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Preparation of New Layered Double Hydroxide, Co-Ti LDH

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Abstract

Layer double hydroxide (LDH) is well known for its ability to intercalate anionic compounds. Most popular LDH is prepared only conventionally with bivalent and trivalent cations. In this study, Co-Ti LDH consisting of bivalent and tetravalent cations was prepared and characterized by chemical analysis, X-ray diffraction, IR spectra, thermal analysis and Scanning Electron Microscope (SEM). The experimental results indicate that the ageing procedure plays a vital role in the formation of Co-Ti LDH. The insertion of a cyanate anion into LDH was confirmed by chemical analysis and IR spectra. XRD patterns of the prepared LDH (Co-Ti-CNO) showed that the interlayer spacing of the LDH was 0.79 nm. The spacing was similar to that of usual LDH in which chloride or bromide anion is the guest. SEM images show that the morphology of Co-Ti LDH was a plate-like structure or a fibrous structure depending on the preparation conditions.

Introduction

LDH is an inorganic layered compound having the ability to intercalate anionic compounds, because LDHs are constituted by infinite sheets of brucite-type material charged positively, where divalent cations are replaced in a fraction of x by trivalent cations in octahedral coordination. The general formula for these compounds is $(M2_{1-x}M3_x\,(OH)_2)^{x+}\cdot(A^-)^x\cdot n\,H_2O$, where M2 and M3 are divalent and trivalent cations, respectively and "A^-" represents interlamellar anions that restore the electro neutrality of the intercalation compounds. The distance between two adjacent layers depends mainly on the nature of the interlayer species and their electrostatic interaction with the main layers

An increasing interest exists in layered double metal hydroxides, which are or may be used as catalysts [1–6], photo catalysts, catalyst supports [7, 8], adsorbents [9, 10], anion exchangers [11, 12], medicine [13, 14] and bonding materials. We have been interested in the application of layered materials as preferential intercalation of isomers [15–18] and as novel, cost-effective and environmentally friendly separation materials [19–22]. Thermal decomposition of LDH containing carbonate anion to metal oxides results in a useful catalyst for a number of peripheral base-catalyzed reactions. A widespread application of LDHs is anticipated by the reason of the pronounced anion-exchange capacity toward inorganic and organic anions.

We recently reported that preparation of Zn-Ti LDH consisting of bi- and tetra-valent cations is possible [23]. The present work examines the possibility to prepare other LDH consisting of bi- and tetra-valent cations. The object of this work is not only preparation of new LDH, but also intercalation of a new guest anion. This new LDH structure contains Co^{2+} and Ti^{4+} cations in host layers and cyanate anion as the guest (Co-Ti-CNO). The effect of the ageing procedure on the formation of the LDH structure is clarified.

Experimental

Materials

The Co-Ti LDH was prepared by co-precipitation of cobalt and titanium salts from a homogeneous solution [23]. A solution of cobalt nitrate and titanium chloride (0.047 mole) were mixed with a urea solution (0.5 mole) under vigorous stirring and heated for a long time at 90 °C. The percentage of titanium is 17–27 mole%. After filtration and washing several times in distilled water, the products were dried under vacuum at room temperature. For simplicity, the samples are designated hereafter as CoTi-x-y, where x means the percentage of titanium and y means the ageing time with stirring and heating.

Characterization

Powder X-ray diffraction (XRD) spectra were recorded on Rigaku, RINT 2200 using CuKα (filtered) radiation (λ = 0.154 nm) at 40 kV and 20 mA between 1.8 and 50°. Thermal analyses (TG, DTG and DTA) of powdered samples up to 800 °C were carried out at a heating rate of 10 °C/min in flow of nitrogen using a Seiko SSC 5200 apparatus. FT-IR spectra (KBr disc method) were recorded on a Horiba FT-720. SEM was performed with JEOL: JSM-6330F, (15 kV/12 mA).

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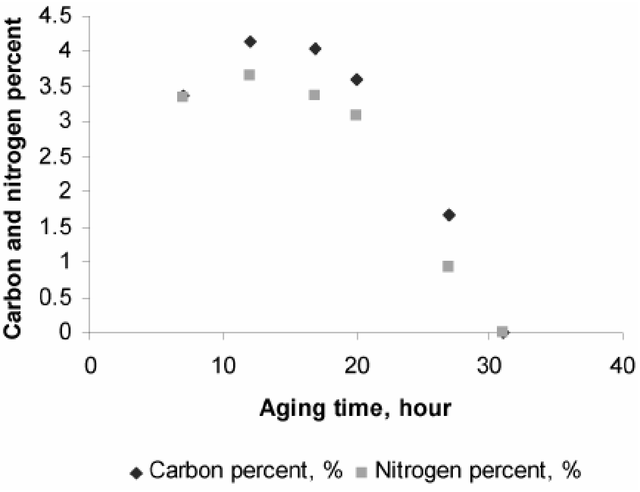

Figure 1. The effect of ageing time on the carbon and nitrogen percentages of CoTi-27 LDH.

Results

Chemical analysis

Chemical analysis (CHN) suggests the following chemical composition for CoTi-27-12:

$$Co_{0.75}Ti_{0.25}(OH)_2(CNO^-)_{0.3}(CO_3)_{0.1} \cdot 0.4H_2O.$$

It is considered that the CoTi-27 LDH structure is formed by an ageing procedure for 12–17 h, as shown in Figure 1. Figure 1 shows a clear relationship between the percentage of carbon and nitrogen of the samples during the ageing procedure. The presence of carbon and nitrogen indicates the presence of anion between the layers and the formation of LDH structure. Figure 1 also shows that the percentage of carbon reached maximum and was approximately constant in the ageing time for 12–17 h, suggested the preparation of the CoTi-27 LDH structure.

It is noted that the percentage of nitrogen and carbon of CoTi-27 LDH started to decrease with the increase of the ageing time after 17 h. This indicated that the LDH structure started to collapse. At ageing time for 31 h, the LDH structure completely disappeared, as suggested by XRD patterns.

