Supplementary information

Carbonates stabilize interstratified α/β intermediates in the preparation of nickel hydroxide

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Tab. S1. Synthesis conditions. Nature of the precipitation solutions, composition of the aging system, temperature of aging and drying, phases formed.

			Aging system (mol L^{-1})			aging	drying	phase
sample	receiving bath	pH control	Ni	NO_3	CO_3	T /°C	T/°C	$Ni(OH)_2$
N14-C15-W126	2M NaOH	3M NaOH	0.34	0.67	0.05	25	25	α
N25-C14-W55	2M NaOH	3M NaOH	0.34	0.67	0.05	25	80	α
N02-C03-W06	2M NaOH	3M NaOH	0.34	0.67	0.01	80	80	β
N13-C06-W36	2M NaOH	3M NaOH	0.19	0.38	0.01	25	25	IS+β
N19-C05-W21	2M NaOH	3M NaOH	0.19	0.38	0.01	25	80	IS+β
N01-C02-W06	2M NaOH	3M NaOH	0.19	0.38	0.00	80	80	β
N01-C31-W109	0.1M Na_2CO_3	0.5M NaOH	0.19	0.38	0.06	25	25	α
N02-C21-W78	0.1M Na_2CO_3	0.5M NaOH	0.19	0.38	0.04	25	80	α
N06-C16-W48	0.1M Na_2CO_3	0.5M NaOH	0.19	0.38	0.03	80	80	IS
N02-C14-W28	0.25M Na_2CO_3	2M NaOH	0.31	0.63	0.12	80	80	IS
N00-C40-W129	0.25M Na_2CO_3	3M NaOH	0.34	0.67	0.13	25	25	α
N02-C16-W37	0.25M Na_2CO_3	3M NaOH	0.34	0.67	0.13	80	80	IS

Samples denomination by composition: percent molar ratios NO_3/Ni (N), CO_3/Ni (C) and interlayer water/Ni (W)

Table S2. Results of nitrogen and carbon analysis and thermogravimetry

sample	Flash C-N analysis			TG data	
	N%	C%	H%	mass loss % 200° C	mass loss % final
N14-C15-W126	1.79	1.61	2.35	20.7	43.3
N25-C14-W55	3.08	1.52	2.28	9.7	35.1
N02-C03-W06	0.31	0.37	2.22	1.1	21.6
N13-C06-W36	1.75	0.76	2.02	6.4	30.8
N19-C05-W21	2.64	0.63	1.97	3.5	28.3
N01-C02-W06	0.20	0.28	2.16	1.1	21.2
N01-C31-W109	0.16	3.24	2.48	17.1	39.0
N02-C21-W78	0.25	2.30	2.56	12.8	35.4
N06-C16-W48	0.80	1.90	2.10	8.4	29.9
N02-C14-W28	0.31	1.66	2.03	3.8	25.0
N00-C40-W129	0.00	3.80	2.94	18.3	41.0
N02-C16-W37	0.20	1.85	2.40	6.3	28.0

Interpretation of the XRD pattern of interstratified $Ni(OH)_2$

The study of the diffraction pattern of mixed layered materials has been early developed in the field of clays, where several phases with compatible structure in the *ab* plane can frequetly be formed together. The xrd pattern of the mixed material strongly depends on the type and ordering of the layer stacking. In the case of a physical mixture, *viz*. the superposition of oriented individual crystallite of two different phases, the pattern will essentially correspond to the addition of the patterns of the two phases. In the case of the regular alternation of layers of two phases (degree of ordering $R = 1$), a superstructure will be formed, with 001 spacing corresponding to the sum of the 001 spacings of the two phases. Additional reflections will be formed, defined as rational, as their spacings obey the Bragg law.

