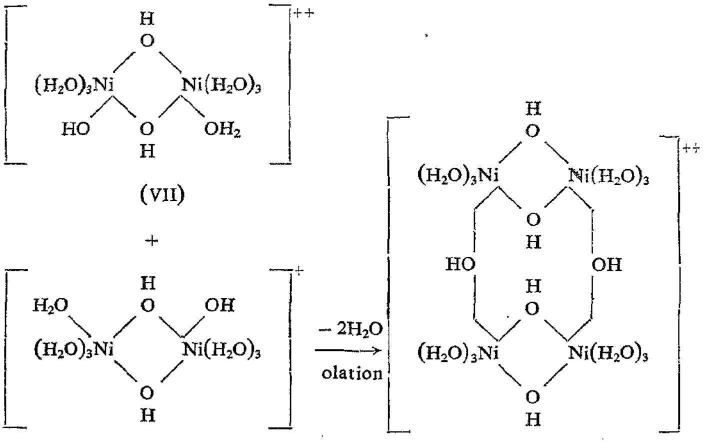
(XI)

The carbonate salt of the corresponding derivative of (XI) with four groups coordinated to each nickel atom would have the configuration (XII).



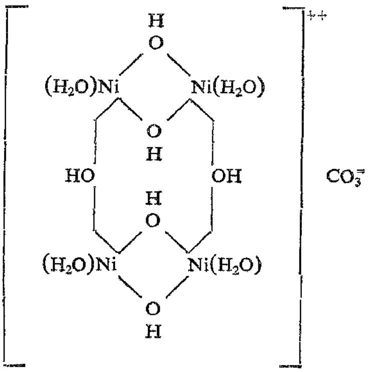
(XII)

Instead of the formation of the linear tetranuclear complex, as pictured above, a tetranuclear complex of the same composition may be pictured to be formed by the olation of the binuclear complex (VII) in a lateral fashion giving rise to a ring complex (XIII) in which all the nickel atoms are identical. This can take place as follows :



(VII) + (VII) → (XIII)

The carbonate salt of the derivative of (XIII) with four groups of coordinated to each nickel atom would have the arrangement as shown in (XIV).



(XIV)

The carbonate salts of both the complexes, (XII) and (XIV) correspond to the molecular formula $4NiO.CO_2.7H_2O$. In both configurations, four molecules of water are coordinated directly to nickel atoms and the other three molecules of water are bound more firmly in the skeleton unit as six bridging hydroxyl groups. However, in the configuration (XII), only the extreme nickel atoms of the linear chain have the water molecules coordinated as such to them, two per nickel atom. In the other arrangement (XIV), each of the four nickel atoms has a molecule of water coordinated to it.

It has already beed pointed out that if the precipitation of the basic carbonate is carried out at elevated temperatures, the product tends to be more and more basic. Thus nickel carbonates with compositions $14NiO.CO_2.16H_2O$ and $17NiO.CO_2.21H_2O$ could be prepared by mixing nickel salt and alkali carbonate at 97°C in the ratio 1 : 1 and 1 : 3 respectively[4]. In addition to the effect of olation and hydrolysis on the composition of the precipitate, mixed bridging may also modify the basic character of the precipitate. The formation of mixed bridges may be envisaged during precipitation at these higher temperatures[10]. In these basic compounds too, it has been shown from thermal studies[5] that the water contained in these samples is not uniformly bound. From the above two compounds, 5 and 6 molecules of water, respectively, are lost earlier in the first stage of thermal decomposition. In each unit, this amount of water may be considered as coordinated to nickel atoms. On losing this water the basic carbonates would have the compositions $14Ni.CO_2.11H_2O$ and $17NiO.CO_2.15H_2O$ respectively. Alternately, the compound $14NiO.CO_2.16H_2O$ may be regarded as $NiCO_3.11Ni(OH)_2.2NiO.5H_2O$ containing 5 molecules of easily removable water, 22 *ol* bridges and 2 *oxo*-bridges in each unit. Similarly, compound $17NiO.CO_2.21H_2O$ may be represented as $NiCO_3.15Ni(OH)_2.NiO.6H_2O$ with 6 molecules of water coordinated to nickel atoms, and involving 30 *ol* bridges and *oxo*-bridge per unit.

If these products are washed with boiling water, the compositions change to $16NiO.CO_2.14H_2O$ and $22NiO.CO_2.18H_2O$ respectively. Thermal studies[5] of these compounds indicate that these also contain 5 and 6 molecules of water respectively, coordinated to nickel atoms. The alternate structures for these compounds are respectively, $NiCO_3.9Ni(OH)_2.6NiO.5H_2O$ and $NiCO_3\cdot 12Ni(OH)_2.9NiO.6H_2O$ involving 6 and 9 *oxo*-bridges respectively. The ramification in these samples seems to be much more complicated as the samples are not easily attacked by dilute mineral acids. It is known that anions also participate as bridging groups in polynucleate ions[11] and therefore they do not always react as simple anions otherwise do. Perhaps similar formation of mixed bridges with carbonate ions may be responsible for its resistance towards dilute mineral acids. Similar phenomena have been observed by several workers earlier[12, 13] and they are of the opinion that there is a fairly strong covalent character for the bond between the metal atom and the anion. In mixed bridges of the above type, the coordinating groups are the oxygen atoms of the oxy-anion, in this case the carbonate; and these metal-oxygen bonds may be expected to have a fairly large degree of covalent character.

It is of interest to find out the arrangement of the different units in the solid basic nickel carbonates. In the case of the carbonate, $4NiO.CO_2.7H_2O$, the first stage of decomposition, in which 4 molecules of water are lost per unit, causes a three-fold increase in the amount of nitrogen adsorbed[6]. At the end of the second stage of decomposition, however, the surface area is again of the same order as that of the original sample. The precipitates obtained at 97°C show that there are only slight increases in the amounts of nitrogen adsorbed at the end of the first and second stages of decomposition.

It is therefore suggested that in the solid basic nickel carbonates prepared at 25°C units of (VI), (IX), (XII) or (XIV) are arranged, with carbonate ions in between two units, in a cross-linked manner along three dimensions. In such a case, the loss of coordinated water, during the first stage of decomposition, would create empty space in the form of cracks and capillaries and hence cause the surface area to increase several-fold. Such a frame-work would be rigid and relatively stable[14], as is found to be the case for these basic carbonates. If, on the other hand, the various units constituting the basic nickel carbonates were arranged in the form of chains or layer lattices, on removal of the coordinated water, there should be a contraction due to lateral shrinkage which therefore results in little or no increase in adsorptive capacities of the solids as was found by Barrer in the case of zeolites[14]. The basic carbonates formed at 25°C are hard and massive and undergo no visible shrinkage at the end of the first stage of decomposition, but instead has a much larger surface area. These basic carbonates may therefore be expected to consist of units forming cross-linked chains along three dimensions. On the other hand, the basic carbonates precipitated at 97°C are either linear, or two-dimensional chains since they are easily powdered, contract on decomposition and show only slight increase in surface area on undergoing decomposition[6]. This is also in accord with the behaviour of the wet precipitate in contact with distilled water. The process known as deoxolation, is known to occur in cases where long-chain polymers containing *oxo*-bridges are broken up at the *oxo*-bridges into smaller particles of colloidal dimensions[10]. In contact with distilled water, the basic carbonates prepared at 97°C cause the water to be turbid, indicating the redispersion of the precipitate.

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