

THE PREPARATION AND PROPERTIES OF LANTHANUM-PROMOTED NICKEL-ALUMINA CATALYSTS:  
 STRUCTURE OF THE PRECIPITATES

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Precursors of La-promoted Ni-alumina catalysts have been prepared by precipitation from their nitrate solutions at pH 7 using solutions of  $\text{NH}_4\text{HCO}_3$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ . The preparation was carried out either by coprecipitation from a mixed salt solution or by sequential precipitation of  $\text{Al}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{Ni}^{2+}$  in succession. In the absence of promoter, the precipitate with Ni/Al ratio of 2.5 is of the pyroaurite structure and has the composition  $\text{Ni}_5\text{Al}_2(\text{OH})_{14}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . Two types of lanthanum-containing precipitate were made in which either extra La was added (Ni/Al kept constant at 2.5) or the proportion Ni/(Al+La) was kept constant at 2.5. The majority of these precipitates were single compounds which also had the pyroaurite structure. At high La contents, the series in which La is added gives separation of the compounds  $\text{La}_2\text{O}(\text{CO}_3)_2$  and  $\text{LaONO}_3$  in addition to the layer structure; with the series in which the La is substituted for Al, all the samples appeared to have the pyroaurite structure, even one in which no Al was present. The sequential precipitation route yields smaller crystallites than does coprecipitation. Materials precipitated with  $\text{NH}_4\text{HCO}_3$  in all cases contained  $\text{NH}_4\text{NO}_3$  while those precipitated with  $\text{Na}_2\text{CO}_3$  gave inclusion of  $\text{NaNO}_3$ . In both cases, the presence of the nitrates causes a decrease of crystallinity of the layer compound. Potassium is not included in the precipitate in any of the samples examined. A model is presented for the structure of the lanthanum-containing precipitates.

1. INTRODUCTION

Nickel-aluminium catalysts prepared by coprecipitation are commonly used for the steam reforming of hydrocarbons and for the methanation of CO.<sup>1</sup> We are interested in the various factors, such as the method of precipitation,<sup>2</sup> which influence the activity and stability of such materials and in the effect of promoters.<sup>3</sup>

One such promoter is lanthanum which improves both the activity and stability of the catalysts. We have previously discussed the effect of lanthanum addition: improved specific activity, increased resistance to carbon deposition and higher stability in comparison to unpromoted materials.<sup>2-4</sup> We also showed that the method of precipitation is of prime importance in determining the properties of the catalysts. For example, materials prepared by coprecipitation (i.e. all the metal ions were precipitated at the same time by the reaction with alkali) were much more stable than others prepared by a sequential route.<sup>2,5</sup>

The precipitation of a mixture of a nickel salt and an aluminium salt (Ni/Al=3) in the absence of a lanthanum salt using a carbonate solution yields the compound  $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  which has a layer structure of the hydro-talcite type, as was reported by Kruissink et al.<sup>3</sup> (See Figure 1). The layer structure can

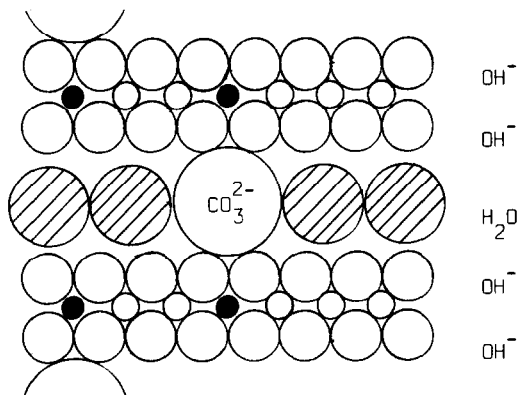


FIGURE 1  
 Structure of  $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot n\text{H}_2\text{O}$ .<sup>3</sup>  
 Small solid circles:  $\text{Al}^{3+}$ ; small hollow circles:  $\text{Ni}^{2+}$

tolerate a variation of the Ni/Al ratio; if the precipitates are hydrothermally aged, the ratio lies from 2 to 3. With a Ni/Al ratio less than 2, aluminium hydroxide separates; with a ratio of more than 3, nickel hydroxide is formed in addition to the layer structure.<sup>3</sup> The inter-layer of the structure shown in Figure 1 contains water molecules, hydroxide ions, nitrate

present a more detailed model for the structure of the precipitates.

