# Alternative Approach to Incorporation of Nickel into Layered Structure of Mg–Al Double Hydroxides: Intercalation with $[Ni(edta)]^{2-}$ Species

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Coprecipitation reaction of $Mg^{2+}$ and $Al^{3+}$ with pre-formed $[Ni(edta)]^{2-}$ complex ($H_4$edta = ethylenediaminetetraacetic acid) gives rise to a new layered double hydroxide phase.

Layered double hydroxides (LDHs) represent an important class of inorganic materials with many useful properties.[1] In the field of catalysis, they found potential for development of catalyst precursors and catalysts of high surface area, finely dispersed active component(s), various basic and redox properties.[2–5] Ni-containing catalysts are of especial concern as they are considered as an efficient low-cost alternative to supported noble metal catalysts widely used in industrially significant reactions.[6–9]

The traditional way to prepare nickel-containing Mg–Al LDHs involves coprecipitation of Mg(II), Al(III) and Ni(II) cations at neutral to basic pH with counter-ion (usually carbonate). Two-valent nickel isomorphously substitutes $Mg^{2+}$ ions in brucite-like layers giving lamellar structures very similar to Mg–Al LDHs referred also as hydrotalcites.

Our suggested approach completely differs from the above. It is based on two experimental findings. The first deals with the strong ability of LDHs to incorporate and retain multiply charged anions like carbonate or sulfate in their structure.[10] Another one comes from aqueous chemistry of edta which is known to form chelates of 1:1 stoichiometry with many transition metal cations.[11,12] The key feature of such chelates is their high stability in solutions with neutral and moderately high basic pH. Thus, for $[Ni(edta)]^{2-}$ complex, the logarithm of stability constant is 18.62 while for edta chelates of Mg(II) and Al(III) the corresponding log K values are 8.79 and 16.3.[13] These data show that $Ni^{2+}$ ion forms a chelate which is about two orders of magnitude more stable than that of aluminium and much more stable than $[Mg(edta)]^{2-}$ complex. It also implies that when the reaction of coprecipitation of $Mg^{2+}$ and $Al^{3+}$ is to take place in an aqueous solution of preformed $[Ni(edta)]^{2-}$, the dissociation of $[Ni(edta)]^{2-}$ complex and the formation of chelates of Mg and Al will hardly proceed to notable extent.

Summary of experimental details for preparation of Ni-containing LDHs is presented in Table 1. Synthesis of MgAl-Ni(edta) was carried out at pH of 10.5 in order to ensure the complete ionization of the chelating agent to $edta^{4-}$ in aqueous solution.[14] The resultant solid had pale blue color which was fully due to $[Ni(edta)]^{2-}$ species involved. On the contrary, when Ni was introduced together with Mg and Al as cationic species (see entry 2 in Table 1), the precipitate formed was light green in color that is typical of two-valent nickel compounds.

The difference was further strengthened by the results of XRD measurements (Figure 1). As can be seen in figure, diffractogram of MgAl-Ni(edta) shown as pattern A strongly differs from those of reference LDHs (patterns B to D). The presence of three symmetrical peaks at 6.2, 12.2 and 18.6° corresponding to basal spacings *d* of 14.2, 7.2 (as *d*/2) and 4.8 Å (as *d*/3) strongly suggested that the newly synthesized double hydroxide phase has a layered structure. However, the X-ray diffractogram of the sample shows broadened lines which indicated that the crystallinity is distinctly smaller than that of the reference samples. Subtraction of 4.8 Å as of brucite sheet thickness from the maximum calculated *d* value results in a gallery height of 9.4 Å which can be attributed to Mg–Al LDH with compact $[Ni(edta)]^{2-}$ ions residing in the interlayer space.

The results of thermal analysis of MgAl-Ni(edta), three reference LDHs and pure $Na_2Ni(edta)\cdot 2H_2O$[15] are shown in Figure 2. Thermogravimetry (TG) profile recorded for MgAl-Ni(edta) (curve A in Figure 2a) shows that thermal decomposition of sample occurs in two consecutive steps which is typical of Mg-Al LDHs. However, such TG profile is markedly different from those of reference LDHs (compare with curves B to D in Figure 2a) showing especially fast reduction in sample weight at tem-

**Table 1.** Ways to introduce nickel into Mg–Al double hydroxides[a]

| | Starting atomic ratio of coprecipitated cations[b] | Counter-ion (anion X)[c] | Molar ratio X to $Al^{3+}$ | Precipitation pH[d] | Compound formula[e] | Sample legend |
|---|---|---|---|---|---|---|
| 1 | $Mg^{2+} : Al^{3+}$ 3 : 1 | $[Ni(edta)]^{2-}$[f] | 10 : 1 | 10.5 | $[Mg_7Al_2(OH)_{18}][Ni(edta)]$ | MgAl-Ni(edta) |
| 2 | $Ni^{2+} : Mg^{2+} : Al^{3+}$ 1 : 5 : 2 | $CO_3^{2-}$ | 3 : 1 | 10.0 | $[NiMg_5Al_2(OH)_{16}]CO_3$ | NiMgAl-$CO_3$ |

[a]Degassed and deionized water was used throughout the work. Resultant suspensions were stirred at 63 °C for 1 h and then aged without stirring at the same temperature for 18 h. Precipitates were filtered, washed with water and dried in air at 80 °C for 16 h, followed by storage under vacuum in a dessicator at room temperature. [b]Metal nitrates were used as starting compounds. [c]Sodium salts were used. [d]pH of aqueous suspension was controlled by dropwise addition of 1M solution of NaOH. [e]Derived from the results of elemental analysis by ICP emission spectrometry. Water content is not shown. [f]Aqueous solution of $[Ni(edta)]^{2-}$ chelate was prepared by dropwise addition of equimolar amount of Ni(II) nitrate to $Na_4$edta solution prior to the coprecipitation of Mg and Al cations.