From the chemical analysis of CoTi-17-17 LDH, the following chemical composition is suggested:

$$Co_{0.81}Ti_{0.19}(OH)_2(CNO^-)_{0.32}(CO_3)_{0.03} \cdot 0.5H_2O.$$

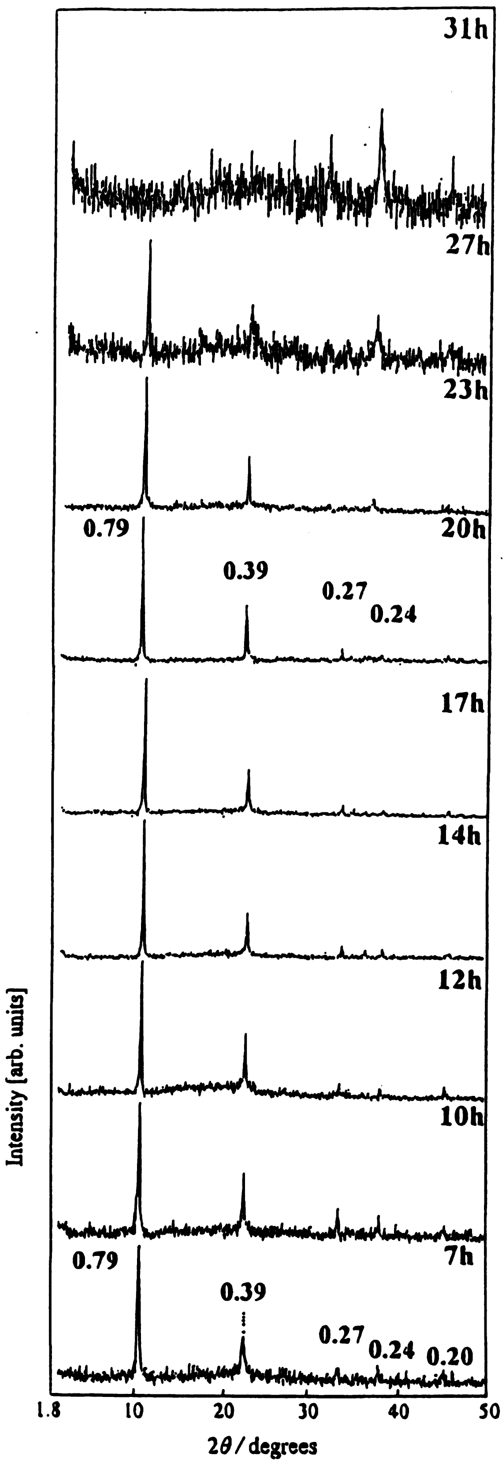

Figure 2. X-ray diffraction patterns of CoTi-27 LDH at different ageing times.

X-ray diffraction

Powder X-ray diffraction patterns of CoTi-27 LDH at different ageing times are shown in Figure 2. The XRD patterns showed two or three sharp peaks. These peaks exhibit some common features of layered materials such as narrow, symmetric, strong peaks at low $2theta$ values and weaker, less symmetric lines at high $2theta$ values. For layered, hydrotalcite-like materials, these peaks (0.79, 0.39, and 0.26 nm) corresponded to diffraction by planes (003), (006), and (009), respectively. The value for the (003) peak at 0.79 nm is significantly larger than the value reported for natural hydrotalcite whose value is 0.76 nm in the case of the carbonate anion as the guest [24–25, 1]. However, it agrees thoroughly with synthetic hydrotalcite in the case of chloride or bromide as a guest [26–28]. This value is related to the thickness of the brucite-like layers (0.48 nm for hydrotalcite), as well as the size of the anion (and, in some cases, its orientation) and the number of water molecules existing in the interlayer.

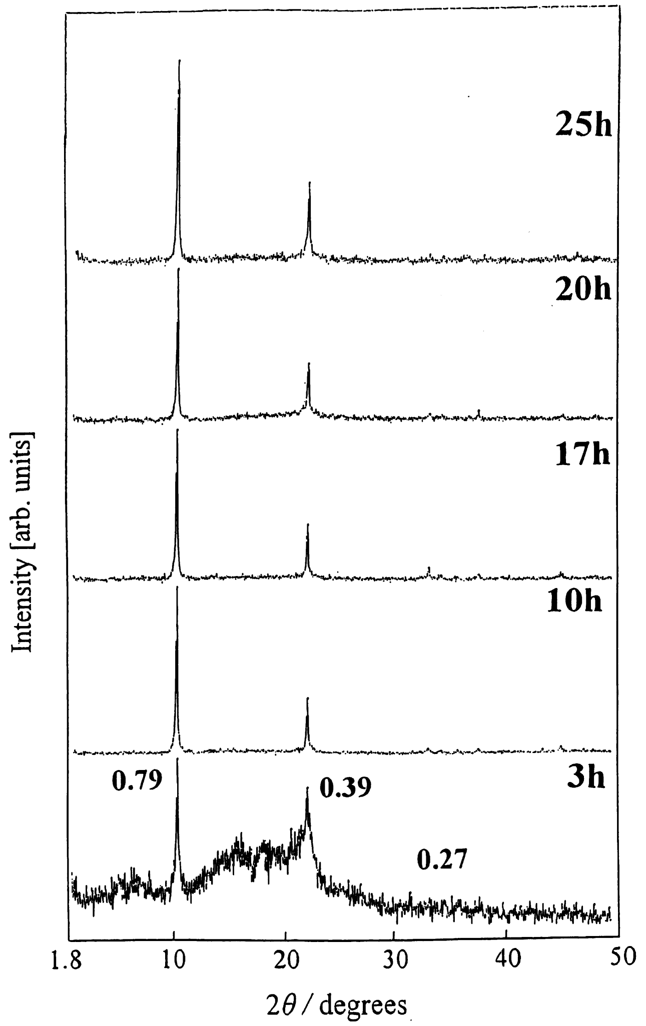

Figure 3. X-ray diffraction patterns of CoTi-17 LDH at different ageing times.

