

Hydrotalcite-like compounds obtained by anion exchange reactions

M. A. ULIBARRI, M. J. HERNANDEZ

Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Universidad de Córdoba, 14004 Córdoba, Spain

J. CORNEJO

Instituto de Recursos Naturales y Agrobiología, CSIC, Sevilla, Spain

The synthesis of nickel aluminium hydroxypicrate, $[\text{Ni}_3\text{Al}(\text{OH})_8] (\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$, and lithium aluminium hydroxypicrate, $[\text{Al}_2\text{Li}(\text{OH})_6] (\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$ by anion exchange is described. Picric acid and the corresponding hydroxycarbonates were used as starting materials. The new compounds were characterized by chemical analyses, electron microscopy, infrared spectroscopy and X-ray diffraction. The results obtained indicate that both are hydrotalcite-like compounds where the picrate anion lies between the basic layers. The thermal decomposition of the compounds was studied by differential thermal and thermogravimetric analysis.

1. Introduction

Hydrotalcite-like compounds are mixed metal hydroxides of formula $[\text{M}_1^{2+}_{1-x}\text{M}_2^{3+}_x(\text{OH})_2]^{x+} \text{X}_{x/n}^{n-} \cdot m\text{H}_2\text{O}$ where $\text{M}^{2+} = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}$, etc., $\text{M}^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}$, etc., $\text{X}^{n-} = \text{CO}_3^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{SO}_4^{2-}$, etc. and $0.2 \leq x \leq 0.33$. Their structure consists of positively charged brucite-like layers, $[\text{M}_1^{2+}_{1-x}\text{M}_2^{3+}_x(\text{OH})_2]^{x+}$, alternating with negatively charged interlayers containing anions and water molecules, $[\text{X}_{x/n}^{n-} \cdot \text{H}_2\text{O}]^{x-}$ [1–3]. M^{2+} and M^{3+} are randomly distributed at the octahedral positions in the basic layer.

$[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ is a laminar hydrotalcite-like compound whose structure consists of positively charged layers with Al^{3+} cations arranged as in gibbsite, $\text{Al}(\text{OH})_3$, vacancies (one-third of the octahedral positions) being occupied by Li^+ cations. Al^{3+} and Li^+ are largely ordered in the octahedral layer. Anions and water molecules fill the interlayer spaces [4–6]. The general formula of hydrotalcite-like compounds should be extended to include the monovalent Li^+ cations.

Hydrotalcite-like compounds feature well-known anion-exchange capabilities [7–9]. They are some of the few known inorganic anion exchangers. Their anion-exchange properties are governed by the anion size, its electric charge and the molar $\text{M}^{2+}/\text{M}^{3+}$ ratio. A number of small anions ($\text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-$, etc.) have been used in exchange reactions. The interlayer spacing of these compounds varies with the size of the intercalated anion. The intercalation of large anions is of some interest to adsorption and catalysis. Polyoxometallates [10] and anionic complexes were recently intercalated [11].

The aim of the present work was to gain further knowledge about the intercalation of large anions into the interlayer spacing of hydrotalcite-like compounds

by intercalating picrate anions via anion-exchange reactions.

2. Experimental procedure

Two different hydrotalcite-like compounds were used in the anion-exchange reaction with picrate, namely $[\text{Ni}_3\text{Al}(\text{OH})_8]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ and $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$.

Ni–Al hydroxycarbonate was prepared as described elsewhere [12] by coprecipitation from Ni^{2+} and Al^{3+} salt solutions by slowly adding an NaOH solution until a suitable pH of 10 to 12 was reached. The resulting gel was hydrothermally treated to improve crystallinity. The synthesis of the Al–Li hydroxycarbonate was conducted by slow addition of an aluminium carbonate (0.1 M) to a saturated LiOH solution up to pH 12.5 [13]. In both experiments, the gels were treated hydrothermally to improve crystallinity.

An amount of 0.5 g of $[\text{Ni}_3\text{Al}(\text{OH})_8]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ and 1 g of $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ was suspended in 500 ml of 0.05 and 0.1 M picric acid solutions, respectively. The water employed was free from CO_2 . The suspensions were kept under continuous stirring for 48 h. The resulting products were washed and dried at 60 °C.

