

## Preparation and Characterization of Organic–Inorganic Layered Nanohybrid, Hydroxyl Double Salts (HDSs)—Isomer Separation via Preferential Intercalation into Layered Framework

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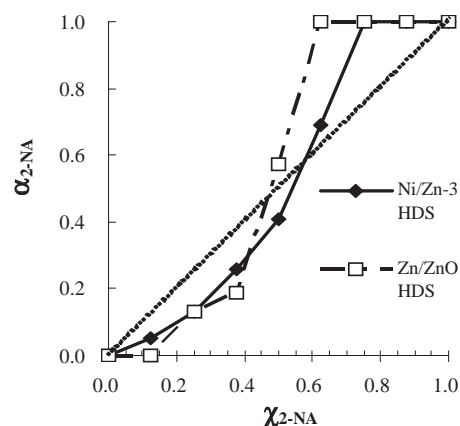
A novel attempt in exploring the isomer separation capability of Hydroxyl Double Salts (HDSs), layered nanohybrids is conducted via competitive intercalation. Typical Zn HDS and new formulated Ni/Zn type HDSs demonstrated unique but reverse intercalation preference towards an equal mole isomeric mixture solution of 1-naphthoate and 2-naphthoate anions solution. The research successfully exemplified the feasibility of controlling the intercalation chemistry of HDSs by formulating their metal composition.

Hydroxyl Double Salts (HDSs) and Layered Double Hydroxide (LDH) are two layered nanohybrids which have unique intercalation chemistry,<sup>1,2</sup> a subfield of the host–guest chemistry. Previous studies indicated two well-characterized classes of HDSs compounds, Zn and Cu types.<sup>3</sup> The general formulae of Cu type and Zn type are  $M_2(OH)_3A^-$  ( $M = Cu, Co,$  and  $Ni$  in tetrahedral environment) and  $M_3(OH)_8(A^-)_2 \cdot nH_2O$  ( $M = Zn$  in octahedral arrangement), respectively. Between brucite interlayers,  $A^-$  anion exists as free ion in Zn-HDSs but in coordinated form of Cu-HDSs. Though mixed-metal-type HDSs have been synthesized and analyzed structurally, their intercalation chemistry remains unexplored.<sup>4</sup> For LDH, enormous researches have been carried out in its application as catalyst, absorber, anion exchanger, isomer separation medium, and gene carrier system.<sup>5–9</sup> However, effort on HDSs remains scarce. In this study, selective anion exchange characteristics of mono and mixed-metal types HDSs are discussed and feasibility studies on controlling the intercalation affinity of the HDSs are presented.

Zn and Ni/Zn types HDSs, as host compounds, are synthesized by using metal salt–metal oxide method as reported in the literature.<sup>10</sup> Basal spacing and metal composition of each HDS are characterized by powder X-ray diffraction (PXRD) and inductive couple plasma spectrometry (ICPS) techniques, separately. Studied guests are 1-naphthoic (1-NA) and 2-naphthoic (2-NA) acids. 0.1 g of HDSs, at optimized host–guest ratio 1:2 (by mole), is reacted with 20 mL (7:3 of acetonitrile: distilled water by volume ratio) neutralized isomeric mixture solution

of 1-NA and 2-NA (totally 0.1 g) anions. Eight mixture combinations of the guest anions are analyzed, from ratio 8:0 till 0:8 with an interval of 0.125. Intercalation is conducted at 65 °C for 8 h. Then, time-resolved PXRD analysis is carried out to characterize the changing interlayer spacing of the intercalates. Moving on, deintercalation step is performed quantitatively by adding diluted hydrochloric acid and followed by acetone to the intercalate powder in order to extract and dry the intercalated naphthoic acids for <sup>1</sup>H NMR quantitative analysis.

