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IMMOBILISATION OF A PHENOLATE DERIVATIVE WITH A MECHANO-HYDROTHERMAL TECHNIQUE AIDED BY ULTRASONIC IRRADIATION

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ABSTRACT

The combination of mechanochemical method enhanced with ultrasonic treatment, proved to be fast synthetic and intercalation techniques, providing efficient and comfortable tools for the preparation of hierarchically-ordered nanostructures.

During the ultrasonic-enhanced, mechanochemically-assisted method of layered double hydroxide (LDH) synthesis, first, the starting metal-hydroxides had to be pre-milled before the ultrasonic treatment. The success of preparation and intercalation was verified by a range of instrumental methods (X-ray diffractometry (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energy dispersive X-ray analysis (EDX) and infrared (IR) spectroscopy). The amount of adsorbed and intercalated phenolate derivate ions was measured by UV-Vis spectroscopy.

XRD measurements revealed that the layered structures were formed and the organic chemicals were intercalated, indeed. Thermogravimetric measurements also indicated the formation of the LDH structure, and infrared measurements verified the presence of phenolate derivates in the sample. In the SEM images, the flat hexagonal crystal forms of the LDHs were clearly observable, even for the intercalated samples. SEM-EDX elemental maps also indicated the successful preparation of the LDHs. Measurements by UV-Vis spectroscopy attested that nearly half of the added pentafluorophenolate was immobilised by the LDHs.

INTRODUCTION

Layered double hydroxides are of interest recently, because of their special layered structure and their wide-ranging applicability. The most common members of LDHs are hydrotalcites having brucite-like layered structure $[\text{Mg}(\text{OH})_2]$, in which the Mg(II) ions are partly replaced by Al(III) [1]. Caused by the aluminium ions, the layers have positive charge, which is compensated by interlamellar anions. They are exchangeable by other type of anions; thus, nanocomposites with new special attributes may be created. The mayor synthesis method of LDHs is the co-precipitation technique [2]; however, recently, a new method, a mechanochemically-assisted technique has been developed as a fast and easy way of making LDHs. In our research, ultrasonic irradiation was used to improve this technique building on the special stirring ability of the ultrasound.

MATERIALS and METHODS

As starting materials, a 2:1 ratio of $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ was milled in a mixer mill for 1 hour. The ultrasonic treatment was carried out in thermostated ultrasonic bath (35 kHz, 30 W, 313 K). After this, glass centrifuge tubes were filled with the milled metal-hydroxides and as aqueous media, 5 ml of 0.01 M NaOH solution was added. In the intercalation process Na-pentafluorophenolate was used to replace the carbonate ions in the pristine CaAl-LDHs. The Al(III) and the phenolate ions were applied in 1:1 ratio. The time interval of ultrasonic mixed treatment was 4 h. After the preparations, the samples were washed with distilled water and absolute ethanol.

RESULTS

XRD measurements verified the presence of LDH phases both in the pristine and the intercalated samples (Figure 1). It is to be seen that the intercalation only resulted in small increase in the basal spacing (from 0.74 nm of the pristine LDH to 0.75 nm of the LDH treated by pentafluor-phenolate anions). This small increase indicates that the phenolate ions lie parallel to the layers.

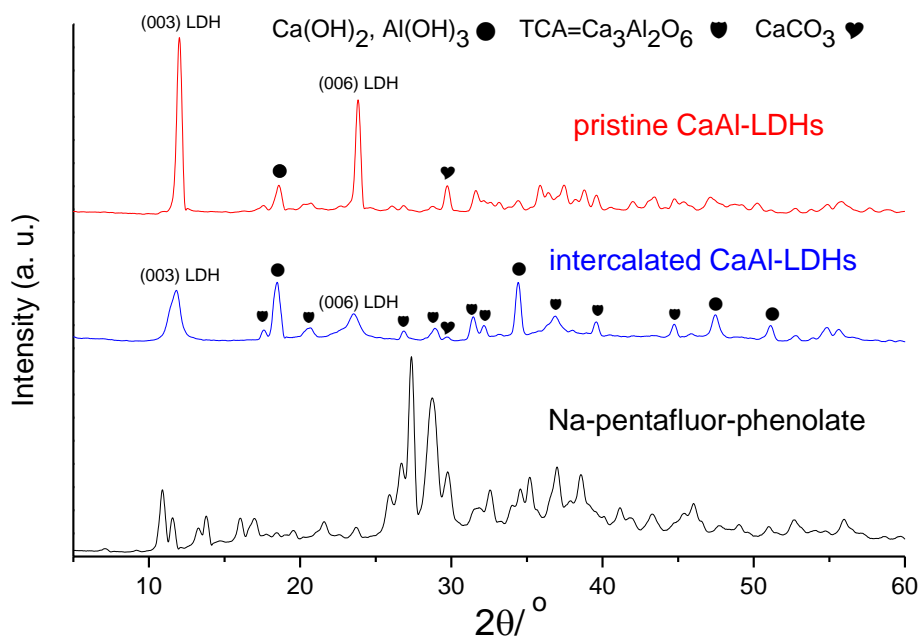


Figure 1: X-ray diffractograms of the various samples.