## 2. EXPERIMENTAL

Preparation of catalyst precursors. The conditions of precipitation of the various series of samples examined here are summarized in Table 1.

TABLE 1: Precipitation Conditions for the Various Series of Precipitates

Series <sup>*</sup>	C10	C20	C30	C40	C50	S1	S40
Base used	NH <sub>4</sub> HCO <sub>3</sub>	NH <sub>4</sub> HCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>
Temp. of precipitation /°C	20 - 80	20 - 80	80	80	80	70	70
Molar ratios of Ni/Al	5:2	1:2, 3:2, 7:2, 9:2	5:2	variable	variable	5:2	variable
Ni/(Al+La)	variable	---	variable	5:2	5:2	variable	5:2
Mol% La	1, 5, 10, 20	0	0, 0.1, 0.5, 15, 20	0.1, 0.5, 1.0, 20, 28.6**	0.1, 5.0, 20	0, 1.0, 5.0, 10	0.1, 0.5, 1.0, 2.0, 5.0
<u>Stock solutions used</u>	/mol dm <sup>-3</sup>						
Ni <sup>2+</sup>	1.00	variable	1.0	0.222	0.25	3.34	0.222
Al <sup>3+</sup>	0.400	variable	0.4	0.089	0.1	1.34	0.089
La <sup>3+</sup>	variable	---	variable	0.089	0.1	1.2	0.089
Base	1.52	1.52	1.5-3.2	0.70	1.0	3.2	0.70

\* C = coprecipitated; S = sequentially precipitated.

\*\* This amount of La corresponds to full replacement of the Al by La

ions and/or carbonate ions, depending on the manner and pH of precipitation. For reasons of electroneutrality, the Al<sup>3+</sup> ions are balanced by the anions in the interlayer: one hydroxide or nitrate ion per Al<sup>3+</sup> or one carbonate ion per Al<sup>3+</sup>.

It is not so clear how the structure of the precipitates is modified by the addition of lanthanum. In a previous paper,<sup>2</sup> we presented a tentative model of how the lanthanum might be incorporated in the hydrotalcite structure. We now present the results of detailed investigations of several series of lanthanum-containing precipitates prepared in various ways and we

Stock solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in the concentrations given in Table 1 were either used as such (sequential method) or mixed to the desired composition (coprecipitation method). The precipitation was performed in a heated and stirred vessel to which the solutions of the precipitating agent (K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> or NH<sub>4</sub>HCO<sub>3</sub>) and of the metal salt solutions were added dropwise; a large amount of water (about 1 dm<sup>3</sup>) was first added so that the pH of the solution could be more easily controlled throughout the precipitation process.

In the coprecipitation method, the mixture

of the metal ions was precipitated at one time; in the sequential method, the  $\text{Al}^{3+}$  ions were precipitated first, then the  $\text{La}^{3+}$  ions and finally the  $\text{Ni}^{2+}$  ions. The precipitation temperature was maintained at 70 or 80°C; an exception was with  $\text{NH}_4\text{HCO}_3$  for which the temperature of precipitation was 20°C but, after addition of the substances, the temperature was then raised to 80°C. The pH during coprecipitation was maintained at pH 7 (+ 0.5); in the sequential series,  $\text{Al}^{3+}$  and  $\text{La}^{3+}$  were precipitated in turn at pH 6 and then  $\text{Ni}^{2+}$  was precipitated, the pH being allowed to rise from 6.5 to 8. After the (co)precipitation was completed, the resultant solids were filtered with suction on a glass filter (D4), washed several times with water at 70 or 80°C and were then dried overnight in air at about 100°C.