As shown in Figure 2, at least eight samples with different ageing times have indicated the formation of CoTi-27 LDH. Among these samples, CoTi-27-17 represents the highest crystallinity of Co-Ti LDHs. The intensity of the basal spacing d (003) increased from 700 to 3000 and became sharper with the increase in ageing time from 7 to 17 h. This may be because of the slow decomposition of urea. It needs efficient time to produce the anions that neutralize the positive charges of Co-Ti layers. Some diffractions such as those of planes of (009) and (012) are not clear in CoTi-27-7. However, they can be clearly observed in CoTi-27-17.

The intensity of the main peak (003) starts to decrease in the case of CoTi-27-20 and CoTi-27-23 as shown in Figure 2 (20 h and 23 h). In the case of CoTi-27-27, the LDH structure started to collapse where the crystallinity became weak and the new phase corresponding to oxide and hydroxide started to increase as shown in Figure 2 (27 h). The LDH structure completely disappeared and the peaks of the new phase became clear in the case of CoTi-27-31, as shown in Figure 2 (31 h). This may be because of the oxidation and decomposition of the anion by heating and/or the oxidation of cobalt (Π). This suggestion agrees with the results of chemical analysis. Also, the thermal analysis and IR spectra confirmed this suggestion, as will be discussed later. In the case of decreasing the percentage of titanium from 27% (CoTi-27 LDH) to 17% (CoTi-17 LDH), the stability of the LDH structure become more stable against ageing time, as shown in Figure 3. This means that CoTi-17 LDH is more stable than CoTi-27 LDH, because the high percentage of titanium increases the concentration of the cyanate anion between the hydroxylated layers. This leads to an increase of

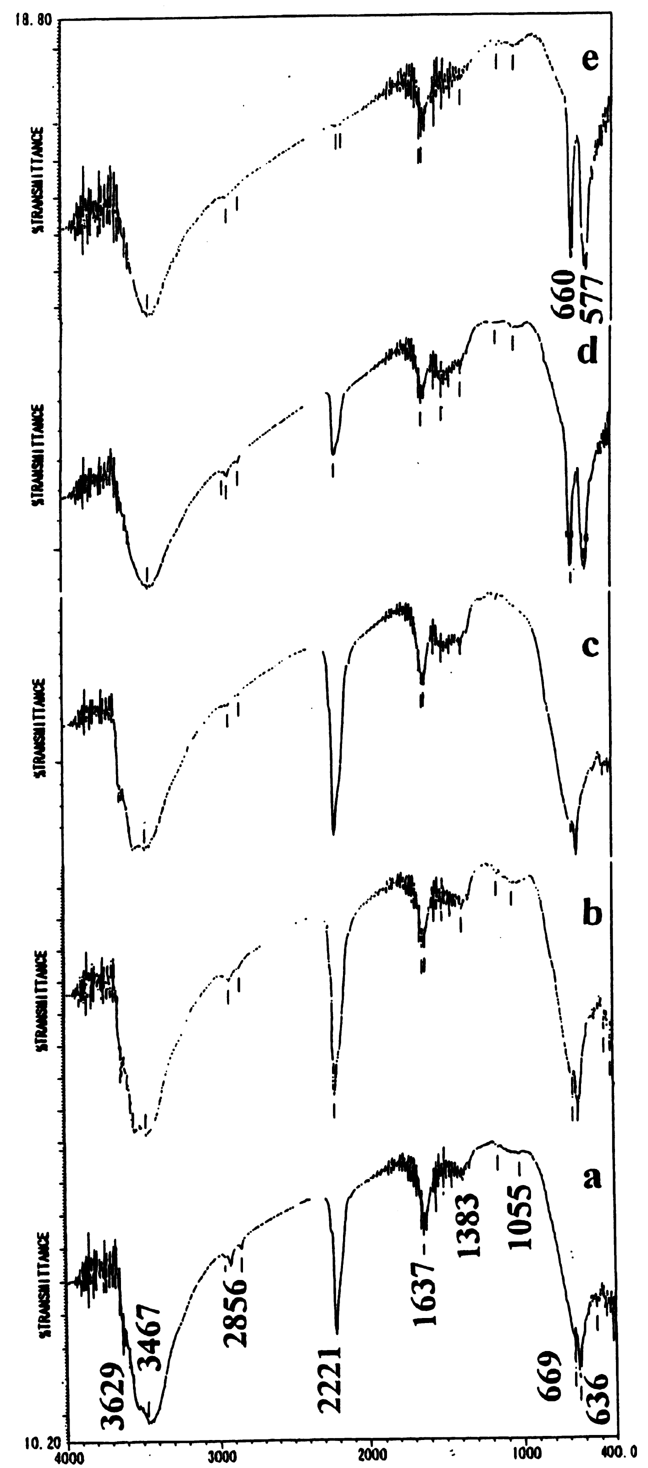

Figure 4. IR Spectra of CoTi-27 LDH at different ageing times: (a) 7 h, (b) 12 h, (c) 17 h, (d) 27 h, and (e) 31 h.

