The Effect of Aging Time on the Properties of Nickel-Aluminium-Carbonate Layered Double Hydroxide Synthesized by Hydrothermal Method

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Layered double hydroxide of nickel-aluminium with carbonate as an interlamellar anion was synthesized by hydrothermal technique (HT) at various aging times, 1 d, 2 d, and 4 d. For comparison, the same material was also prepared by conventional method (CM) using a shaker oil bath at 70 °C and aging for 18 h. The atomic ratio $r = n(\mathrm{Ni}^{2+})/n(\mathrm{Al}^{3+})$ of 4 was chosen in this study. Hydrothermal treatments performed on the aged samples enhanced the crystallinity, surface area, and the Ni content of the resulting materials. The r value of 3.2 was obtained for the sample prepared by CM technique compared to 3.5 for HT technique. Surface area analysis showed that the latter has a higher surface area than the former, 96 compared to around 22 $\mathrm{m}^2\,\mathrm{g}^{-1}$. No aging time-surface area-dependent property can be clearly observed for the materials synthesized by HT technique. Pore size distribution shows that CM technique produced a sample with a sharp single peak centred at around 35 $\mathring{A}$. A more broad pore size distribution was observed when the hydrothermal synthesis was adopted and the sample was aged for a day. On the other hand, a bimodal one was observed when the aging time increased to two days. Further increase of aging time to 3 d resulted in the dominance of the pore size distribution at 90 $\mathring{A}$.

Layered double hydroxide (LDH) is a component of anionic clay [1]. A general formula for LDH or the so-called hydrotalcite-like compound can be written as $[\mathrm{M(II)}_{1-x}\mathrm{M(III)}_x(\mathrm{OH})_2]^{x+}[\mathrm{A}^{y-}_{x/y}] \cdot m\mathrm{H}_2\mathrm{O}$, where M(II) is any divalent ion and M(III) is any trivalent ion, A^{y-} is any anion, such as carbonate, sulfate, chloride, etc. For synthetic LDH, the value of x can be in the range of 0.15—0.34 [2].

LDH can be synthesized by using coprecipitation method in which two solutions of M(II)/M(III) and $\mathrm{NaOH}/\mathrm{Na}_2\mathrm{CO}_3$ are slowly mixed, followed by aging at elevated temperature for 18 h [3]. Alternatively, high-temperature hydrothermal method can be used to achieve different properties of the resulting materials [1]. It was shown that a sequential precipitation of ion occurs during the formation of the Ni/Al LDH. The first precipitate is constituted by the $\mathrm{Al(OH)}_3$ at pH at about 4, and then most of the nickel is precipitated in the mixed hydroxide at pH at about 6 [4] and finally Ni precipitated at much higher pH [5]. The crystallinity and the lattice parameters of the Ni/Al LDH compounds were found to be significantly affected by the composition. The thermal stability of these materials increased with the decrease in Ni/Al atomic ratio [6].

Apart from methods of synthesis, works on the applications of Ni/Al LDH as a catalyst were also done. The Ni-containing layered double hydroxide was used as a soda substitute in the selective aldol condensation of acetone into diacetone alcohol. It was found that the loss of the lamellar structure was the main cause of the catalyst deactivation [7]. Similarly, this material was also used as catalysts for the dehydrogenation of ethylbenzene to styrene. The catalyst was found to be active and highly selective to styrene. With vanadium-containing oxides, a selectivity of 98 % in styrene was achieved with a conversion of 38 % in ethylbenzene [8]. The thermally calcined Ni/Al LDH was also used as catalyst for decomposition of nitrous oxide into nitrogen and oxygen. It showed good activity even at high temperature [9].

Here we discuss the work on the hydrothermal synthesis of nickel-aluminium carbonate LDH (NACAL) and the characterizations of the resulting material. The work focused on the effect of aging time on the properties of the resulting materials, in particular the textural properties, and if hydrothermal method can be used to synthesis of NACAL with relatively pure lamella phase with high r values. Comparison with the properties of the sample prepared by the conventional

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method was also done and will be discussed.