**Analysis.** Nitrate analysis was performed by titration following the Devarda method; the carbonate analysis was done photometrically with a Heraeus "Micro-Rapid CH" titrator.<sup>6</sup> The sodium and potassium content were determined by atomic absorption spectrometry (AAS) using a Varian AA6 instrument. Nickel, aluminium and lanthanum were analysed by X-ray fluorescence (XRF), using a Philips PW 1410 apparatus and also by AAS. X-ray powder diffraction spectra (XRD), using  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5405 \text{ \AA}$ ), were recorded at 40 kV and 30 mA, using a PW 1050 goniometer at 2 degrees/min. ASTM XRD data files served for identification of the various compounds.<sup>7</sup>

### 3. RESULTS

Chemical analyses were carried for samples of Series C30 and 40 and S1 and 40; not every analysis was carried out for each series. The results are given in Table 2 and those for Series S1 and C30 are given in Figures 2a and b respectively as a function of the lanthanum content, defined as:

$$\text{Mol\% La} = 100\text{La}/(\text{Ni}+\text{Al}+\text{La})\%$$

The lanthanum contents determined analytically for Series C30 are close to those of the starting solutions. However, the  $\text{Ni}^{2+}/\text{Al}^{3+}$  ratios for the same series determined by XRF were consistently too high compared with the expected value of 2.5 (see Table 1). This appears to arise from the fact that the  $\text{Al}^{3+}$  contents determined by the method were too low. When one analysis was carried out with AAS, the ratio was as expected (see Table 2).

We now consider the  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{Na}^+$  results for Series C30. At a lanthanum content lower than about 1 mol%, the predominant ion is carbonate. However, at higher contents, the nitrate and sodium ion contents increase as is shown graphically in Figure 2a; as these two species increase in approximately equal molar proportions, we conclude that the precipitate contains  $\text{NaNO}_3$  at higher sodium contents. This was confirmed by XRD (see below). It should be noted that the carbonate contents of the C30 series given in Table 2 have been corrected for this sodium nitrate content. It was found that the sodium nitrate could be washed out of the precipitate only if the precipitate were first dried at about 100°C before further washing. It was also found that any nitrate ions present in the interlayer of the pyroaurite structure could be replaced by carbonate ions by washing the precipitate with sodium carbonate; the dotted line in Figure 2a represents the resultant carbonate compositions, the nitrate (and  $\text{Na}^+$ ) contents having dropped to effectively zero. The carbonate and lanthanum ion contents then increase almost exactly in molar proportion one to the other.

For the S1 series, the predominant ionic species present for all the samples is carbonate (see Table 2 and Figure 2b) and the carbonate content increases linearly with lanthanum content. As the precipitant for this series was  $\text{K}_2\text{CO}_3$ , the  $\text{K}^+$  contents were determined and were found to be negligible; the same applied for

TABLE 2: Chemical Analyses of the Precipitates

Series	C30	C30*	S1	C30	S1	C30	S40	S40	S1	C30
La <sup>3+</sup>	La <sup>3+</sup>	NO <sub>3</sub> <sup>-</sup>		CO <sub>3</sub> <sup>2-</sup>		Na <sup>+</sup>			F <sup>+</sup>	Ni <sup>2+</sup> /Al <sup>3+</sup>
Content	/mol%	/wt%		/wt%		/wt%			/wt%	
(Calculated)										
0	0	3.27	1.46	5.13	10.02	0.26	-	-	0.001	2.65
0.1	0.08	3.22	-	8.16	-	0.24	0.025	-	-	2.75
0.5	0.40	2.70	-	8.24	-	0.28	-	0.026	-	2.87
1	0.92	0.73	1.48	-	10.25	0.57	0.014	-	0.001	3.90
2	1.9	9.64	-	6.41	-	3.9	-	0.049	-	2.83
5	-	-	1.57	-	11.14	-	-	0.020	0.001	-**
10	-	20.75	0.51	-	14.64	11.4	0.021	-	0.001	2.51
15	-	-	0.66	-	15.80	-	0.029	-	0.001	-
20	20.9	25.40	1.31	9.90	18.39	12.6	0.008	-	0.001	3.43
28.6	-	-	-	-	-	-	0.013	-	-	-

\* These values are corrected for the amount of NaNO<sub>3</sub> in the sample (see text).  
 \*\* This analysis was carried out with AAS