Table 1 tabulated the ICP and PXRD results of the synthesized HDSs. As characterized, metal composition of the formed Ni/Zn type HDSs is substantially varied from the theoretical composition, for first 4 Ni/Zn type HDSs. As the maximum Ni ratio is only 53–54%, regardless of the used metal composition; this novel Ni/Zn type HDSs is postulated to have a different but specific brucite microstructure<sup>4</sup> vis-à-vis that of Zn-HDSs. This postulation is further confirmed by the drastic change in basal spacing of the synthesized Ni/Zn type HDSs, between samples Ni/Zn-7 and Ni/Zn-5. As the basal spacing is almost constant

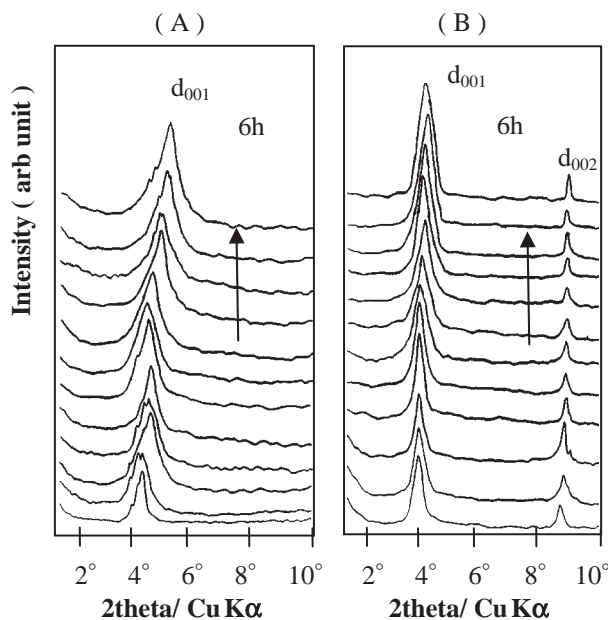


**Figure 1.** Plot of  $\alpha_{2-NA}$  (mole fraction of intercalated 2-NA isomer in HDSs) vs  $\chi_{2-NA}$  (mole fraction of 2-NA isomer in the starting solution of guests).

**Table 1.** Chemical formulae and basal spacing of parent HDSs, as well as new basal spacing of intercalated HDSs

Samples	Ni:Zn ratio		Basal spacing/Å	Chemical formulae of the parent synthesized compounds	Intercalation compound/Å	
	Theoretical <sup>a</sup>	Experimental <sup>b</sup>			1-NA	2-NA
Ni/Zn-1 HDS	0.90:0.10	0.54:0.46	9.19	(Ni <sub>0.54</sub> Zn <sub>0.46</sub> )(OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	20.82	20.53
Ni/Zn-3 HDS	0.70:0.30	0.53:0.47	9.15	(Ni <sub>0.53</sub> Zn <sub>0.47</sub> )(OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	20.83	22.29
Ni/Zn-5 HDS	0.50:0.50	0.34:0.66	9.24	(Ni <sub>0.34</sub> Zn <sub>0.66</sub> )(OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·XH <sub>2</sub> O	21.02	23.99
Ni/Zn-7 HDS	0.30:0.70	0.19:0.81	9.69	(Ni <sub>0.19</sub> Zn <sub>0.81</sub> )(OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	21.53	24.66
Ni/Zn-9 HDS	0.10:0.90	0.09:0.91	9.79	(Ni <sub>0.09</sub> Zn <sub>0.91</sub> )(OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·XH <sub>2</sub> O	21.12	22.79
Zn/ZnO-HDS	0.00:1.00	0.00:1.00	9.92	Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2.1H <sub>2</sub> O	21.32	25.22

<sup>a</sup>Initial metal composition used in the synthesis of HDSs. <sup>b</sup>Actual reacted metal composition in synthesized HDSs.