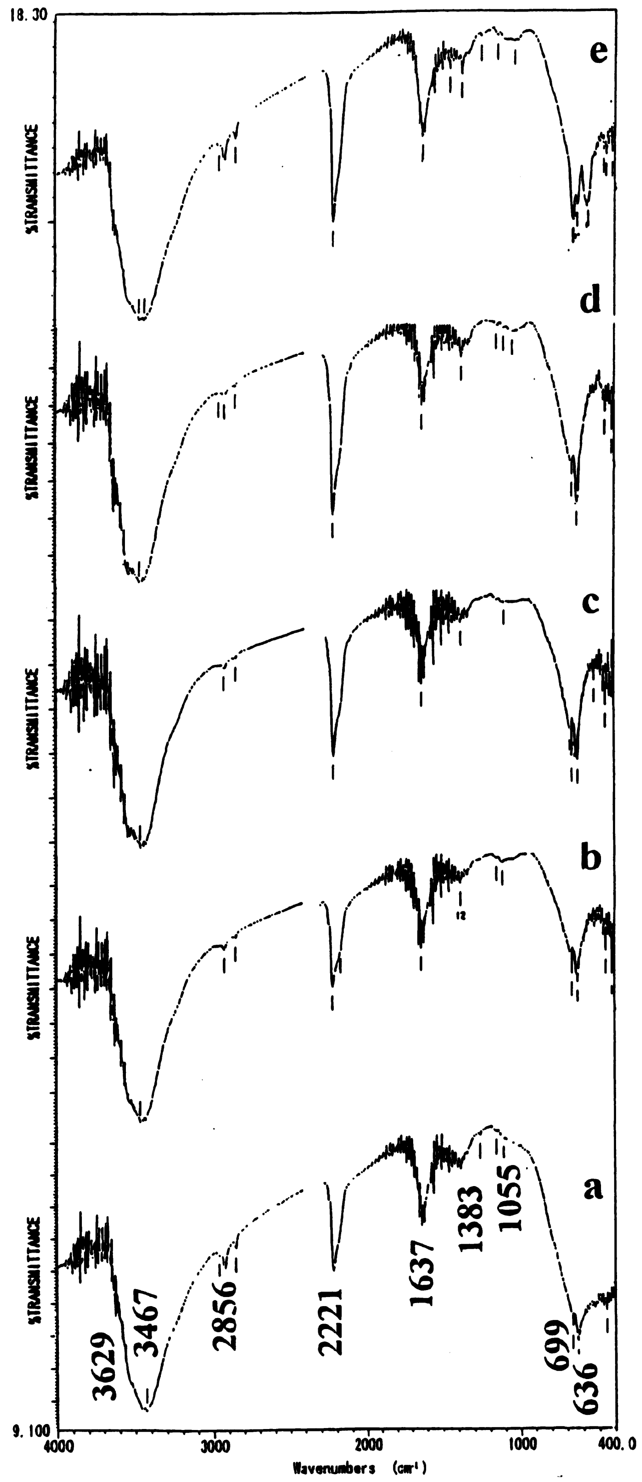

Figure 5. IR Spectra of CoTi-17 LDH at different ageing times: (a) 3 h, (b) 10 h, (c) 17 h, (d) 20 h, and (e) 25 h.

the repulsion between the electron density of the nitrogen of cyanide groups and the stability of LDH structure decrease. So, when the percentage of titanium increases to 30%, the Co-Ti LDH could not be observed.

FT-IR spectroscopy

The FT-IR technique has been used to identify the nature and symmetry of interlayer anions. The insertion of cyanate

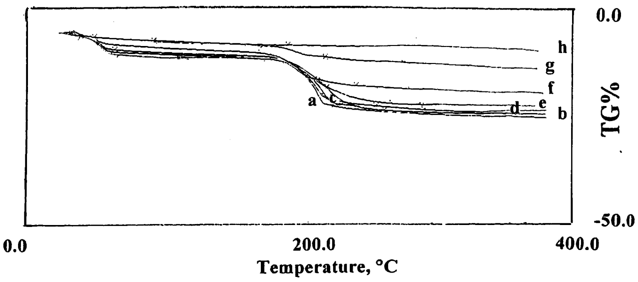

Figure 6. Thermal analysis of CoTi-27 LDH at different ageing times: (a) 7 h, (b) 12 h, (c) 14 h, (d) 17 h, (e) 20 h, (f) 24 h, (g) 27 h, and (h) 31 h.

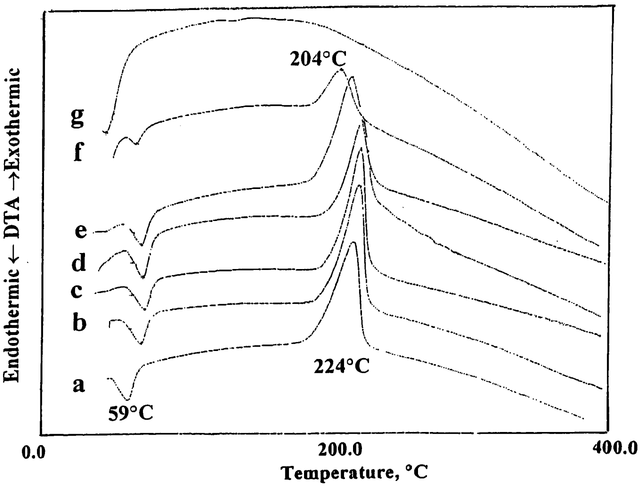

Figure 7. Differential thermal analysis (DTA) of CoTi-27 LDH at different ageing times: (a) 7 h, (b) 12 h, (c) 14 h, (d) 17 h, (e) 20 h, (f) 24 h, (g) 27 h, and (h) 31 h.

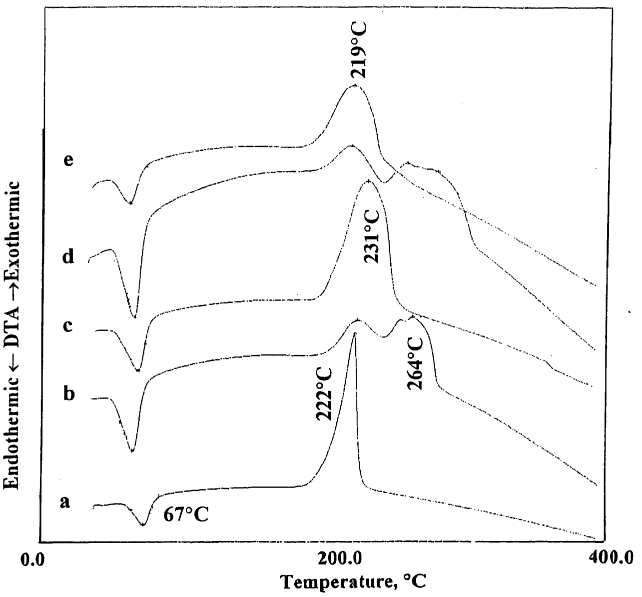

Figure 8. Different thermal analysis (DTA) of CoTi-17 LDH at different aging times: (a) 3 h, (b) 10 h, (c) 17 h, (d) 20 h, and (e) 25 h.