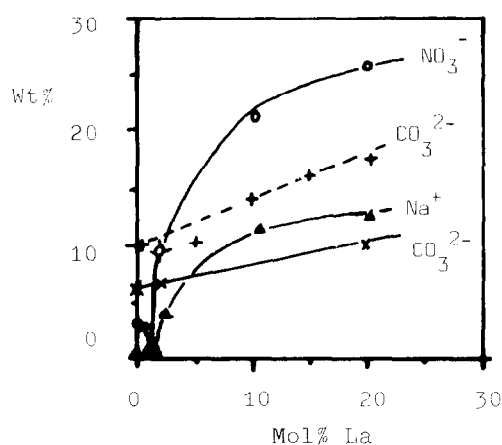


FIGURE 2a  
Content of ions present in the C30 series

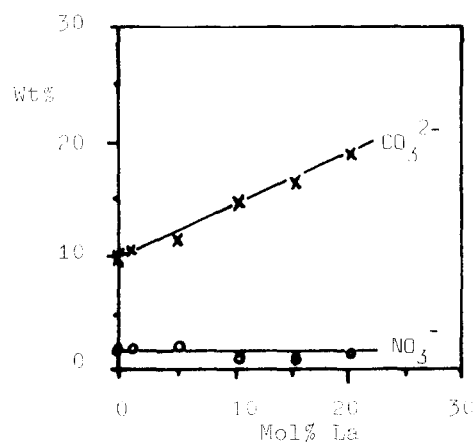


FIGURE 2b  
Content of ions in the S1 series

the Na<sup>+</sup> contents of a series (S40) made with sodium carbonate as precipitant (see Table 2). It would thus appear that the sequential preparation method has the advantage of more easily excluding foreign ions from the precipitates formed.

The results for the sodium ion contents of Series S40 given in Table 2 show that the prob-

lem of the removal of sodium from the precipitate is not so great for samples in which the Ni<sup>2+</sup>/(Al<sup>3+</sup>+La<sup>3+</sup>) ratio is kept constant at 2.5. As the ratio falls for the later members of the C30 series, it would appear that it is very important in determining the retention of sodium and other ions.

Figure 3 gives typical X-ray diffraction

patterns; samples with 1 and 20 mol% La are shown for each of the series, and two of the samples of Series C20 (without La but with varying Ni/Al contents) are also given. For the samples with 1 mol% La, the patterns obtained are identical to those obtained for samples without lanthanum, there being no phases present other than a rather amorphous layered structure of the (rhombohedral) pyroaurite type. At higher lanthanum contents, the structure is more amorphous and less distinct; in the cases of the C10 and C30 series, additional lines also appear, these being identified as being due to distinct  $\text{La}_2\text{O}(\text{CO}_3)_2$  and  $\text{NaNO}_3$  phases. With the S1 series, a trace of  $\text{LaONO}_3$  was identified at 20 mol% La. A summary of the results is given in Table 3 which also shows that  $\text{NH}_4\text{NO}_3$  was identified in the C10 series. For the C20 series, which contains no La, the predominant additional phase was also identified as being  $\text{NH}_4\text{NO}_3$ ; see Table 4.

The crystallite sizes of the pyroaurite particles of the precipitate particles were determined by X-ray line-broadening using the Scherrer formula.<sup>8</sup> For each series, the particle diameter decreased with increasing La content, becoming more or less constant at 10 mol% La and above. (For the C50 and S1 and 40 series, it became constant, for the C30 and 40 series, it continued to drop.) For the C series, the diameter measured dropped from approximately 80 Å to approximately 50 Å while for the S series it dropped from about 40 Å to about 30 Å.

#### 4. DISCUSSION

In a previous paper,<sup>2</sup> we presented some results for the behaviour of the C30 and S1 series of precipitates which are examined in greater detail, together with several more series, in this publication. As a consequence of thermal analytical (TG) studies of the decomposition of the precipitates together with preliminary