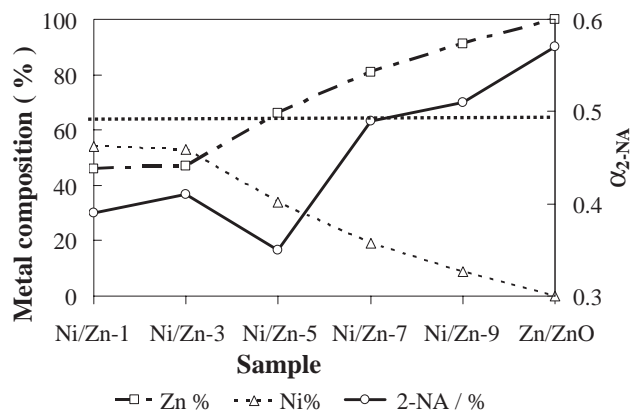


**Figure 2.** Time resolved XRD patterns, from 0.5 to 6 h at an interval of 30 min, of (A) Ni/Zn-3 and (B) Zn types HDSs during intercalation with equal mole isomeric mixture solution of naphthoate anions. XRD spectra from 7 to 8 h are not included as no change is observed.

for the first 3 samples, Ni/Zn-3 is singled out to represent Ni/Zn type HDSs for further competitive intercalation<sup>9,11,12</sup> analyses. Basal spacing of 1-NA or 2-NA intercalates, of each sample, is characterized accordingly to identify representative peak of the respective guests.

Figure 1 is the <sup>1</sup>HNMR result of the deintercalated mole fraction of 2-NA guest, during competitive anion exchange of HDSs with an isomeric mixture solution of both naphthoate guests at various ratios.<sup>13</sup> Dotted line in the curve represents the theoretical result in the case of no preferential intercalation. Based on the result, we learnt that 1-NA anion is exclusively intercalated vis-à-vis 2-NA at its high mole fraction,  $\chi_{2NA}$  lower than 0.5. Interestingly, at  $\chi_{2NA}$  higher than 0.6, 2-NA anion is predominantly intercalated. At  $\chi_{2NA} = 0.5$ , 1-NA is selected as the preferred guest in Ni/Zn-3 versus 2-NA of Zn type HDSs. To understand this unique phenomenon, time resolved XRD patterns are collected at an interval of 30 min, from 0.5 to 8 h during intercalation with equal mole isomeric mixture solution of guests. Result is shown in Figure 2.

For Ni/Zn-3, the first emerging peak, equal to new interlayer spacing of the intercalated HDSs, is detected at 22.5 Å, a peak of purely 2-NA intercalated scenario. Then, the peak shifts to and fro between 22 and 21 Å, before settled down at 20.8 Å which signals exclusive intercalation of 1-NA anion. This trend revealed that readjustment in orientation and arrangement of intercalated 2-NA anion, due to increment of 1-NA anion, took place before 1-NA anion won out as the preferred guest. On the other hand, a constant peak, at around 24.5 Å is detected through out the intercalation reaction, demonstrating predominant intercalation of 2-NA anion for Zn-HDSs. Based on these XRD patterns, coupled with the fact that Ni/Zn and Zn types HDSs have different brucite microstructure; we believed that different orientation of 1-NA and 2-NA anions in interlayers



**Figure 3.** Relationship of metal composition with intercalation affinity of 2-NA isomer in equal mole isomeric mixture solution of 2-NA and 1-NA anions.

of HDSs and varied interaction of host (brucite)–guest are reason behind the alteration in selection of the preferred guest from Ni/Zn-3 to Zn types HDSs.

As such, relationship between preferential intercalation of HDSs and their metal compositions is further analyzed. Figure 3 illustrated the result of this analysis. As shown, the intercalation affinity of 2-NA anion, quantified by  $\alpha_{2NA}$  increased with the ratio of Zn cation, except sample Ni/Zn-5. Below 80% of Zn content, intercalation affinity of 2-NA is inferior to that of 1-NA anion but above this Figure, 2-NA is predominantly intercalated. Lower intercalation affinity of 2-NA for sample Ni/Zn-5 could be attributed to drastic change in brucite microstructure, as mentioned early.

Considering these results, we could draw a conclusion that intercalation character of a HDS is dependent on its metal composition. In other words, intercalation preference of HDSs is controllable by fine-tuning their metal compositions. Hence, by upfront design of microstructure of a HDS; this nanohybrid could be potentially used as an agile isomer separation medium.

#### References and Notes

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- See Supporting Information for characterization in detail.