The cations Ni^{2+} , Al^{3+} and Li^+ were analysed for atomic absorption spectrometry on a Perkin Elmer instrument after dissolving the solids in dilute HCl (0.1 M). The picrate anion was determined on a Lambda 1 spectrophotometer by monitoring the solution absorbance at 354 nm.

X-ray powder diffraction patterns were recorded on a Philips PW 1130 diffractometer using $\text{CoK}\alpha$ radiation and an iron filter. The scanning rate was

$1^\circ 2\theta \text{ min}^{-1}$. Electron micrographs were recorded on a Jeol 200 CX microscope. Infrared spectra were recorded in the range 4000 to 200 cm^{-1} on a Perkin Elmer 599B spectrophotometer by previously diluting samples in KBr.

Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were carried out on a Rigaku-Thermoflex TG-DTA instrument at a heating rate of $10^\circ \text{C min}^{-1}$.

3. Results and discussion

The ion-exchange reaction replacing CO_3^{2-} by picrate yielded similar results for the two hydroxycarbonate-like compounds studied. The X-ray diffraction patterns obtained in both cases (Figs 1 and 2) show increased d_{001} spacings, and hence increased interlayer spacings consistent with the expectations for the replacement of one anion (carbonate) for a bulkier anion (picrate). The increase observed in the d_{002} spacings of the hydroxypicrates with respect to the corresponding hydroxycarbonates (Table I) was 0.57 nm in both cases. The thickness of the interlayer space was calculated by subtracting the thickness of the brucite-like layer (0.477 nm) or gibbsite-like layer (0.485 nm) as required from that of the unit layer d_{002} . The values thus calculated are also listed in Table I.

On the other hand, on comparing the d_{002} spacings of the homoionic samples, it is seen that the Ni-Al compounds feature larger spacings than the Al-Li compounds. This can be related to the positive charges at the octahedral layers, which is of about 0.33 nm^2 per charge for Ni-Al compounds with $M^{2+}/M^{3+} = 3$, and about 0.25 nm^2 per charge for Al-Li compounds with $M^{2+}/M^{3+} = 2$ [4]. The higher charge density at the octahedral layers favours attraction to the anion layers, which decreases the thickness of the unit layer (d_{002}) [12].

The morphology of the hexagonal plates, more or less even, shown by the Ni-Al hydroxycarbonate (Fig. 3) is preserved after the anion exchange of CO_3^{2-} by picrate. The size of the particles is only slightly affected by the anion exchange. On the other hand, the

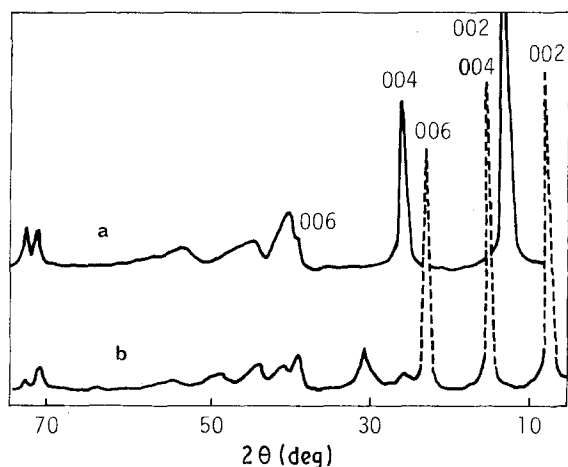


Figure 1 X-ray powder diffraction patterns of: (a) $[\text{Ni}_3\text{Al}(\text{OH})_8]_2(\text{CO}_3) \cdot n\text{H}_2\text{O}$ and (b) $[\text{Ni}_3\text{Al}(\text{OH})_8](\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$.

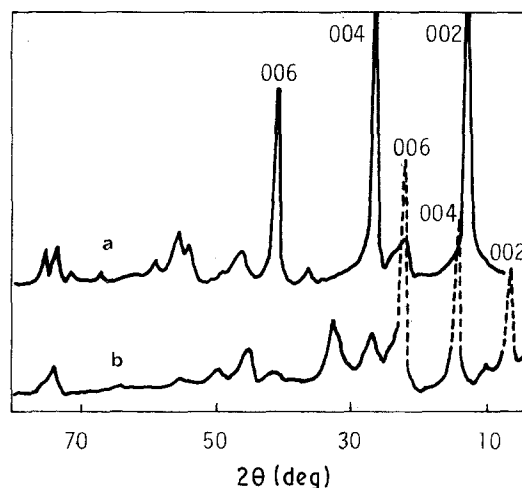


Figure 2 X-ray powder diffraction patterns of: (a) $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ and (b) $[\text{Al}_2\text{Li}(\text{OH})_6](\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$.