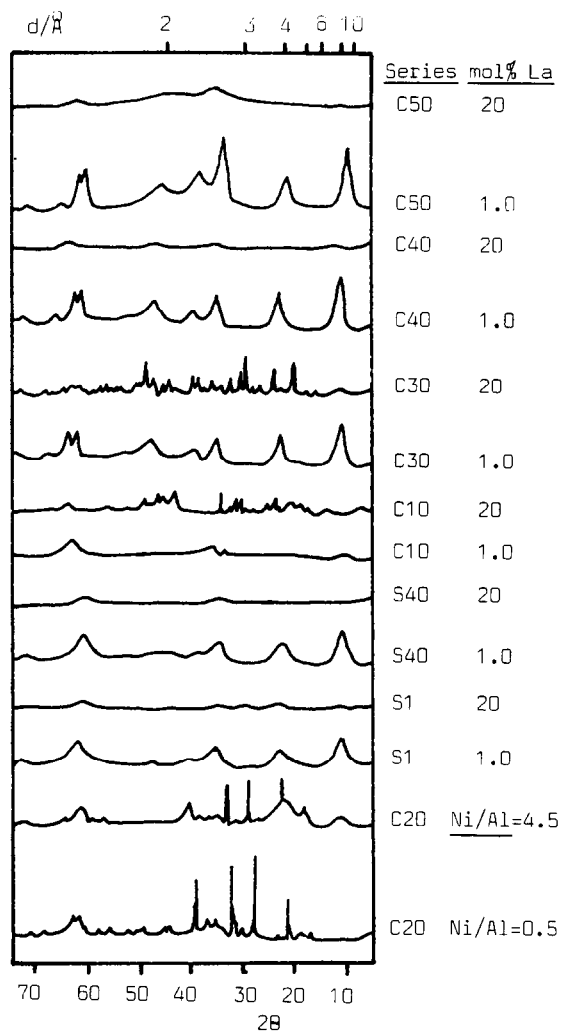


FIGURE 3  
Typical examples of XRD patterns of the precipitates.

X-ray studies, we concluded<sup>2</sup> that the lanthanum did not form a separate phase until higher lanthanum contents. We put forward a possible structure for the precipitates and suggested that nitrate ions incorporated in the precipitate at high lanthanum contents could account for the unexpectedly high weight changes observed for these samples. Figure 5 gives a schematic representation of this suggested structure where an attempt is made to represent two-dimensionally the sizes and posit-

TABLE 3: Phases present in C10, 30, and 50 and S1 and 40 Series as Identified by XRD

Series Mol% La	C10	C30	C40	C50	S1	S40
0	--	pyroaurite	--	pyroaurite	pyroaurite	--
0.1	--	pyroaurite	pyroaurite	--	--	pyroaurite
0.5	--	pyroaurite	pyroaurite	--	--	pyroaurite
1	pyroaurite (+NH <sub>4</sub> NO <sub>3</sub> )*	pyroaurite	pyroaurite	pyroaurite	pyroaurite	pyroaurite
2	--	pyroaurite +NaNO <sub>3</sub>	pyroaurite	--	--	pyroaurite
5	pyroaurite +NH <sub>4</sub> NO <sub>3</sub> ** +u.p.	pyroaurite +LaOHCO <sub>3</sub> +La <sub>2</sub> O <sub>3</sub>	pyroaurite +LaOHCO <sub>3</sub>	pyroaurite	pyroaurite	pyroaurite
10	(pyroaurite) +NH <sub>4</sub> NO <sub>3</sub>	pyroaurite +La <sub>2</sub> O(CO <sub>3</sub> ) <sub>2</sub> +LaNO <sub>3</sub>	pyroaurite +u.p.	--	pyroaurite	pyroaurite
15	--	pyroaurite +La <sub>2</sub> O(CO <sub>3</sub> ) <sub>2</sub>	pyroaurite +u.p.	--	pyroaurite	pyroaurite
20	NH <sub>4</sub> NO <sub>3</sub> +u.p.**	pyroaurite +La <sub>2</sub> O(CO <sub>3</sub> ) <sub>2</sub> +NaNO <sub>3</sub>	pyroaurite	pyroaurite	pyroaurite +(LaONO <sub>3</sub> )	(pyroaurite)
28.6	--	--	(pyroaurite)	pyroaurite	--	(pyroaurite)

\* ( ) indicates very weak diffraction pattern  
 \*\* ( ) indicates very weak diffraction pattern  
 u.p. - unidentified phase

