

Effects of hydrothermal treatment on textural properties of $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$

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A synthetic hydrotalcite-like compound, $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$, was prepared by co-precipitation followed by hydrothermal treatment. The effects of hydrothermal treatment, time and temperature on crystallite size, crystal strain, and specific surface area have been studied. Differences in textural properties found by means of data obtained by X-ray powder diffraction, scanning electron microscopy and nitrogen adsorption techniques are discussed.

1. Introduction

Al-Li hydroxycarbonate, $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$, is a laminar, hydrotalcite-like compound, obtained by hydrolysis of Al^{3+} in the presence of lithium carbonate solutions [1]. The structure consists of positively charged gibbsite-like layers with lithium cations occupying the vacancies in the gibbsite structure. Anions and water molecules are present between the layers to compensate the resultant charge.

A crystallochemical study was carried out by selected-area electron diffraction (SAD), X-ray diffraction (XRD) and infrared analysis [2]. The results are consistent with an ordered distribution of cations (aluminium and lithium) in the octahedral sheets.

Likewise, the thermal stability of this compound has been studied [3] and the ability to give rise to anion-exchange reactions has been shown recently [4, 5], as well as a noticeable antiacid behaviour towards solutions containing low selectivity anions [5]. On the other hand, the textural properties of Al-Li double hydroxides with various mono- and divalent inorganic anions has been studied [6]. It is known that the textural properties of solids are strongly affected by the synthesis methods used to obtain them [6, 7].

In the present paper, a systematic hydrothermal treatment of the Al-Li hydroxycarbonate has been carried out and its influence on the textural properties has been studied by means of X-ray line broadening analysis, scanning electron microscopy (SEM) and nitrogen adsorption techniques.

2. Experimental procedure

The Al-Li hydroxycarbonate was obtained by slow addition of an aluminium carbonate (0.1 M) to a saturated LiOH solution up to pH 12.5 [3]. An aliquot of this suspension was removed, washed to eliminate excess Li_2CO_3 and then dried at 60°C for later use. The remainder was treated hydrothermally at different temperatures and during variable times.

X-ray diffraction powder patterns were obtained on a Philips PW1130 diffractometer, with $\text{CoK}\alpha$ radiation and an iron filter. The line profiles were recorded at a

2θ scanning rate of $1/8^\circ \text{min}^{-1}$. The intensities were read each 0.025° of 2θ . Line profile analyses were carried out on the (002) reflection; this line was chosen for its high peak to background ratio and the absence of overlapping peaks. A highly crystalline silicon sample provided the instrumental profile.

The determination of crystallite size (ϵ) and microstrains ($\langle e \rangle$) was developed by the variance method by employing a computer program to calculate the variance-range function of the profiles [8]. Crystallite size and microstrains were calculated from the slope and intercept of the variance-range plots by means of the equation of Langford and Wilson [9]:

$$W_{2\theta} = \frac{K\lambda}{2\pi^2} \frac{\Delta(2\theta)}{\epsilon \cos \theta} - \frac{\lambda^2}{4\pi^2 \epsilon^2 \cos^2 2\theta} + 4 \tan^2 \theta \langle e^2 \rangle$$

where K is the variance shape factor, λ is the radiation wavelength and θ the angle of the line centroid.

Scanning electron micrographs were obtained with a Philips SEM 501B. Samples were gently dispersed by ultrasonic treatment in acetone, settled on nickel holders and covered with an electrodeposited gold film.

Adsorption-desorption isotherms of N_2 were obtained at 77 K in a conventional volumetric apparatus. The samples were previously outgassed at room temperature and equilibrated under a vacuum better than 10^{-4} torr for at least 2 h before measuring the isotherm. Surface areas were calculated using the BET [10] and α_s -plot [11] procedures assuming a cross-sectional area of 0.162 nm^2 for the N_2 molecule. The α_s -plot method [11] was also used for qualitative assessment of the microporosity of the samples. Mesopore analysis was carried out using the Dollimore and Heal [12] and Lippens *et al.* [13] methods, assuming cylindrical and slit-shaped geometries, respectively, for the pores.

3. Results and discussion

XRD patterns of the samples synthesized show all the spacings corresponding to the Al-Li hydroxycarbonate according to the assignment previously proposed [2].