In the case in which layers of two phases are randomly superposed ($R = 0$), still maintaining common parallel boundaries and good alignment in the 001 direction, the X-rays waves from the components interfere with each other and a composite pattern is produced, which differs from a physical mixture and does not form an ordered superstructure. If the stacking sequences are not periodic, the composite reflections do not follow the Bragg law and are defined as irrational. Methods to calculate the pattern profiles in these cases have been developed, as a function of the degree of order and of the position of the atoms in each layer, and information on appropriate methods and programs is available in the literature cited at the bottom of this section. Their application to IS-$Ni(OH)_2$, formed by interstratification of α- and β-$Ni(OH)_2$, is complicated by incertitudes about the degree of hydration and the position of anions in the α-$Ni(OH)_2$ phase.

However, The position of the compromise reflection, which results from the interference of the patterns of the alpha and beta phases, can be calculated just from the position of the reflections of the parent phases and their ratio, as shown by Méring in 1949. In the general case of the random interstratification of A and B phases, the position of the compromise reflection will be

1) $d_{ave} = x\, d_A + (1-x)\, d_B$

Where $x = A / (A+B)$ is the relative amount of the phases. In the case of IS-$Ni(OH)_2$, we have two compromise reflections, resulting from the interference of d(001) of β-$Ni(OH)_2$ with, respectively, d(001) and d(002) of α-$Ni(OH)_2$ (see Fig. S1). The labelling of the resulting reflections, as systematised by Bailey, indicates the component contributions separated by a slash, with the smaller spacing first. So, we have to define two composite reflections, 001(β-$Ni(OH)_2$)/001(α-$Ni(OH)_2$) and 002(α-$Ni(OH)_2$)/001(β-$Ni(OH)_2$) and we have to write twice the equation (1) as

2) $d_{001/001} = x\, d_{\alpha 001} + (1-x)\, d_{\beta 001}$

3) $d_{002/001} = x\, d_{\beta 001} + (1-x)\, d_{\alpha 002}$

We have no a priori knowledge of the hydration level and the cell parameter of α-$Ni(OH)_2$ but we known d(001) of β-$Ni(OH)_2$ and the position of the compromise reflections. We can write the ratio between d(001) and d(002) of α -$Ni(OH)_2$ as

4) $d_{\alpha 001} = 2\, d_{\alpha 002}$

The solution of the system of the three equations (2), (3), and (4) provides us with the values of the three unknowns $d_{\alpha 001}$, $d_{\alpha 002}$, and x, *viz.*the interlayer spacing of α-$Ni(OH)_2$ and the fraction of its amount in the interstratified material.