TABLE 4: Phases in Series C20 (Variable Ni/Al) as identified by XRD

Molar ratio Ni <sup>2+</sup> /Al <sup>3+</sup>	Phases Present
1:2	(pyroaurite)* + NH <sub>4</sub> NO <sub>3</sub> + u.p.**
3:2	(pyroaurite) + NH <sub>4</sub> NO <sub>3</sub>
7:2	pyroaurite + NH <sub>4</sub> NO <sub>3</sub>
9:2	pyroaurite + NH <sub>4</sub> NO <sub>3</sub>

\* ( ) : very weak diffraction pattern  
 \*\* ( ) : very weak diffraction pattern  
 u.p. : unidentified pattern

ions of the ions present in the structure. The size of the La<sup>3+</sup> ion (1.016 Å) in comparison with that of Al<sup>3+</sup> (0.51 Å)<sup>9</sup> prevents a simple replacement of Al<sup>3+</sup> by La<sup>3+</sup>. However, removal of one OH<sup>-</sup> ion from the brucite layers affords sufficient space to fit the larger cation. The electroneutrality can then be restored by inserting one doubly charged ion (CO<sub>3</sub><sup>2-</sup>) into the interlayer for each La<sup>3+</sup> ion in the structure. Such a model explains the linear relationship between the carbonate content and the La

content shown in Figure 2. Another possibility is that the charge of the La<sup>3+</sup> ion is counter-balanced by substituting a nitrate ion into the interlayer and an O<sup>2-</sup> ion in the hydroxide ("brucite") layer of the structure or an extra hydroxyl ion in the interlayer; there is insufficient room in the interlayer for two nitrate ions per lanthanum ion.

Figure 4 represents the situation where La<sup>3+</sup> ions are substituted in the structure in place of Al<sup>3+</sup> ions, as is the situation for the Series C40 and 50 precipitates. For the C30 series, the lanthanum was added in addition to the aluminium. Thus, with increasing lanthanum content, the interlayer becomes filled by the charge-balancing carbonate anions and a separation of new phases commences (see Table 3); the local environment of the La<sup>3+</sup> ion in the hydrotalcite-like phase for this type of material remains the same as that depicted in Figure 4. A similar phase separation occurred with Ni-Al materials at lower Ni/Al contents,<sup>3</sup> a separate aluminium hydroxide phase being formed.

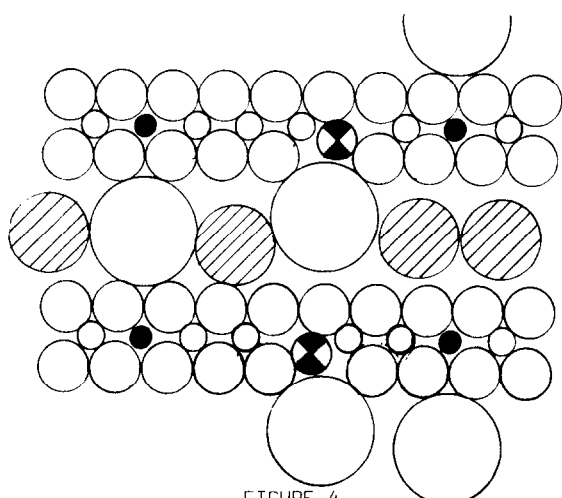


FIGURE 4

Possible structure of  $\text{Ni}_5\text{Al}_2\text{La}_x(\text{OH})_{14+x}(\text{CO}_3)_{1+x} \cdot 4\text{H}_2\text{O}$ .

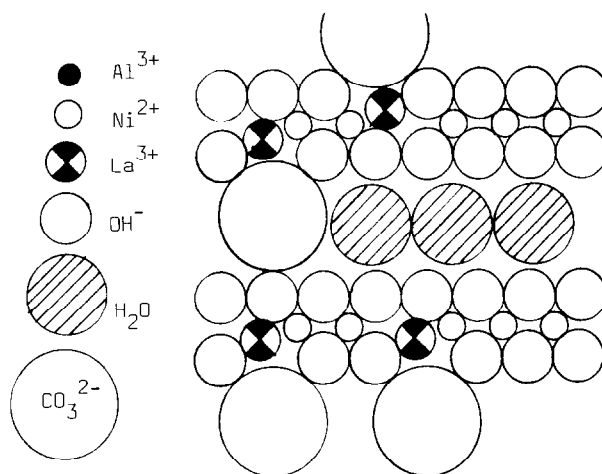


FIGURE 5

Possible structure of  $\text{Ni}_5\text{La}_2(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$