EXPERIMENTAL

Powder X-ray diffraction patterns were recorded on a Shimadzu XRD6000 powder diffractometer unit using CuK_α (filtered) radiation ($\lambda = 1.54$ $\mathring{A}$) at 40 kV and 20 mA. The Ni/Al ratio of the resulting NACALs was determined by an inductively coupled plasma-emission spectrometry (ICP-ES), using a Labtest Equipment Model 710 Plasmascan sequential emission spectrometer. Fourier transform infrared (FTIR) spectra were recorded using a Perkin—Elmer Model 1725X spectrophotometer in the range of 400—4000 cm^{-1}. TGA and DTG thermal analyses of powdered samples were recorded up to 1000 °C, at a heating rate of 10 °C min^{-1} in a flow of N_2 gas using a Perkin—Elmer TGA 700 thermal analysis system. The surface area and pore size distributions were carried out by employing the BET N_2 adsorption-desorption method at 77 K using a Micromeritics ASAP 2000 porosimeter.

Layered Double Hydroxide

NACAL was prepared by standard coprecipitation method [3]. A solution of $Ni(NO_3)_2$ and $Al(NO_3)_3$ was prepared by dissolving the salts in deionized water. The initial atomic ratio, r_i ($r = n(Ni^{2+})/n(Al^{3+})$) of the solutions was adjusted to 4 by adjusting the concentration of the salts in the mother liquor. Another solution of NaOH and Na_2CO_3 was also prepared, into which the Ni/Al solution was slowly added. The resulting precipitate was stirred and aged at 70 °C for 18 h in a shaker oil bath, cooled at room temperature, filtered and washed several times with deionized water, dried at 80 °C in an oven overnight and kept in a sample bottle for further characterizations.

Similar method was adopted for hydrothermal technique. However, at the end of NaOH/Na_2CO_3 addition, instead of aging for 18 h at 70 °C, the resulting solution was kept in a teflon liner in a Parr bomb for 1, 2, and 4 d, and heated in an oven at 140 °C. The sample was then cooled at room temperature, filtered and washed several times with deionized water, dried at 80 °C in an oven overnight and kept in a sample bottle for further characterizations.

RESULTS AND DISCUSSION

Powder X-ray diffraction (PXRD) patterns for NACALs prepared by using conventional method (NACAL0) and hydrothermal method aging for 1 d (NACAL1), 2 d (NACAL2), and 4 d (NACAL4) are shown in Fig. 1. The basal spacing for all the samples is essentially similar of around 7.8—7.9 $\mathring{A}$, summarized in Table 1. As shown in the figure, all of them afford well-crystallized hydrotalcite-like mate-
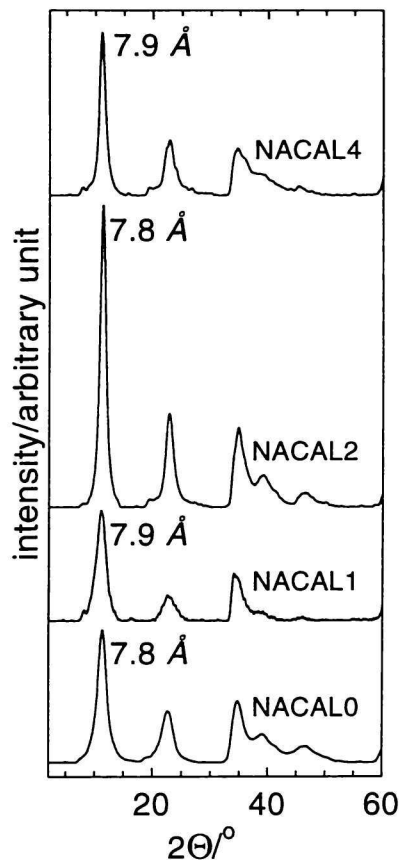

Fig. 1. Powder X-ray diffraction patterns for samples synthesized by the conventional method, 18 h in a shaker oil bath (NACAL0) and hydrothermal method at various aging times, 1 d (NACAL1), 2 d (NACAL2), and 4 d (NACAL4).

rial (JCPDS 22-700). In the hydrothermal method, the sample aged for 2 d (NACAL2) shows the highest intensity of the 003 peaks at around 7.8 $\mathring{A}$, compared to the other two. This peak is also stronger in intensity than NACAL0, indicating a better stack of Ni-Al layered inorganic hydroxide obtained for this particular sample.