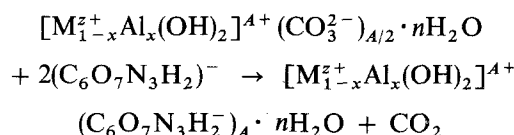
TABLE I Variation of d_{001} spacings and interlayer thickness with the anion

Sample	d_{002} (nm)	d_{004} (nm)	d_{006} (nm)	Interlayer thickness (nm)
Ni-Al- CO_3	0.79	0.39	0.264	0.313
Ni-Al-picrate	1.36	0.68	0.45	0.883
Al-Li- CO_3	0.76	0.378	0.254	0.275
Al-Li-picrate	1.33	0.66	0.44	0.845

$\text{Ni}^{2+}/\text{Al}^{3+}$ cation ratio also remains constant. This can be regarded as a topotactic reaction, which is consistent with the findings of other authors in anion-exchange reactions involving other hydroxycarbonate-like compounds [14]. The micrographs of the Al-Li hydroxycarbonates studied in this work show similar results.

Further information about the intercalated anion can be obtained by infrared spectroscopy. In Figs 4 and 5 are shown the IR spectra of the hydroxycarbonates and the corresponding hydroxypicrates. In both cases, the typical bands of the interlayer CO_3^{2-} anion [5] (one of greater intensity at 1360 to 1370 cm^{-1} and others, less intense, at 1050 , 870 and 680 cm^{-1}) are absent, and new bands which can be ascribed to picrate (C-H 3080 to 3030 cm^{-1} ; C-C 1625 to 1475 cm^{-1} ; NO_2 1560 to 1490 cm^{-1} , 1260 to 1180 cm^{-1}) [15] are observed. The regions characteristic of AlO_6 octahedra (370 to 750 cm^{-1}) and LiO_6 or NiO_6 (200 to 350 cm^{-1}) are similar to those reported elsewhere [4, 5], and the presence of sharp bands in this region suggests the occurrence of cation ordering in Al-Li hydroxycarbonates, but not in those of Ni-Al.

The above results indicate that a replacement of the interlayer CO_3^{2-} anion with picrate occurred during the anion exchange experiment. The anionic exchange reaction can be represented by the following scheme:



