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One-Step Synthesis of Organic LDH and Its Comparison with Regeneration and Anion Exchange Method

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A novel one-step method has been developed to synthesize organically modified layered double hydroxide under ambient condition and without requirement of carbonate-free condition. This method has been found to be effective in the presence of several competitive anions and provides modified products with improved homogeneity, crystallinity, etc., as compared to other commonly known methods such as anion exchange and regeneration. The critical control of the pH value of the reaction medium is a key aspect of this method and provides a high degree of intercalation of the surfactant without forming any pure LDH phase. WAXS and FTIR analysis prove the homogeneous nature of the modified LDH. In contrast to the regeneration method, the chemical environment of the metal hydroxide layers remains identical to that of the unmodified LDH, as confirmed from the solid-state ^{27}Al MAS NMR spectroscopy.

1. Introduction

Layered double hydroxide (LDH) is a host−guest material consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules.[1] They can be represented by a general formula, $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}A^{n-}{}_{x/n}\ yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Mg^{2+} and Al^{3+}, respectively, and A^{n-} is interlayer anions, such as $CO_3{}^{2-}$, Cl^- and $NO_3{}^-$.[2] Because of a wide field of potential applications, such as catalysts,[3,4] medical materials,[5,6] gene delivery,[7,8] and polymer nanocomposite,[1,9,10] LDH materials have generated serious research activities in area of their synthesis and modifications.[11−16] One of the most recent applications being investigated extensively is the use of LDH as nanofiller for polymer matrix to improve flame-retardancy and mechanical properties.[17,18] However, to be used as nanofiller for polymers, the organic modification of LDH is necessary. The current methods employed for modification of LDH such as anion exchange,[7] regeneration,[1] in situ synthesis,[8] etc., are either complex or yield products with inferior qualities in terms of crystallinity, homogeneity, and composition. For example, the regeneration method is a two-step procedure, often interfered by the presence of other ions in the system. In addition, changes in composition and/or crystallinity can occur after regeneration.[19] Similarly, direct anion exchange and in situ synthesis methods do not yield very efficient intercalation of anionic surfactant under ambient conditions due to the interference with $CO_3{}^{2-}$, which has very strong affinity for LDH layers. The coprecipitation method has been also reported for in situ synthesis of polymer nanocomposites, where the intercalation of high molecular weight polymers

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occur within the LDH sheet during the formation of the metal hydroxide layers.[20,21] However, the up-scaling of this method to produce greater volume of materials and also the efficiency in polyolefin based system are still questionable. Thus, the significantly increased cost of the organo-LDH in comparison to very cheap and natural parent materials becomes a limiting factor for their large scale industrial application. A design of a novel simple and low-cost on an industrial scale synthesis of organo-LDH is a major challenge for material scientists. Therefore, a one-step method to synthesize organo-LDH would be the right approach, efficiency of which should be assessed regardless of the nature of the starting reactants (more specifically, different competitive anions) and the anionic surfactant.

In this report, we present a one-step synthesis method to prepare organo-LDH. A common surfactant, sodium dodecylbenzenesulfonate (DBS), has been employed as an organic modifier. No additional measures other than controlling the pH of the medium were required to obtain a high degree of intercalation by the surfactant retaining the high crystallinity independent of the presence of other anions, like NO_3^-, CO_3^{2-}, and Cl^-. The prepared organo-LDH has been characterized in detail by WAXS, FTIR and ^{27}Al NMR and ^{1}H MAS NMR and compared with those obtained by the common modified methods such as regeneration and ion-exchange for the first time.

2. Materials and Experimental Method

2.1. Materials. The metal nitrate salts, metal chloride salts, sodium hydroxide, sodium carbonate and sodium dodecylbenzenesulfonate (DBS) used for synthesis of organic Mg−Al LDH by one-step route were obtained from Aldrich Chemical Co. and used without further purification. The Mg−Al LDH (PURAL MG 63 HT, Mg:Al = 2:1) used for preparing modified LDH by regeneration method was supplied by the SASOL GmbH, Germany.