Table 1 compares the Ni/Al ratio of NACALs. As shown in the table, the final Ni/Al ratio, r_f, *i.e.* the ratio in the resulting layered inorganic structure, is 3.2 and 3.5, for NACAL prepared by hydrothermal method and conventional method, respectively. The initial value (r_i), *i.e.* the value at the beginning of the reaction in the mother liquor is 4. A slightly lower r_f value than r_i indicates that less amount of Ni^{2+} ion in the mother liquor was used for the formation of the positively charged layers of the inorganic metal double hydroxide during the formation of LDH.

Fig. 2 shows the FTIR spectra for NACALs. All of them show a broad strong, hydroxyl stretching band at around 3000—3800 cm^{-1} and the two strong carbonate bands at around 1450 cm^{-1} [10]. The lower values of the hydroxyl stretching band in NACALs
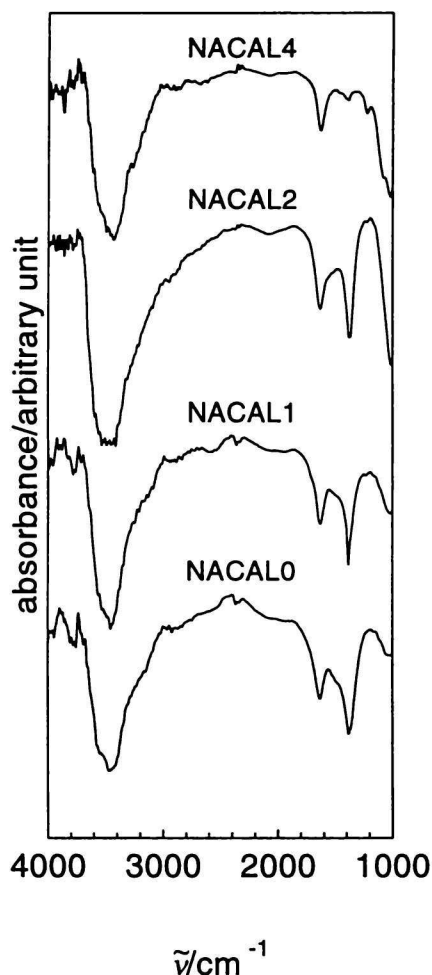
Fig. 2. FTIR spectra for samples synthesized by the conventional method, 18 h in a shaker oil bath (NACAL0) and hydrothermal method at various aging times, 1 d (NACAL1), 2 d (NACAL2), and 4 d (NACAL4).
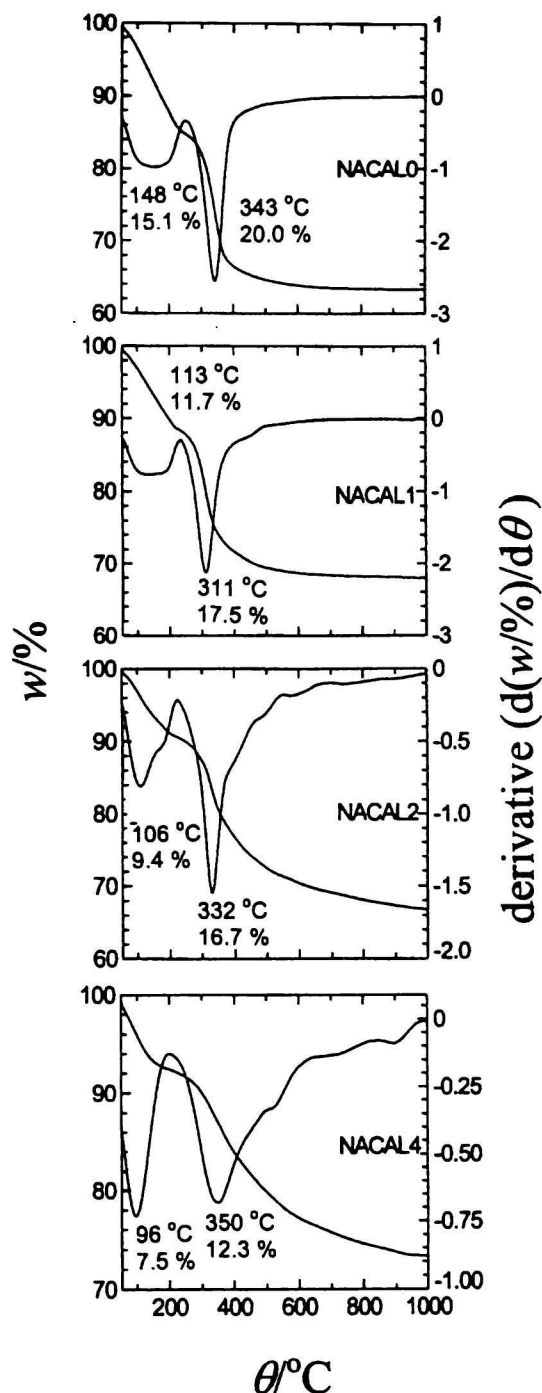