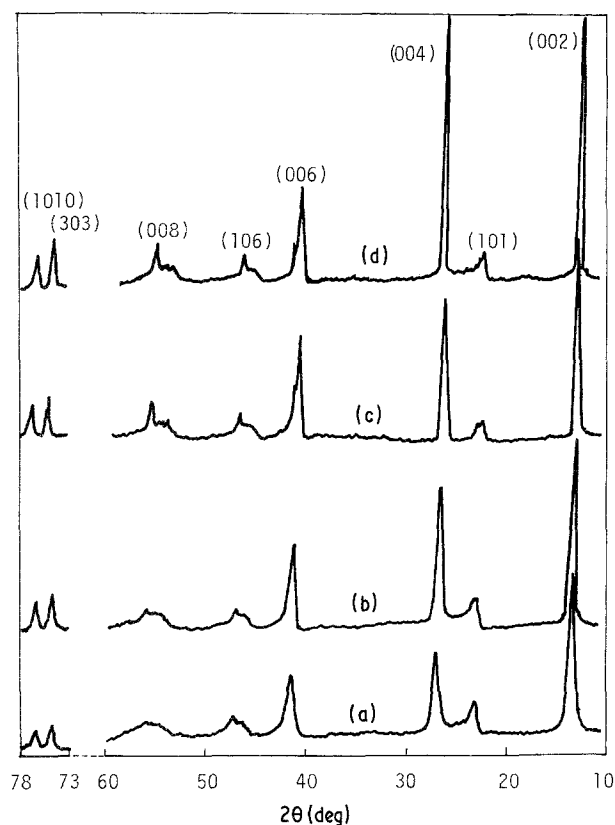


Figure 1 X-ray powder diffraction patterns for various selected samples: (a) untreated; (b) 48 h, 60°C; (c) 48 h, 80°C; (d) 48 h, 100°C.

Fig. 1 shows X-ray diffractograms of various samples subjected to different hydrothermal treatments. An increasing sharpness of the peaks can be observed as the indicated treatment progresses, indicating a higher crystallinity for these samples. A similar behaviour has been found recently for analogous compounds [6].

In order to obtain more quantitative results to evaluate this variation of crystallinity, an X-ray line broadening analysis of the (002) reflection was carried out. Table I shows the crystallite sizes and microstrains resulting from the variance analysis for samples treated hydrothermally and varying the time, while Table II shows the same parameters as a function of the temperature of the hydrothermal treatment.

The crystallite size increased markedly in the first 5 h of treatment at 130°C (Table I), and this increase progresses very slowly up to 24 h of hydrothermal treatment; between 5 and 24 h at 130°C the crystallinity can be considered, in practice, constant. Instead, after 33 h the crystallite size increased noticeably and it is also maintained when the treatment advances up

TABLE I Effects of hydrothermal treatment time on the crystallite size (ϵ) and microstrains ($\langle e \rangle$) in the (002) plane

Temperature (°C)	Time (h)	ϵ (nm)	$\langle e \rangle \times 10^3$
25	0	2.4	30.8
130	5	9.7	5.7
130	9	10.7	5.6
130	24	10.9	5.4
130	33	31.0	0.7
130	48	31.9	1.3

to 48 h. Microstrains decrease progressively with the hydrothermal treatment. An analogous behaviour has been found for other hydrocalcite-like compounds [14].

The increasing of crystallite size and decreasing of microstrains lead to a growth of the particle size as is shown in the electron micrographs of Figs 2a, to c. This variation in the particle size must have an influence on the adsorption properties, as we shall discuss below.

Table II shows the effects of the treatment temperature for samples treated for 48 h. The crystallite size increased progressively with temperature and this affected the particle size (Figs 2d to f) and, consequently, the adsorption properties.

The N_2 adsorption-desorption isotherms of samples studied are shown in Fig. 3. The isotherms corresponding to the untreated sample and the one hydrothermally treated for 48 h at 60°C may be considered as Type IV in the BDDT classification [15] and show hysteresis loops in the region from $P/P_0 = 1$ to $P/P_0 = 0.6$ to 0.85, suggesting the presence of mesoporosity. The rest of the isotherms are reversible over the range considered (i.e. up to $P/P_0 \sim 0.95$) belonging to Type II of the above-mentioned classification.