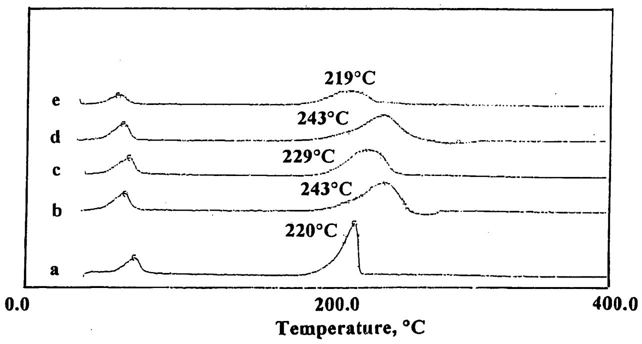

Figure 9. Differential thermo-gravimetric (DTG) of CoTi-17 LDH at different aging times: (a) 3 h, (b) 10 h, (c) 17 h, (d) 20 h, and (e) 25 h.

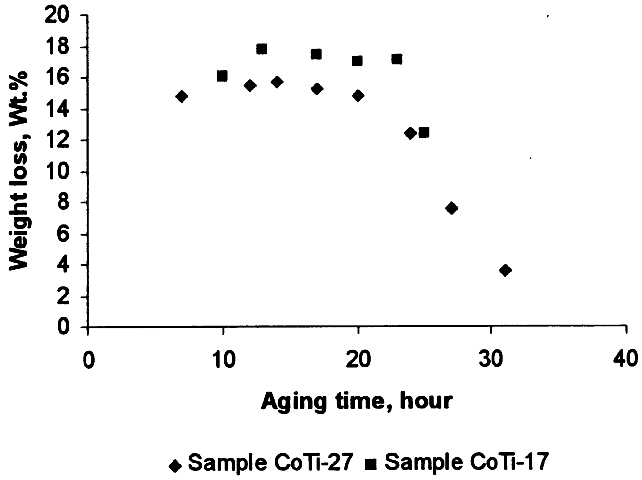

Figure 10. The effect of ageing time on the weight loss in the range at 67-300 °C of CoTi-27 LDH and CoTi-17 LDH.

anion (NCO^-) into CoTi-27 and CoTi-17 LDH was clearly demonstrated by the appearance of the ν_1 vibration in 2230–2105 cm^{-1}, the ν_2 vibration in the 600–650 cm^{-1} and the ν_3 vibration in the 1190–1220 cm^{-1} [29].

The IR absorption peak at 2221 cm^{-1} was assigned to the symmetrical stretching vibration mode of CNO^-. Figures 4 and 5 indicate the presence of the interlayer anion (NCO^-) in CoTi-27 and CoTi-17. However, this peak became small in CoTi-27-27 and disappeared in CoTi-27-31. This indicated the collapse of the LDH structure. As can be noted in Figures 4 and 5, a small amount of carbonate into the interlayer space is confirmed by the presence of a weak absorption peak at 1383 cm^{-1} [29,30] for all samples and was also supported from the chemical composition. This peak became clear in CoTi-27-17, as shown in Figure 4c.

An important phenomenon for the presence of cyanate anion into the interlayer space is the change of ν_{OH} (OH stretching vibration at around 3500 cm^{-1} [31, 32]. It is noted that the broad OH vibration band is clearly resolved into two components in case of CoTi-27-7, CoTi-27-12 and CoTi-27-17, which has been attributed to the presence of the CN group near hydroxyl group. According to the proposed model, the peak of the hydroxyl group affected by the cyanide group shifted to a low wavenumber (i.e., 3467 cm^{-1}) due to the lowering of the O–H bond electron density, while the unaffected hydroxyl groups appeared at high value (i.e., 3629 cm^{-1}). This phenomenon agrees with the effect of nitrate ion on the IR peaks of LDH as described in the literature [33]. Furthermore, the δ-mode of O–H groups jumps to 669 cm^{-1}. In the case of CoTi-27-27 and CoTi-27-31, this phenomenon was not observed, as shown in Figures 4d and e. These results, due to the decomposition of the cyanate anion were also confirmed by chemical analysis, XRD and thermal analysis, which will be discussed later.

A weak peak recorded around 2856 cm^{-1} has been ascribed to the OH stretching mode of interlayer water molecules hydrogen-bonded to interlayer carbonate and cyanate anions [30, 34]. The bending mode band of the water molecules observed was close to 1637 cm^{-1} [35].

The weak band observed at 1055 cm^{-1} can be ascribed to the ν_1 mode of carbonate anion. Although this band is IR-inactive if the carbonate anion is free, it is activated owing to the lowering of the symmetry of the carbonate anion in the interlayer [36].