In the sample of Series C40 containing 28.6 mol% La, there is no longer any aluminium present. Nevertheless, the structure appears from the X-ray results to be unchanged in comparison to that of hydrotalcite apart from the fact that the material is much more amorphous. Figure 5 represents the possible structure of the compound in which all the aluminium is replaced by lanthanum:  $\text{Ni}_5\text{La}_2(\text{OH})_{12}(\text{CO}_3)_2 \cdot n\text{H}_2\text{O}$ , where  $n$  is a small number. The removal of a  $\text{OH}^-$  ion from the hydroxide layer causes a loss of the characteristic regularity of the original structure. As regularity of the structure is a prerequisite of a well-defined X-ray pattern, this would offer an explanation of the changes of the diffraction pattern observed on increasing the lanthanum content (see Figure 3).

As shown in Table 2 and Figure 2, surprisingly large amounts of nitrate and sodium ions are retained by the precipitates of the C30 series, especially at high lanthanum contents. We previously suggested<sup>2</sup> that nitrate ions might be included in the interlayer in place of carbonate ions; although this is clearly the case at low La contents, as shown by the fact (Table 2) that the nitrate content far exceeds

the sodium content, at higher La contents the majority of the nitrate appears to be present as  $\text{NaNO}_3$ . As this only appears as a separate phase at higher La contents, it is possible that some of it is present within the layer structure of the hydrotalcite-like phase or is associated with the  $\text{La}_2\text{O}(\text{CO}_3)_2$  phase. The fact that the sodium content is not easily reduced by washing argues that the sodium nitrate must be locked in some way in the precipitate, it being necessary to destroy the gel-like structure by drying before it can be removed. As the C40 series precipitates, which do not contain the extra lanthanum oxycarbonate phase, have much lower sodium contents than those of the C30 series, this seems to indicate that the retention of sodium nitrate is associated with the oxycarbonate phase. In work on Ni-Al precipitates with high Ni contents, it has been observed that sodium is equally difficult to remove from these materials.

The X-ray results for the C10 series (Tables 3 and 4) show that  $\text{NH}_4\text{NO}_3$  can be retained in the precipitate in the same way as can  $\text{NaNO}_3$ , regardless of whether or not there is La present. In the case of the C10 series, there

was no separate oxycarbonate phase identified. Thus, it is possible that the ammonium and nitrate ions can be incorporated in the inter-layer, possibly by hydrogen bonding with the water species also present. The C50 series precipitated by  $K_2CO_3$  shows no evidence of separate phases (see Table 3) and this is comparable with the results for the C40 series. Preliminary results for the methanation activities of catalysts of the C50 series show these to be extremely active materials. It would thus appear that the relatively poor activities of materials of the C30 series at high La contents reported previously<sup>2</sup> must be attributed to the high sodium contents of the catalysts. The poisoning effects of sodium on the activities of Ni-Al materials have previously been discussed in some detail.<sup>10</sup>

The materials prepared by the sequential route also seem to give rise to the hydroxalcalite structure although, as the crystallite sizes of the materials produced are smaller, the X-ray patterns are less distinct. The S1 series gives separation of an oxynitrate phase at higher La contents (Table 3) but no separate phase is observed in the S40 series, a consequence of the fact that the Ni/(Al+La) ratio is kept constant at 2.5 in the latter and varied in the former. The fact that a lanthanum oxynitrate phase is formed is probably a consequence of the preparation method; this involves addition of the excess La as nitrate after precipitation of the aluminium component, when nitrate ions are more likely to be retained. The sequentially prepared materials are less stable than the coprecipitated materials although the initial activities are somewhat higher.<sup>2</sup> As there is generally a relationship between the crystallite size of the active catalyst and that of the precipitate, this difference in initial activities would be expected from the differences in crystallite sizes of the two series.

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