Fig. 3. DTA and DTG thermograms for samples synthesized by the conventional method, 18 h in a shaker oil bath (NACAL0) and hydrothermal method at various aging times, 1 d (NACAL1), 2 d (NACAL2), and 4 d (NACAL4).

compared to that of free OH groups (> 3650 cm^{-1}) indicate that all the OH groups are involved in hydrogen bonding with the Ni/Al double metal hydroxide interlayer [11].

The absence of a strong absorption band at around 1385 cm^{-1} indicated that the samples are free from nitrate, the coanion present in the mother liquor, as nitrate salts were used for the source of metal ions, nickel and aluminium. This shows that carbonate is more readily intercalated compared to nitrate into the interlayer space of the Ni/Al LDH.

The TGA and DTG for NACALs are shown in Fig. 3. The results of various mass losses and DTG peaks are reported in Table 1. In general, the TGA/DTG thermograms for all the samples show a two-step mass loss. The first one occurred in the temperature range of 55—200 °C with a temperature maximum (θ_{max}) at around 100 °C, as shown by its corresponding DTG thermogram. This mass loss is attributed to surface or physically adsorbed water or in-

terlayer water. The second mass reduction is basically due to dehydration process together with the evolution of carbon dioxide [12]. This is observed at θ_{max} at around 300 °C in the temperature range of around 200—450 °C.

NACALs prepared by HT technique showed that

Table 1. Comparison of the Properties of Ni-Al-carbonate LDHs Synthesized by Conventional and Hydrothermal Technique

Parameter	Technique			
	Conventional	Hydrothermal		
Samples' label	NACAL0	NACAL1	NACAL2	NACAL4
Aging time/h	18	24	48	96
Basal spacing/$\mathring{A}$	7.8	7.9	7.8	7.9
r_f	3.5	3.2	3.2	3.2
Thermal property				
θ_{max1}/°C	148	133	106[a], 90 s[b]	96
θ_{range1}/°C	50—250	50—235	50—225	50—200
$w(1)$/%	15.1	11.7	8.3[a], 1.1[b], 9.4[t]	7.5
θ_{max2}/°C	343	311	332	350
θ_{range2}/°C	250—450	235—430	225—450	200—490
$w(2)$/%	20.0	17.5	16.7	12.3
θ_{range3}/°C	450—1000	430—1000	450—1000	490—1000
$w(3)$/%	1.7	2.9	7.1	7.8
$w(\text{total } (1+2))$/%	35.1	29.2	26.1	19.8
Surface area and porosity				
BET surface area/(m^2 g^{-1})	22	92	105	93
BJH desorption pore volume/(m^2 g^{-1})	0.04	0.20	0.21	0.16
BJH desorption average pore/$\mathring{A}$	41.3	49.4	55.3	54.5

s – shoulder, t – total value, a – value for a, b – value for b.
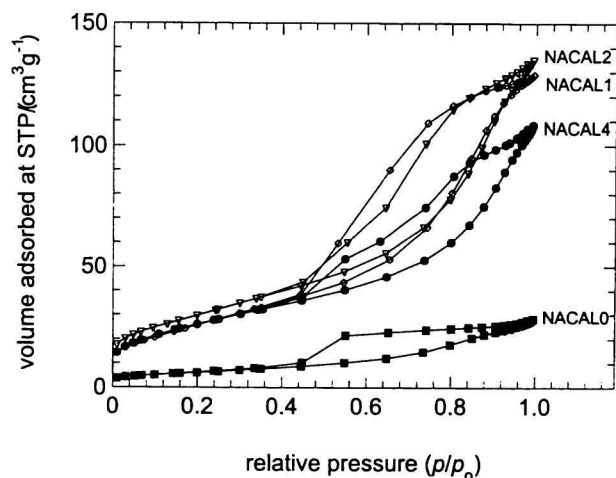