Thermal analysis

TG diagrams of CoTi-27 at different ageing times except CoTi-27-27 and CoTi-27-31 have similar patterns, as shown in Figure 6. Major weight losses occur in three steps. The first weight loss is due to the elimination of surface water and the second weight loss is due to the elimination of interlayer water, whereas the third weight loss corresponds to the dehydroxylation of layers and loss of the interlayer anions. These weight losses are definitely smaller in the samples CoTi-27-24 and CoTi-27-27 and disappear in the sample CoTi-27-31. This fact means that the amount of anions in CoTi-27-24 and CoTi-27-27 were small and that there were no interlayer anions in CoTi-27-31. These results coincide with chemical analysis, XRD and IR spectra. DTA curves of CoTi-27 show two peaks, as shown in Figure 7. The first peak at 60–80 °C is endothermic and agreed with the first weight loss. The second peak at 224 °C is exothermic and agreed with the third weight loss. This exothermic peak corresponded to a series of reactions such as decomposition of anions (endothermic event), the reaction of cyanate anion (exothermic event) and partial oxidation of cobalt (exothermic event). This means that the exothermic events compensate the endothermic event and overcome it. The third weight loss is exothermic peak. This is accompanied by the third weight loss and becomes clear in CoTi-17-14 and CoTi-17-23, as shown in Figure 8b and d. The DTA curves of CoTi-17-14 and CoTi-17-23 show another exothermic peak at 264 °C and which is accompanied by weight gain. This weight gain confirms the occurrence of the reaction of the cyanate anion with the environment (nitrogen gas).

Also, the DTG curves of CoTi-17-14 and CoTi-17-23 in Figure 9 show the shift in the third weight loss temperature from 220 °C to 243 °C, followed by shoulder indicating weight gain.

Figure 10 shows the presence of a clear relationship between the ageing treatment and the weight loss of Co-Ti LDH. This relation indicates that the formation of stable Co-Ti LDH occurred in the range of the ageing time of 12–17 h.

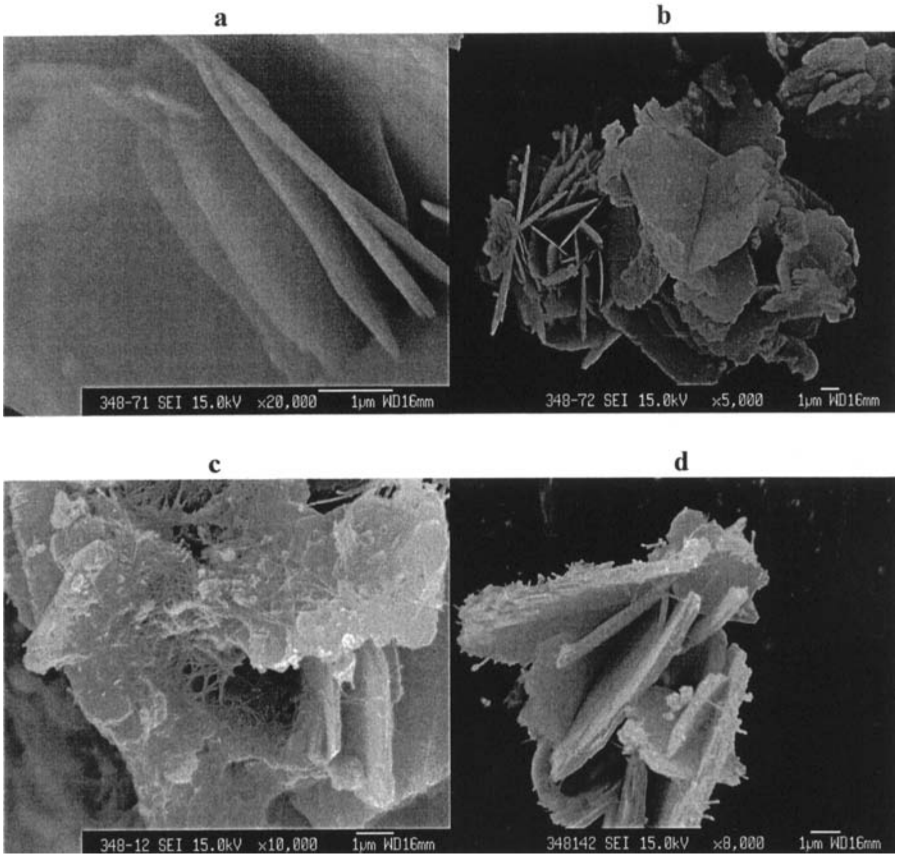

Figure 11. SEM images of CoTi-27 LDH at different ageing times: 7 h × 20,000, (b) 7 h × 5,000, (c) 12 h × 10,000, and (d) 14 h × 8,000.