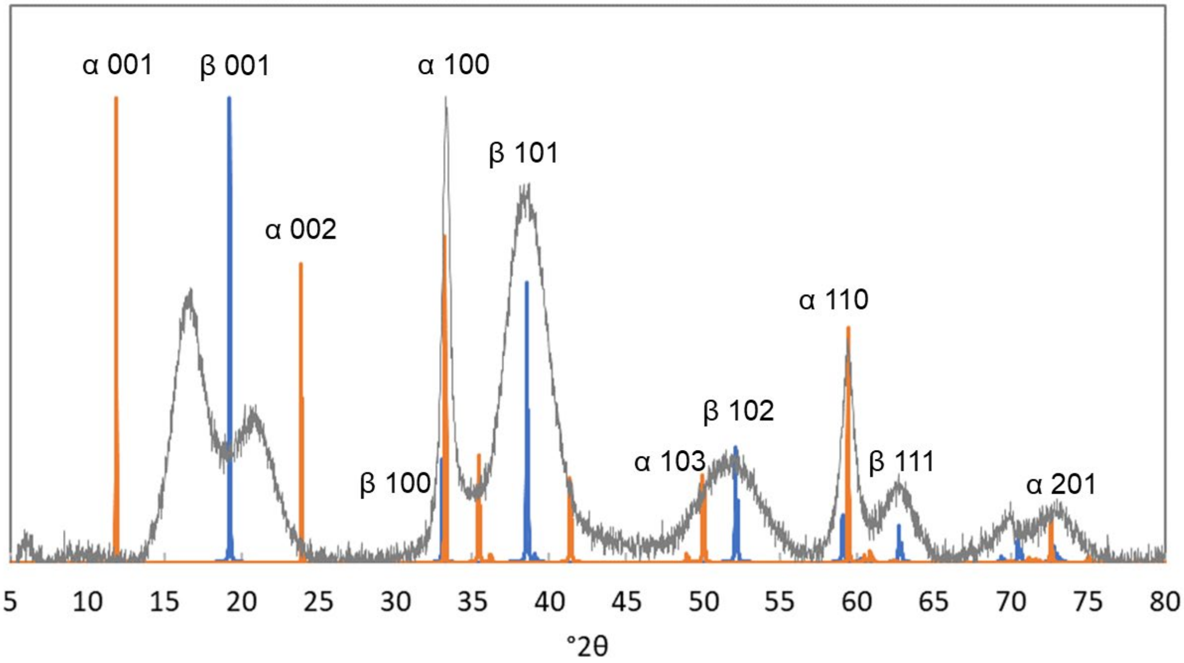

Fig. S1. XRD pattern of mixed-layered α/β-$Ni(OH)_2$, $Ni(OH)_{1.66}(NO_3)_{0.2}(CO_3)_{0.16}\cdot 0.37\ H_2O$, R0, 38 % α, and the locations of the reflections for pure parent phases.

Useful literature:

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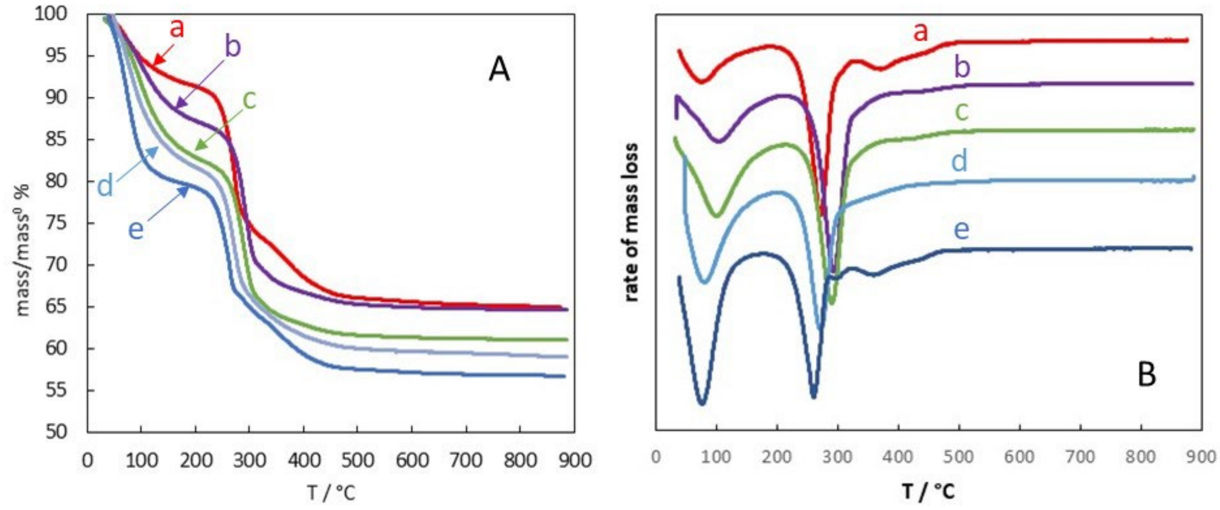