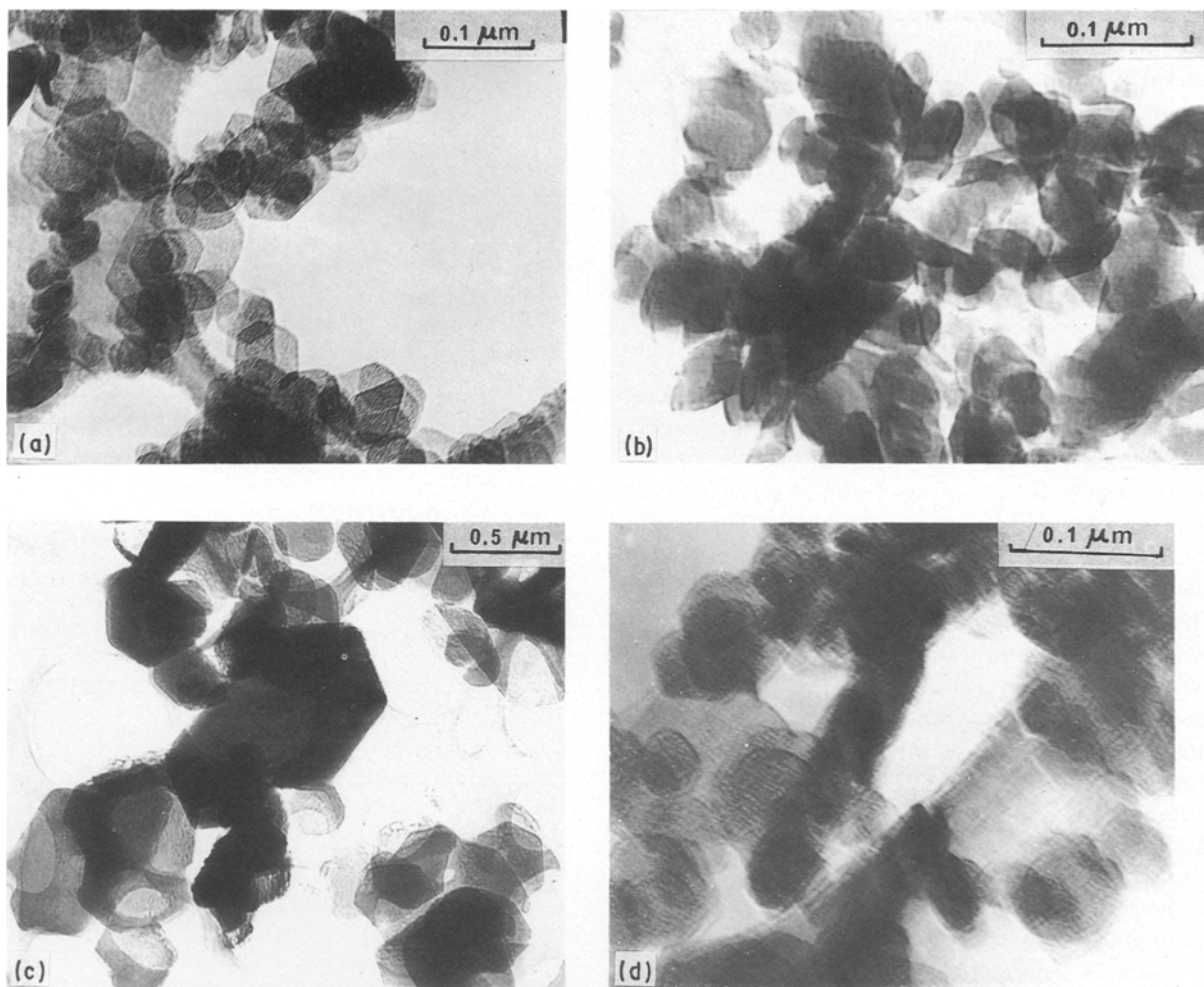


Figure 3 Transmission electron micrographs (TEM) of: (a) $[\text{Ni}_3\text{Al}(\text{OH})_8]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$; (b) $[\text{Ni}_3\text{Al}(\text{OH})_8](\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$; (c) $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$; (d) $[\text{Al}_2\text{Li}(\text{OH})_6](\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$.

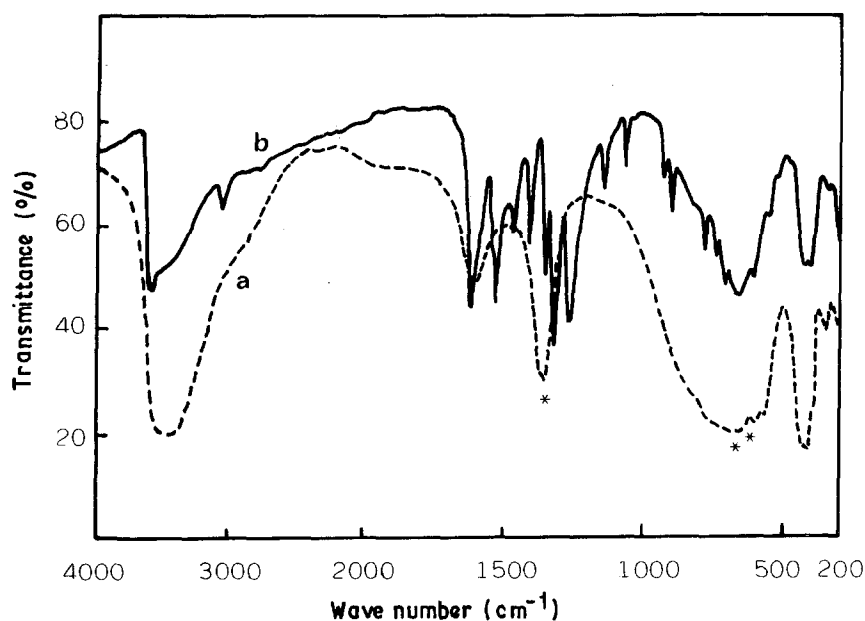


Figure 4 Infrared spectra of $[\text{Ni}_3\text{Al}(\text{OH})_8]^+ X_{n/m}^{m-} \cdot n\text{H}_2\text{O}$: $X^{m-} = \text{CO}_3^{2-}$ (dashed line) and $\text{C}_6\text{O}_7\text{N}_3\text{H}_2^-$ (solid line). (*) Molecular vibrations due to carbonates.

in which $\text{M}^{z+} = \text{Ni}^{2+}$ or Li^+ ; $A = x = 0.25$ for Ni^{2+} and $A = 2x - 1 = 0.33$ for Li^+ .