Fig. 4. Adsorption-desorption isotherms of nitrogen at 77 K for the samples synthesized by the conventional method, 18 h in a shaker oil bath (NACAL0) and hydrothermal method at various aging times, 1 d (NACAL1), 2 d (NACAL2), and 4 d (NACAL4).

the first-step mass loss and θ_{max} decreased with aging time. The corresponding values for the sample prepared by the conventional method were found to be higher than the values for the samples prepared by the hydrothermal method. This is shown in Table 1 and Fig. 4. This indicates that NACALs prepared by HT technique revealed in less percentage of surface or

physically adsorbed water or interlayer water and the water content decreased with the aging time.

A decrease in percentage mass loss with aging temperature of the sample prepared by hydrothermal method was also observed for the second-step mass loss but with the increase of θ_{max}. Noteworthy also is that the DTG curves became broader as the aging time increased, and shoulders were also observed, especially for NACAL2 and NACAL4. This is probably due to the decomposition of the remaining NO_3^- from the sample. In addition, the existence of CO_3^{2-} could not be ruled out as the CO_3^{2-} absorption band is hardly distinguishable from the NO_3^- bands in the FTIR spectra given in Fig. 2. As it is known that NO_3^- is more stable than CO_3^{2-}, and obviously decomposed at higher temperature, then the second mass loss should also include the decomposition of NO_3^-, which is corresponding to the third mass loss in Table 1. Therefore the total mass loss becomes 20.4, 23.8, and 20.1 % for NACAL1, NACAL2, and NACAL4, respectively. This indicates that the mass loss of the samples prepared by hydrothermal method is more or less similar to the one prepared by conventional method, NACAL0.

As shown in Table 1, there is an increase of θ_{max} for the decomposition of CO_3^{2-}, from NACAL1 to NACAL4. Detailed observation of Fig. 1 also shows the presence of additional XRD lines with low intensity at 2Θ around 19.5°, near to the 006 reflection at 2Θ around 22.8° for NACAL2 and NACAL4. The lat-

ter sample also exhibits weaker CO_3^{2-} bands in the FTIR spectrum (Fig. 2), and a very specific shape for the TG/DTG profile (Fig. 3). These results suggest that a Ni-containing phase is possibly formed in the samples prepared by hydrothermal method, in addition to the lamellar phase. Therefore, the increase in the Ni/Al ratio, r_f, from NACAL1 to NACAL2 and NACAL4 is presumably due to this phase.

Also shown in Table 1 is that the decomposition temperature of CO_3^{2-} is increased from 311 to 332 and 350 °C, for NACAL1, NACAL2, and NACAL4, respectively. This is due to the enhancement of the electrostatic attraction between the layers and the anions.

The presence of a Ni-containing phase could also explain the trend in intensity of the XRD lines, i.e. it is decreased from NACAL2 to NACAL4, which is due to the formation of high amount of the additional phase. Therefore, an additional phase is likely to be formed in the samples prepared by the hydrothermal method.

The surface area and porosity of the NACALs were studied by nitrogen adsorption-desorption method. The nitrogen adsorption-desorption isotherms for the samples are shown in Fig. 4. In general, all of the adsorption isotherms are of Type II in the classification of *Brunauer et al.* [13], representing unrestricted multilayer adsorption on a heterogeneous mesoporous material.

However, at a close look at the isotherm, especially at low relative pressure, it is clear that NACAL0 actually has a lower adsorption capacity, compared to the other three samples prepared by the hydrothermal method. This indicates that the former has a lower surface area than the latter.