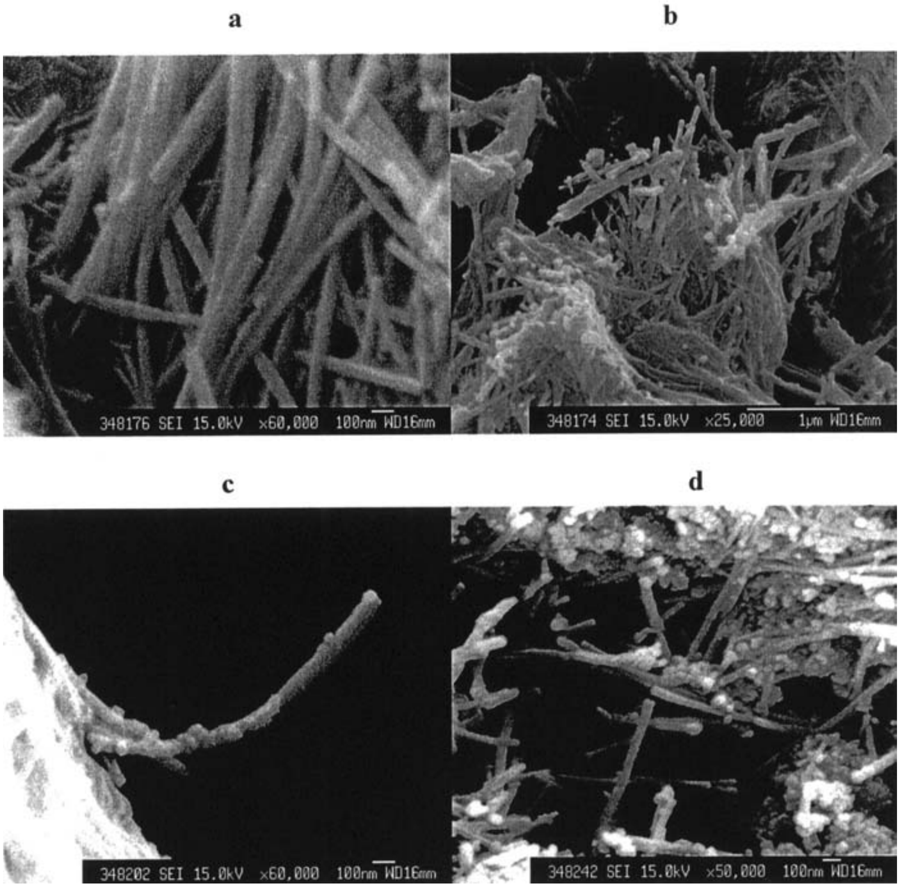

Figure 12. SEM images of CoTi-27 LDH at different ageing times: 17 h × 60,000, (b) 17 h × 25,000, (c) 20 h × 60,000, and (d) 24 h × 50,000.

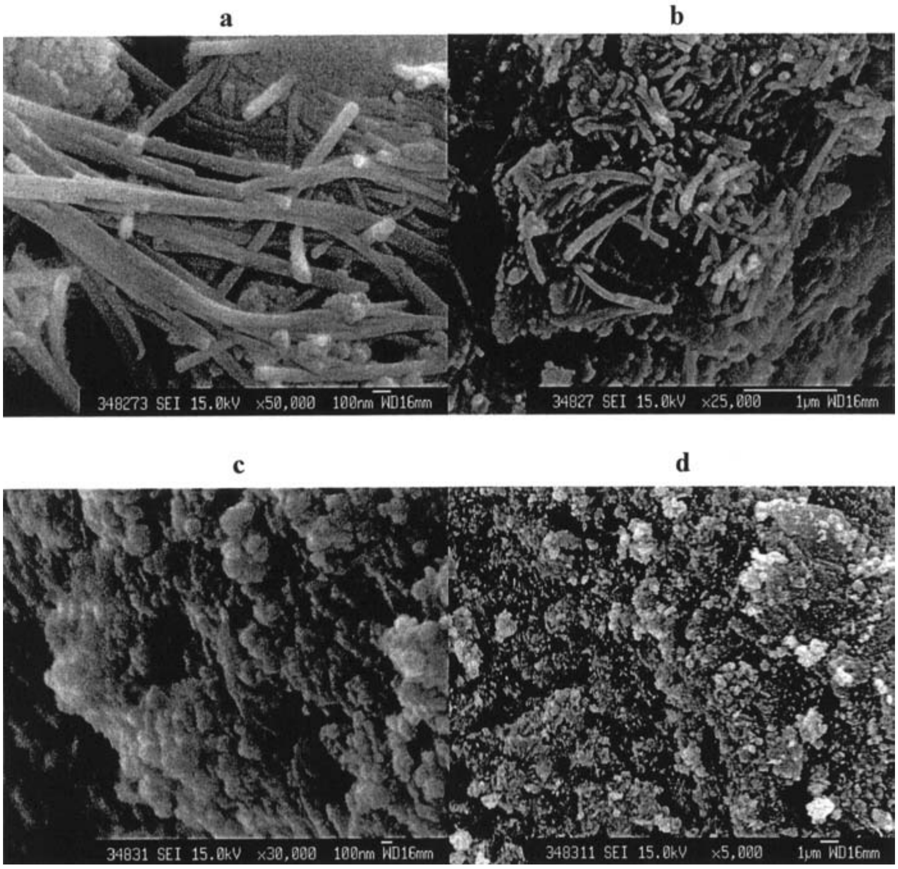

Figure 13. SEM images of CoTi-27 LDH at different ageing times: 27 h × 50,000, (b) 27 h × 25,000, (c) 31 h × 30,000, and (d) 31 h × 5,000.

Scanning electron microscope (SEM)

SEM images of CoTi-27 at different ageing times are shown in Figures 11, 12 and 13. They show that the morphology of Co-Ti LDH clearly depends on the ageing time. For CoTi-27-7, the SEM image shows a clear plate-like morphology, which was typical for the LDH morphology as shown in Figure 11a and b. SEM images of CoTi-27-12, CoTi-27-14 and CoTi-27-17 are shown in Figures 11c, d and 12a, b. They are a mixture of plate-like morphology and fibrous morphology. CoTi-27-20 shows a similar morphology with CoTi-27-12, CoTi-27-14 and CoTi-27-17, but fibrous structures have some modifications. CoTi-27-20 has nodes, as shown in Figure 12c. CoTi-27-24 and CoTi-27-27 show fibrous structures besides new structures consisting of small balls as shown in Figures 12d and 13a, b. In the SEM image of CoTi-27-31, there is no fibrous structure and only small balls are shown, as shown in Figure 13c, d.

Overall, it can be concluded that the best ageing time producing Co-Ti LDH with a plate-like structure is 7 h, and the best ageing time giving Co-Ti LDH with a fibrous structure is 12–17 h. This agrees with the results of XRD, IR spectra and thermal analysis.

Discussion

The powder XRD patterns are not of sufficiently high quality to allow us to carry out structure determination. However, the value of interlayer spacing and the size of the guest ions suggested the orientation of guest ions. Layer thickness was known as 0.48 nm. Therefore, the interlayer spacing available for the anion was calculated as 0.31 nm. The size of cyanate anion is 0.34 nm. So, it was considered that the cyanate anion makes an angle of 65.7° with the Co-Ti layer and connects with the Ti cation through two different sides (above and below the Co-Ti layer) in order to neutralize the positive charge of the titanium cation, as shown in Figure 14. The experimental results show that two anions are intercalated into the interlayer space of Co-Ti LDH indicating that one interlayer spacing is 0.79 nm. The first intercalated anion is cyanate, which was produced from the decomposition of urea as shown in Equation 1:

$$\text{Urea} \rightarrow \mathrm{NH_4^+CNO^-}. \qquad (1)$$

Earlier investigators [36–38] confirmed this equation and consider that the ammonium cyanate is an intermediate with decomposition of urea. Recently, Coebel *et al.* [39–40] mentioned that the thermal decomposition of urea can yield a variety of products, apart from ammonia and isocyanic acid.