The hysteresis loops have characteristics like those described as Type H_1 in the case of the untreated sample (Fig. 3) and H_3 for the 60°C sample in the IUPAC classification [16]. These shapes of hysteresis loop are associated with specific pore structures. Type H_1 loops are often obtained with agglomerates of compacts of particles of fairly uniform size and array, as observed in the SEM micrograph of Fig. 2a. On the other hand, Type H_3 has been obtained with adsorbents having plate-like particles as it seems to be shown in the corresponding SEM micrograph of the sample treated at 60°C for 48 h (Fig. 2d).

The α_s -plots (not shown) have been constructed in the manner previously described by Sing [11]. The non-porous sample obtained by hydrothermal treatment at 130°C for 48 h of the original sample, outgassed at room temperature, was used as a standard. In every case a straight line passing through the origin is obtained at low relative pressure. For the mesoporous samples (Fig. 2a and b) the corresponding α_s -plots exhibited a considerable upward deviation, indicating an absence of microporosity and capillary condensation.

Values of the surface area calculated by the BET and α_s methods (S_{BET} and S_α , respectively) are given in Tables III and IV. As expected from previous findings [6] satisfactory agreement has been obtained between corresponding values of S_{BET} and S_α .

TABLE II Effects of hydrothermal treatment temperature on the crystallite size (ϵ) and microstrains ($\langle e \rangle$) in the (002) plane

Temperature (°C)	Time (h)	ϵ (nm)	$\langle e \rangle \times 10^3$
25	0	2.4	30.8
60	48	5.1	6.3
80	48	13.2	2.1
100	48	26.6	4.8
130	48	31.9	1.3