IR spectra indicate the formation of LDH structure even if phenolate ions were intercalated (Figure 2). At 3670 cm^{-1} , one can see an intense absorption peak of monomeric OH of layers. For the pristine as well as the modified LDHs, signals of the carbonate ions appear at around 1365 cm^{-1} showing presence of these ions between sheets. However, this absorption band is much weaker in the intercalated sample, indicating the replacement of the carbonate ions by the added phenolate ions. Furthermore, shifts in the vibration signals of pentafluorophenolate (1214 , 1244 cm^{-1} from the ring torsion, 1481 , 1681 cm^{-1} from the symmetric and asymmetric stretching

vibrations of carboxylate groups) are also clearly seen, providing additional proofs of the successful intercalation.

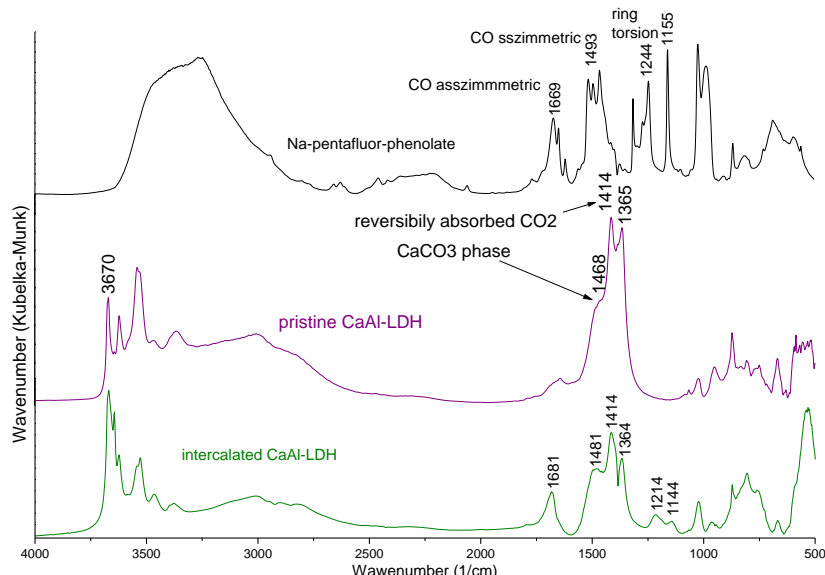


Figure 2: IR spectra of the phenolate derivate, the pristine and the intercalated LDHs.

The thermal behaviour of pristine LDH in air is demonstrated in Figure 3. The curve is the thermogram of a carbonate-containing CaAl-LDH. The removal of physisorbed water occurs between 110–180 °C, while that of the interlayer water molecules takes place in the 200–335 °C temperature region. The final peak is in temperature range of 390–455 °C; it indicates the decomposition, *i.e.*, the dehydroxylation of the layers.

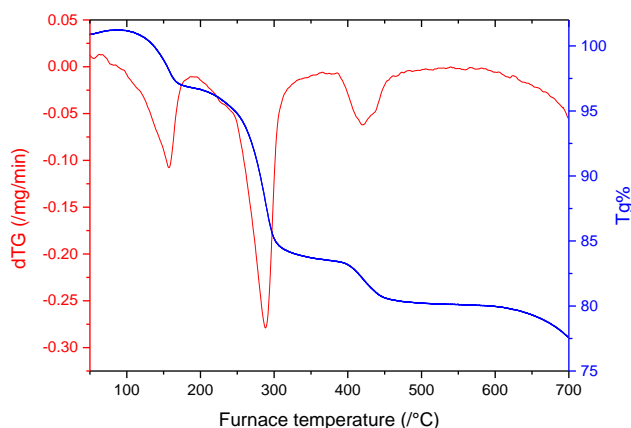


Figure 3: The thermal behaviour of the pristine CaAl-LDH.

Scanning electron microscopy images show the typical structural features of LDHs – hexagonal plate-like morphology is seen (Figure 4). The amount of immobilised phenolate ions was calculated from UV-Vis spectrum of the filtrate in the washing procedure. It was found that 1 g LDH could bind 0,39g pentafluorophenolate ion.

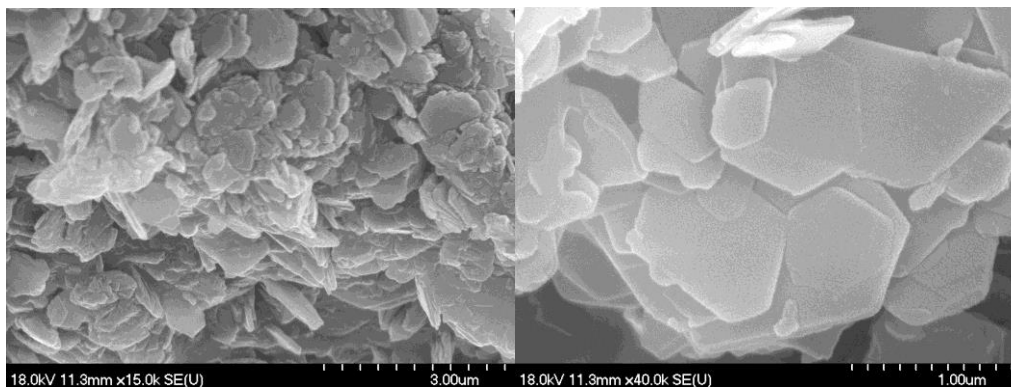


Figure 4: SEM images of the pristine LDH.

CONCLUSIONS

The XRD, SEM and TG measurements proved the formation of CaAl-LDH, IR spectra revealed the presence of pentafluorophenolate ions between layers. Finally, the UV-Vis spectroscopy results quantified the phenolate immobilisation ability of CaAl-LDH, indicating that this material could be useful in waste-water treatment.

Acknowledgements

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