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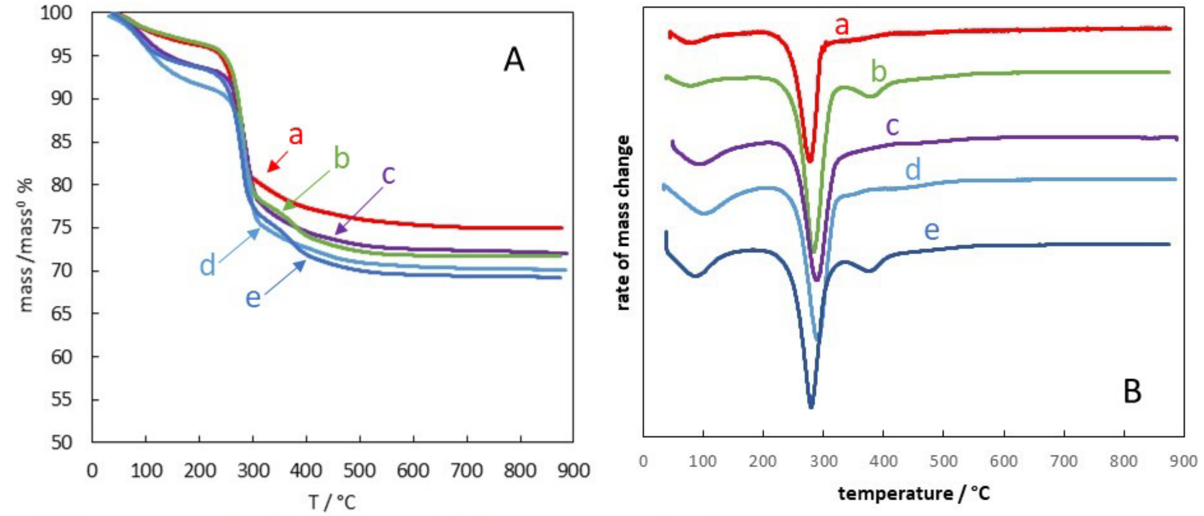

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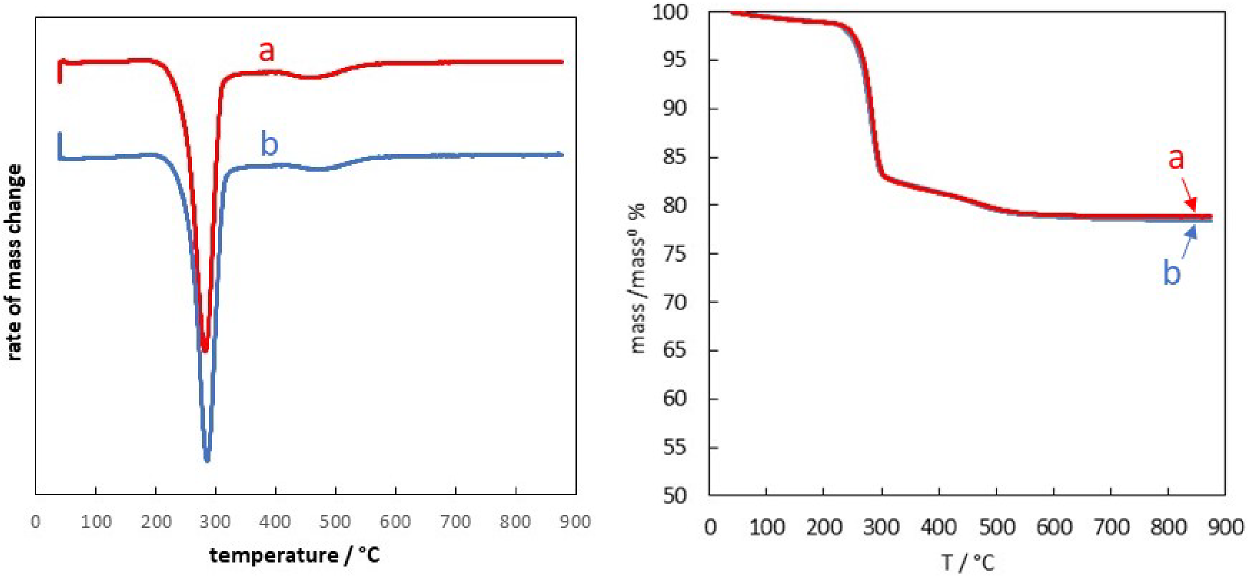

Fig. S4. TG and DTG traces of β-$Ni(OH)_2$ N02-C03-W06 (a), N01-C02-W26 (b).