Also shown in the figure are the hysteresis loops of adsorption-desorption isotherms. For all of them, the hystereses are essentially of Type B, characterized by open slit-shaped capillaries with a parallel wall [14]. Although the Type II isotherm for NACAL0 was retained in NACALs prepared by the hydrothermal method, however, wider hysteresis loops were observed. This is shown in Fig. 4. A wider hysteresis loop indicated that although the mesoporous structure was retained, the pore size distribution changed and this will be discussed in the following section.

Fig. 5 shows plots of BJH desorption pore size distribution for NACALs. As shown in the figure, a sharp single-peaked pore size distribution was observed for NACAL0, centred at around 35 Å. However, the character of a sharp single-peaked pore size distribution in NACAL0 changed to a broad one when hydrothermal synthesis was introduced by aging the sample for one day (NACAL1). Longer aging time (2 d) resulted in a bimodal pore size distribution with an additional broad high-intensity distribution at 90 Å, as observed for NACAL2. Further increase in the aging time to 4 d, resulted in the observation of a broad low intensity of the pore size distribution at 90 Å, as shown for
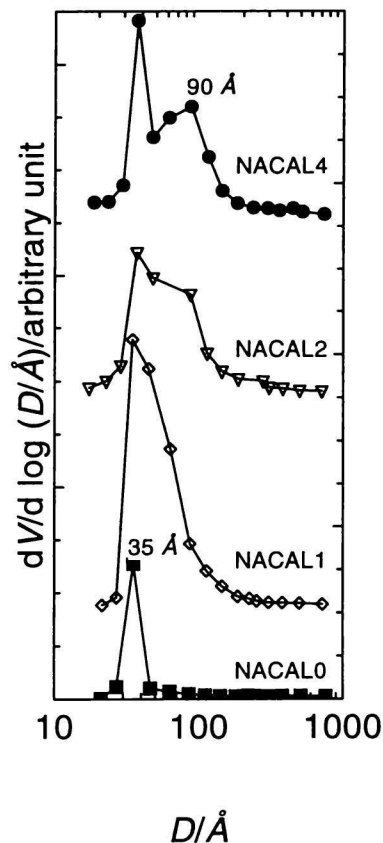

Fig. 5. Pore size distribution for samples synthesized by the conventional method, 18 h in a shaker oil bath (NACAL0) and hydrothermal method at various aging times, 1 d (NACAL1), 2 d (NACAL2), and 4 d (NACAL4).

NACAL4. At the same time the single-peaked pore size distribution centred at around 35 Å became more pronounced. The formation of more mesopores during the aging process of the mother liquor for the hydrothermal method is thought to be the reason why a bimodal pore size distribution was obtained. As the aging time increased, the formations of interstitial pores in the crystallite became more important. As more crystallites grow, the voids between them became more diverse in size, resulting in a broader pore size distribution. The formation of these voids proceeded with time, resulting in the more pronounced pore size distribution at 90 Å. This probably explained why a change from a single mode to a bimodal one was observed when hydrothermal method at longer aging time was introduced.

The dependence of BET surface area on the method and aging time is given in Table 1. As shown in the table, the BET surface area for the sample synthesized by using conventional oil bath method is 22 m^2 g^{-1}, and it increased to more than 3 folds, to 92 m^2 g^{-1}, 105 m^2 g^{-1}, and 93 m^2 g^{-1} for samples prepared by the hydrothermal method, aging for 1 d, 2 d, and 4 d, respectively.

Such a behaviour is presumably due to the formation of mesopores during the aging process of the mother liquor and the formation of interstitial pores in the crystallite, as it was explained in the previous section. In addition, the formation of better crystal as a result of the coarsening of the structure and the elimination of the amorphous grain-boundary phase as was proposed earlier [15], presumably contributed to the larger surface area values for Ni/Al LDH synthesized at longer aging time by the hydrothermal method.

CONCLUSION

This study shows that Ni/Al LDH with carbonate as the interlamellar anion could be synthesized by the hydrothermal method. The hydrothermal aging treatment performed on the resulting samples enhanced crystallinity, surface area, and Ni content, compared to the one synthesized by the conventional method. However, for the hydrothermal method, no significant difference in the surface area of the resulting materials was obtained for different aging times, they are in the range of 92—105 m^2 g^{-1} compared to 22 m^2 g^{-1} for the conventional oil bath method.

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