In the two hydrotalcite-like compounds studied, the exchange of CO_3^{2-} by picrate at the interlayer results in few changes in their decomposition temperatures. Fig. 6 shows the DTA and TG curves of Ni-Al hy-

droxypicrate. The DTA curve shows a sharp exothermic effect in the range 300 to 500°C, coinciding with the pyrolysis of the picrate ion. The TG curve shows a very slow weight loss (2% of the sample) starting at 100°C and extending up to 300°C. This first weight loss is very small compared with that occurring in the

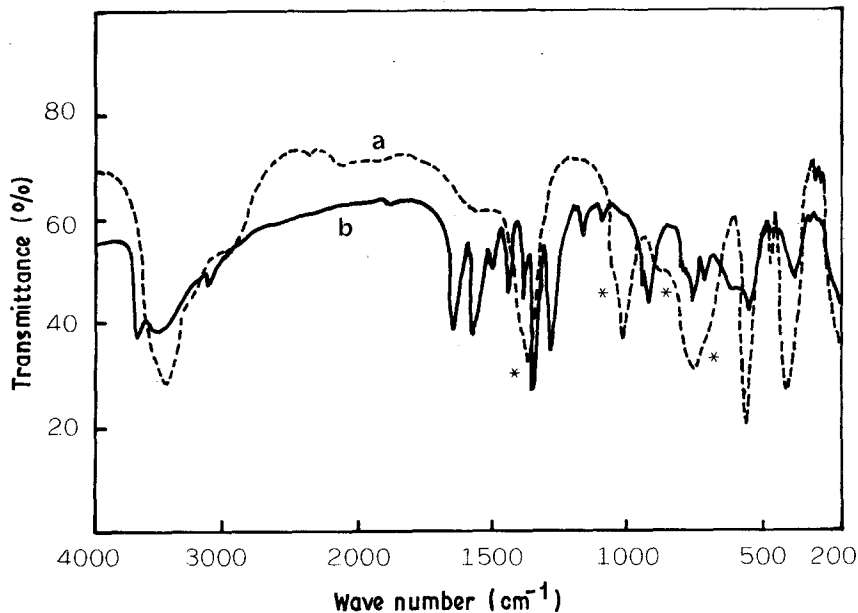


Figure 5 Infrared spectra of $[\text{Al}_2\text{Li}(\text{OH})_6]^+$ $X_{n/m}^m \cdot n\text{H}_2\text{O}$: $X^m = \text{CO}_3^{2-}$ (dashed line) and $\text{C}_6\text{O}_7\text{N}_3\text{H}_2^-$ (solid line). (*) Molecular vibrations due to carbonates.

corresponding hydroxycarbonate (9.2%) which is attributed to interlayer water [12]. Probably, the need of each CO_3^{2-} anion to be replaced by two picrate anions at the interlayer prevents a larger number of water molecules from occupying it.

This is supported by the fact that, while the Ni-Al hydroxycarbonate shows decreased (d_{001}) spacings as a result of the loss of interlayer water [12], the XRD pattern of the Ni-Al hydroxypicrate heated at 300°C (Fig. 7) does not show such a decrease. Likewise, the IR spectra (Fig. 4) show the bands corresponding to the hydroxyl stretching vibrations (3700 to 3500 cm^{-1}), and the bending vibrations (1600 cm^{-1}) of the interlayer H_2O are more intense when the interlayer anion is CO_3^{2-} than when it is picrate, thus indicating the occurrence of larger amounts of interlayer water in the former case. Similar results have been found for other anions [16].