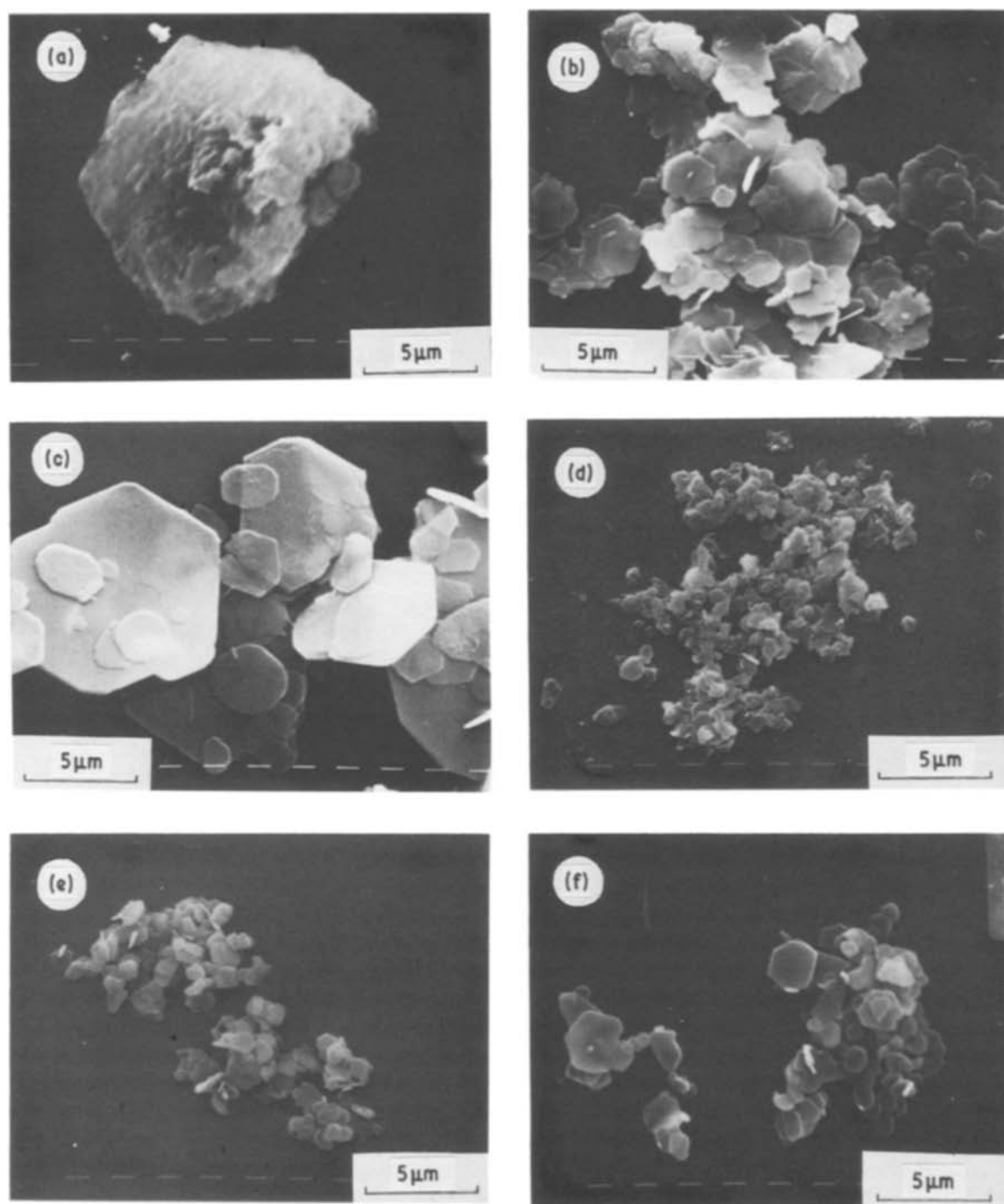


Figure 2 Electron micrographs for: (a) untreated sample; (b) 9 h, 130°C; (c) 48 h, 130°C; (d) 48 h, 60°C; (e) 48 h, 80°C; (f) 48 h, 100°C.

TABLE III Effects of hydrothermal treatment time on N_2 adsorption at 77 K

Temperature (°C)	Time (h)	S_{BET} ($m^2 g^{-1}$)	S_z ($m^2 g^{-1}$)	S_{cum} ($m^2 g^{-1}$)	S'_{cum} ($m^2 g^{-1}$)	V_p ($ml g^{-1}$)
25	0	55.5	54.8	45.3	28.7	0.2528
130	5	20.0	19.7	—	—	0.0387
130	9	18.8	18.5	—	—	0.0384
130	24	13.3	13.4	—	—	0.0376
130	33	5.3	5.0	—	—	0.0125
130	48	5.5	5.1	—	—	0.0125

TABLE IV Effects of hydrothermal treatment temperature on N_2 adsorption at 77 K

Temperature (°C)	Time (h)	S_{BET} ($m^2 g^{-1}$)	S_z ($m^2 g^{-1}$)	S_{cum} ($m^2 g^{-1}$)	S'_{cum} ($m^2 g^{-1}$)	V_p ($ml g^{-1}$)
25	0	55.5	54.8	45.3	28.7	0.2528
60	48	21.4	21.3	15.2	20.6	0.0680
80	48	12.3	12.1	—	—	0.0306
100	48	7.5	7.6	—	—	0.0147
130	48	5.5	5.1	—	—	0.0125