The second intercalated anion is carbonate ion, which was produced from the complete decomposition of urea as shown in Equation 2:

$$\mathrm{NH_4^+CNO^-} + 2\mathrm{H_2}O + 2\mathrm{H^+} \rightarrow \mathrm{NH_4^+} + \mathrm{H_2CO_3} \qquad (2)$$

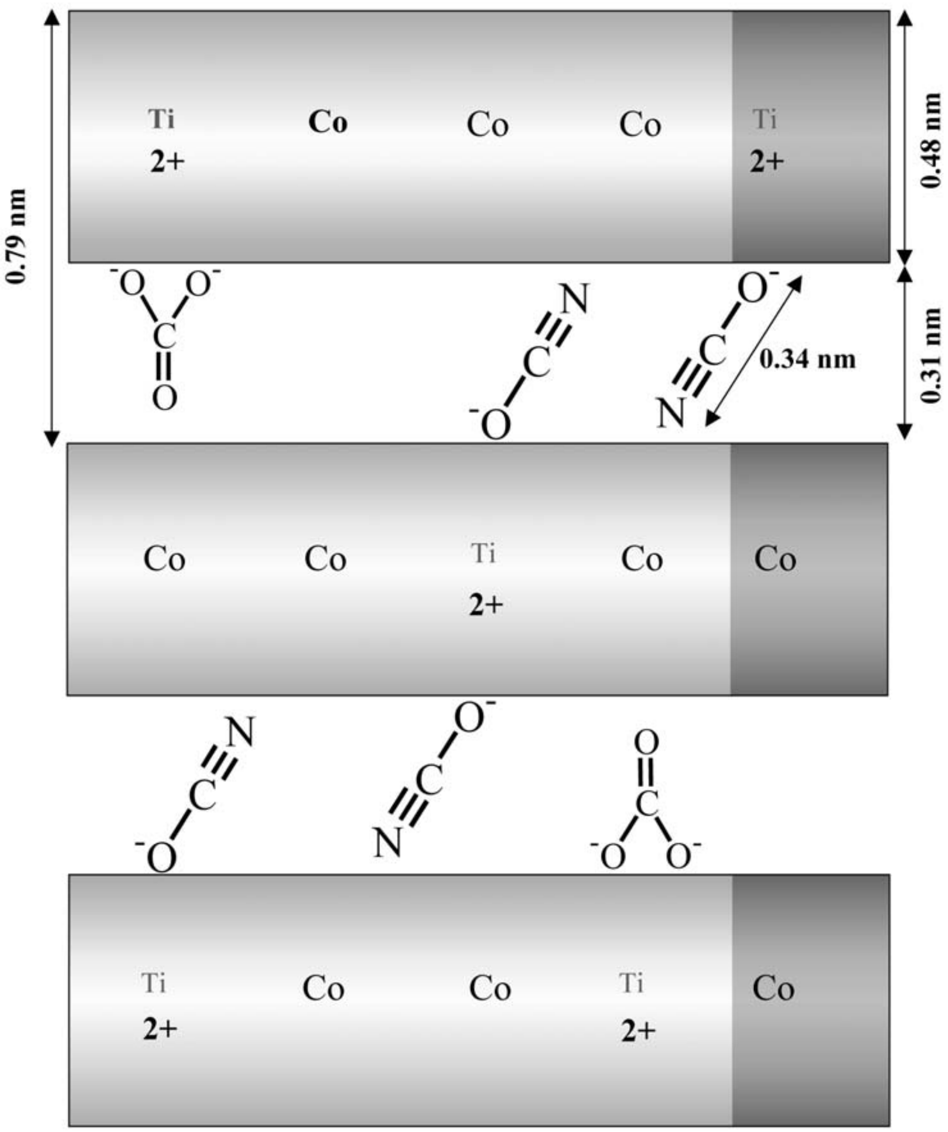

Figure 14. Schematic representation of Co-Ti LDH for plate-like morphology.

The earlier investigators [36–38] indicated that the decomposition of urea is complete only in acidic conditions as shown in Equation 2. According to the preparation conditions of this study, the decomposition of urea is not complete. This leads to a higher concentration of cyanate than the concentration of carbonate ion in the interlayer spacing of Co-Ti LDH, especially at an ageing time of 7 h. Only a trace amount of carbonate anion exists besides cyanate anion. At ageing treatment 7 h, the C/N ratio of Co-Ti LDH is 1, indicating that the intercalated anion is mainly cyanate. SEM images of this sample show only plate-like structure. By increasing the ageing treatment to 12 h, 14 h and 17 h, the C/N ratio increased to 1.2, suggesting that the carbonate anion starts to increase besides cyanate anion. SEM images of these samples show that the fibrous structures start to grow also. This means that there is a relationship between the appearance of the fibrous structure and the presence of carbonate anion besides cyanate anion in the interlayer space of Co-Ti LDH. According to the slow decomposition of urea, Equations 1 and 2, we can explain the effect of the ageing time on the formation of Co-Ti LDH. The schematic representation of Co-Ti LDH, Figure 14, was valid only for the plate-like structure. In the case of the fibrous structure, it needs some modification and further experiments. The morphology of Co-Ti LDH will be the subject of a future publication.

Conclusion

In this study, layered double hydroxides consisting of bivalent and tetravalent have been prepared. The Co-Ti LDH has interlayer spacing 0.79 nm. The insertion of a cyanate anion was successful for the first time. Experimental results indicate that the formation of Co-Ti LDH strongly depends on the ageing treatment and suggests that the best ageing treatment is 12–17 h. SEM images show that the Co-Ti LDH was a plate-like structure and/or a fibrous structure depending on the preparation conditions.

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