Between 300 and 400°C there is a sharp weight loss (TG curve) of 78% corresponding to the pyrolysis of

picrate anions and the dehydration of the compound with destruction of the laminar compound. The XRD pattern of the compound heated at 450°C (Fig. 7) shows the largest spacings of poorly crystalline NiO. Above 750°C the interaction between nickel and aluminium oxides starts to form the spinel NiAl_2O_4 . The XRD pattern of the compound heated at 1000°C

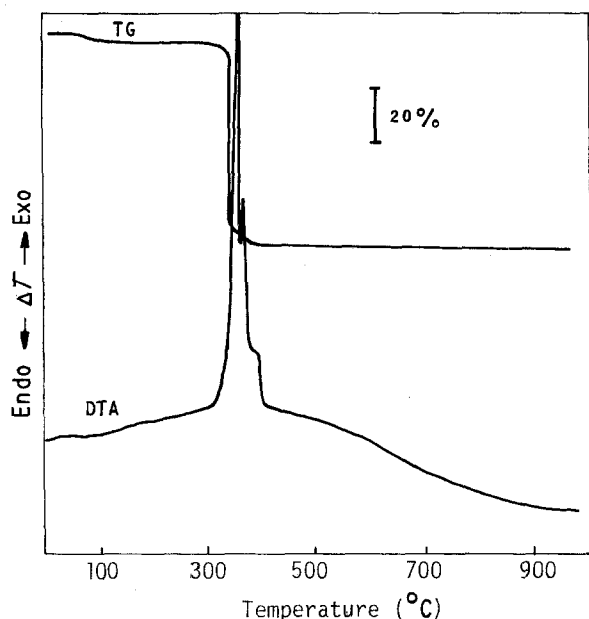


Figure 6 DTA and TG curves of $[\text{Ni}_3\text{Al}(\text{OH})_8] (\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$.

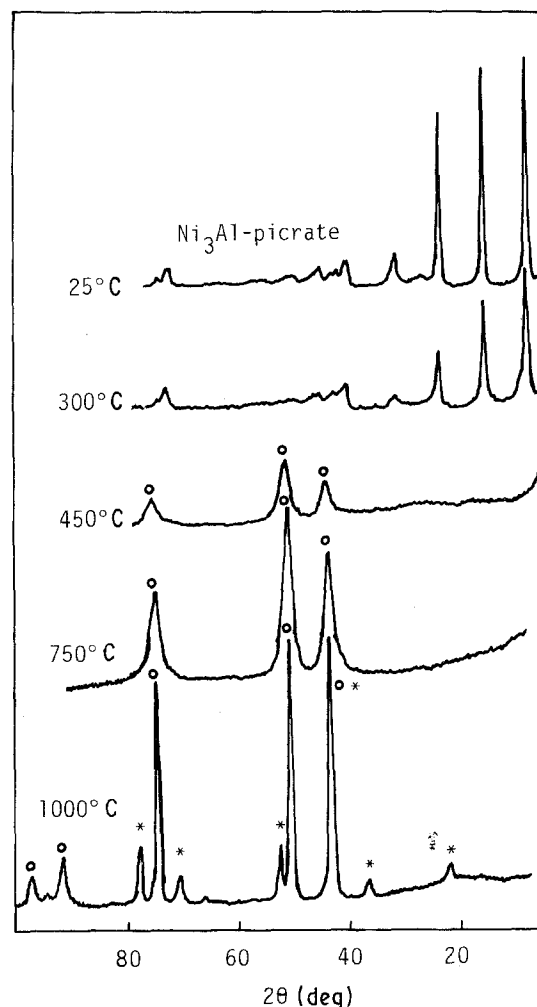


Figure 7 X-ray powder diffraction patterns of $[\text{Ni}_3\text{Al}(\text{OH})_8] (\text{C}_6\text{O}_7\text{N}_3\text{H}_2) \cdot n\text{H}_2\text{O}$ heated at various temperatures. (○) NiO, (*) NiAl_2O_4 .

clearly shows the spacings corresponding to NiO and to spinel.

The decomposition of the Al-Li hydroxypicrate takes place similarly to that of the Ni-Al hydroxypicrate, with an exothermic peak in the DTA curve between 300 and 500°C and the formation of the mixed oxides γ -LiAlO₂ and LiAl₅O₈ above 700°C [17]. The formation of these transitional aluminas with the incorporation of other metal atoms, of considerable general interest, has also been detected in the decomposition of other hydrotalcite-like compounds [18, 19].

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Received 2 February
and accepted 19 February 1990