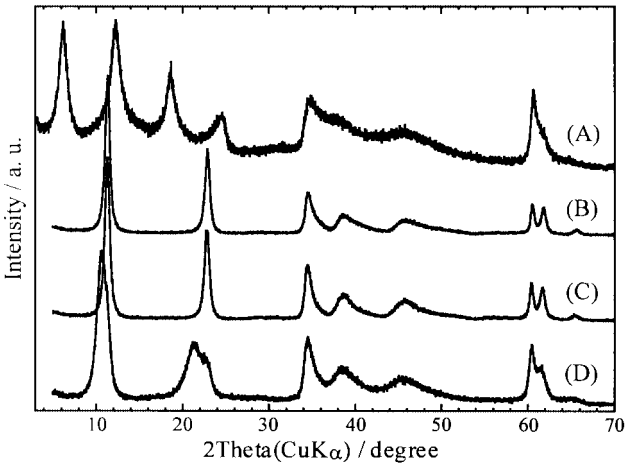


**Figure 1.** Powder XRD patterns of Mg-Al double hydroxides: (A) MgAl-Ni(edta), (B) NiMgAl-$CO_3$, (C) $[Mg_6Al_2(OH)_{16}]CO_3$ and (D) $[Mg_3Al(OH)_8]NO_3$.

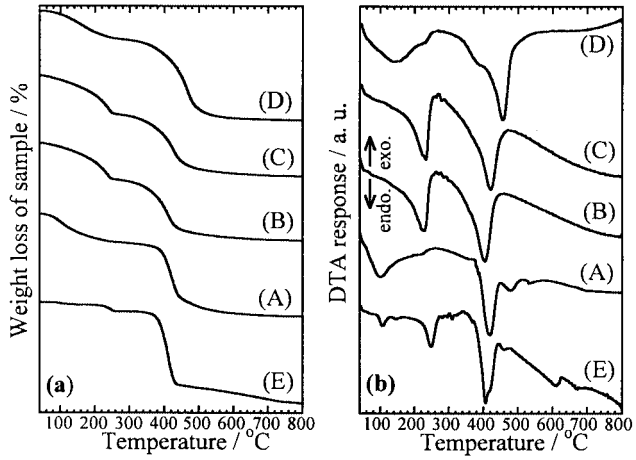


**Figure 2.** Profiles of (a) thermogravimetry and (b) differential thermal analysis for synthesized and reference compounds: (A) MgAl-Ni(edta), (B) NiMgAl-$CO_3$, (C) $[Mg_6Al_2(OH)_{16}]CO_3$, (D) $[Mg_3Al(OH)_8]NO_3$ and (E) pure $Na_2Ni(edta)\cdot 2H_2O$. Samples were heated in $N_2$ flow (20 $cm^3\cdot min^{-1}$) with 10 °C·$min^{-1}$ temperature rate.

peratures of 380 to 440 °C. Very similar behavior in such temperature interval was observed with pure $Na_2Ni(edta)$ as it is shown by curve E in Figure 2a. Differential thermal analysis (DTA) profile for MgAl-Ni(edta) (shown as curve A in Figure 2b) also resembles those of reference LDHs (curves B to D in Figure 2b). It shows two main endothermic peaks centered at 102 and 420 °C. The first one corresponds to the desorption of physisorbed and structural water while the latter is attributed to the dehydroxylation of metal hydroxides (giving water as a product), collapse of LDH structure and decomposition of entrapped $[Ni(edta)]^{2-}$ species releasing $CO_2$ and $NO_X$. Such order of thermal decomposition was confirmed by additional TG–DTA trial performed under He atmosphere with on-line monitoring of effluent gases by ion-selective mass detection. It should be noted that the decomposition of $[Ni(edta)]^{2-}$ species involved into LDH structure proceeded at temperature a little higher than that of pure $Na_2Ni(edta)$ (406 °C) which can be seen from the comparison of curves A and E in Figure 2b. Such an increase in chelate stability can be attributed to interactions of carboxylic functional groups of intercalated $[Ni(edta)]^{2-}$ species with basic MgO formed from Mg hydroxide upon thermal decomposition of Mg-Al LDH. The less intensive endothermic peak at 478 °C may be assigned to some structural changes occurring in MgAl-Ni(edta) after thermal decomposition of both layered structure of double hydroxide and entrapped Ni-containing species.

In summary, the successful synthesis of Mg-Al LDH with nickel involved into lamellar structure as negatively charged edta chelate suggests that the reported approach can potentially be applied to introduce other transition metal cations able to form stable complexes with edta or other similarly functioning chelating agents. In addition to coprecipitation, ion-exchange and rehydration[16] techniques, it widens the set of methods by means of which multicomponent LDHs can be synthesized.

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**References and Notes**

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