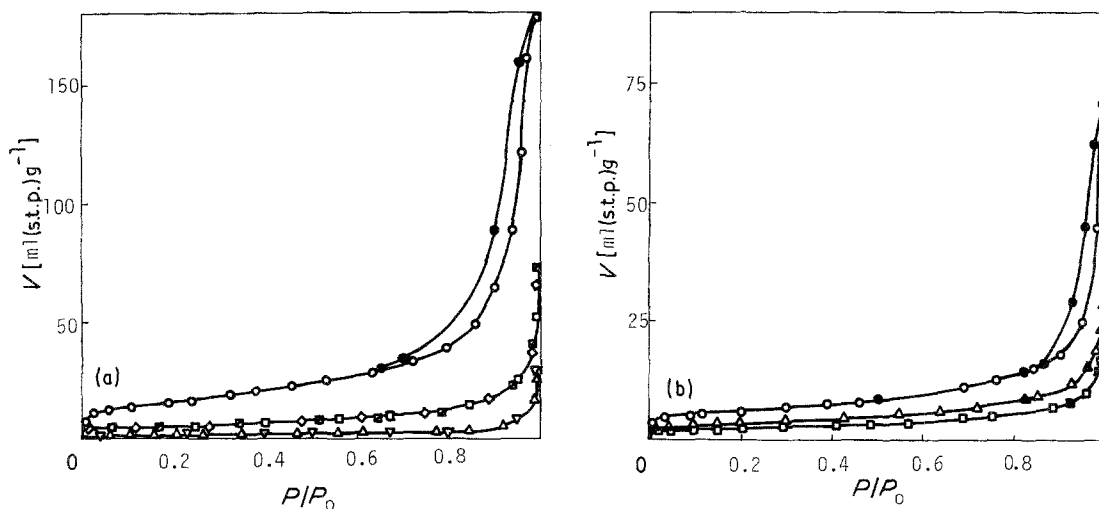


Figure 3 N_2 adsorption isotherms at 77 K (open symbols, adsorption; full symbols, desorption). (a) (O) untreated; (\square) 5 h, 130°C; (\boxtimes) 9 h, 130°C; (\diamond) 24 h, 130°C; (\triangle) 33 h, 130°C; (∇) 48 h, 130°C; (b) (O) 48 h, 60°C; (\triangle) 48 h, 80°C; (\square) 48 h, 100°C.

Cumulative surface areas, S_{cum} and S'_{cum} (Tables III and IV) were obtained for mesoporous samples following the Dollimore and Heal [12] and Lippens *et al.* [13] methods, respectively. t -values used in this analysis have been obtained from the N_2 adsorption isotherm on the non-porous reference sample used as a standard. S_{BET} (or S_z) values agree much better with the corresponding S_{cum} than with S'_{cum} for the original sample. The opposite has been found for the sample treated at 60°C for 48 h. This indicates that the pore shape of the original Al_2Li-CO_3 sample can be explained by assuming a cylindrical (or interstices between closed-packed particles) geometry according to the Dollimore and Heal [12] calculation, whereas slit-shaped (or parallel-plate) mesopores can be assumed for treated sample (d) according to the

Lippens *et al.* [13] calculation. Both samples exhibited the highest specific surface area of the respective series, mainly due to their mesoporous character and small particle size.

The effect of hydrothermal time at 130°C on the specific surface area of the original sample is shown in Table III. A progressive diminishing in S_{BET} values is observed up to 33 h and then maintained at 48 h. These S_{BET} values (Table III) are well correlated with the corresponding crystallite size (Table I) and corroborated by their respective SEM micrographs (Figs 2a to c). Similar comments can be made on the effect of hydrothermal treatment temperature for 48 h on the specific surface area of the original sample (Tables II and IV, and Figs 2a, d, e and f).

Fig. 4 shows variations of specific surface area of $[Al_2Li(OH)_6]_2CO_3 \cdot nH_2O$ samples with hydrothermal treatment time and temperature. The surface area of this sample undergoes a similar variation when subjected to any of these treatments.

On the basis of the above results and discussion, it is considered that both described methods could be used to grow crystals of $[Al_2Li(OH)_6]_2CO_3 \cdot nH_2O$. The two methods are equivalent because the crystallite size, particle size and specific surface area of the sample change in a similar way independently of the method used.

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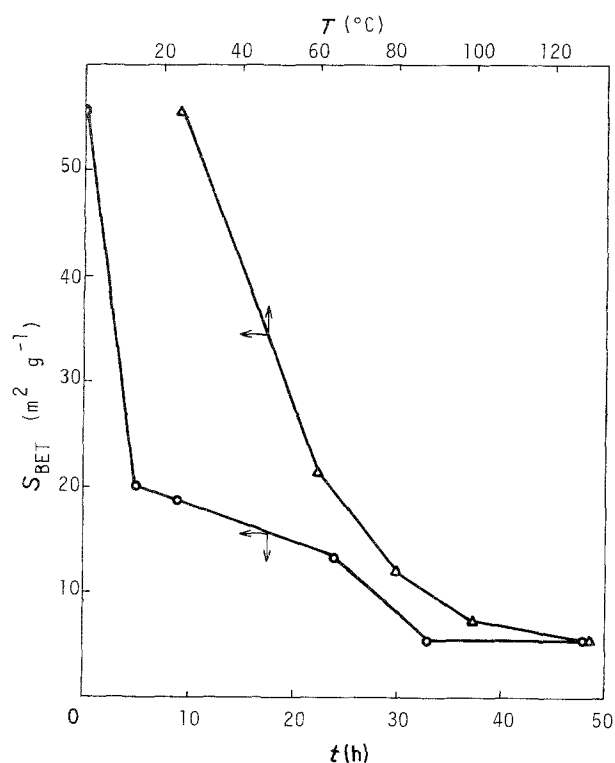


Figure 4 Plot of S_{BET} against time and temperature of hydrothermal treatment.

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