2.2. One-Step Synthesis of Organic LDH (LDH-CO_3-DBS, LDH-Cl-DBS, and LDH-NO_3-DBS). The organic Mg−Al LDHs with three different anions were prepared by one-step route. The synthesis was carried out by the slow addition of a mixed metal (Mg^{2+} and Al^{3+}) salt solution (with Mg^{2+}:Al^{3+} equal to 2:1 and a total metal ion concentration of 0.3 M, either metal nitrate salts or metal chloride salts as original source) to a DBS solution under continuous stirring maintaining the reaction temperature at 50 °C. During the synthesis the pH value was kept at 10 ± 0.2 by adding suitable amount of 1 M NaOH solution (product called LDH-Cl-DBS or LDH-NO_3-DBS) or mixed solution of NaOH and Na_2CO_3 (product called LDH-CO_3-DBS) of a molar ration equal to 5. After the addition of the mixed metal salt solution, the resulting slurry was continuously stirred at the same temperature for 0.5 h and then was allowed to age in a heater at 75 °C for 18 h. The final products were filtered and washed several times with distilled water to get rid of nonreacted surfactant molecules until the pH of the supernatant solution was about 7. The material was then dried in an oven at 80 °C until the constant weight was achieved.

2.3. Modification of LDH by Regeneration Method and Anion Exchange. Modification of LDH by regeneration method: The pristine LDH was calcined at 500 °C for more than 3 h. The calcined product was dispersed in a 0.1 M aqueous solution of DBS with solid/solution ratio 1 g/50 cm^3 and the dispersion was stirred by magnetic stirrer at 25 °C for 24 h. The white mass was then filtered, washed with distilled water several times, and finally dried in oven at 80 °C until constant weight, called LDH-DBS (regeneration).

Modification of LDH by anion exchange: The carbonate-based LDH was synthesized by the same procedure with a one-step method for LDH-CO_3-DBS except there no introducing DBS in the solution. The carbonate-based LDH was dispersed in a 0.1 M aqueous solution of DBS with a solid/solution ratio 1 g/50 cm^3, and the dispersion was stirred by magnetic stirrer at room temperature and reflux, respectively, for 24 h. The white mass was then filtered, washed with distilled water several times, and finally dried in oven at 80 °C until constant weight, called LDH-DBS (anion exchange-RT) and LDH-DBS (anion exchange-reflux), respectively.

2.4. Characterization Techniques. Wide angle X-ray scattering (WAXS) was performed using 2-circle diffractometer XRD 3003 θ/θ (GE Inspection Technologies/Seifert-FPM, Freiberg) with Cu Kα radiation (λ = 0.154 nm) in the range of 2θ = 0.5−25 ° using the step length of 0.05°. The crystallite size of the LDH materials was determined using the Scherrer equation in its simplified version (lattice distortions are neglected)

$$L = (\lambda\kappa)/(\beta\cos\theta)$$

where L is the thickness of the crystallite in the direction perpendicular to the plane of metal hydroxide sheet in LDH materials, κ is a factor between 0.87 and 1.00, β is the full-width at half-maximum (fwhm), and θ is the scattering angle. β was calculated on the basis of the Lorentzian profile of the reflections and Gaussian corrected peak broadening (due to the instrument function). The determination of the broadening for the first-order diffraction, i.e., (003), is difficult because of its asymmetric shape, so the calculation was made with respect to the second order diffraction, i.e., (006). The interlayer distance in the LDH materials was calculated using the Bragg's equation and averaged over the first four orders of diffraction.

The Fourier transform infrared spectra (FTIR) of the LDH materials were obtained using the BRUKER VERTEX 80 V spectrometer over the wavenumber range of 400−4000 cm^{-1}. The powdered samples were mixed with KBr and pressed in the form of pellets for the measurement of FTIR analysis.

Thermogravimetric analysis was done using a TA Instruments TGA Q 5000 in the range between room temperature and 800 °C at a heating rate of 10 K/min in a nitrogen atmosphere.

Scanning electron microscopy (SEM) (microscope model: LEO 435 VP, Carl Zeiss SMT) was used to study morphological features of the powdered samples. The samples were placed on a sample holder using conducting carbon cement and then coated with a thin layer of platinum (layer thickness 15 nm) using a sputter coater (BAL-TEC SCD 500 sputter coater).

For NMR measurements, the samples were placed in 4, 3.2, and 2.5 mm (o.d.) zirconium rotors. All NMR spectra were performed on a (11.7T) Bruker Advance 500 spectrometer with a resonance frequency of 130.34 MHz for ^{27}Al and 500.13 MHz for ^{1}H. ^{27}Al MAS NMR spectra were recorded at a spinning speed of 14kHz employing a BL4 MAS probe-head. A recycle delay of 1 s and 256 repetitions were used. A single pulse of 1 μs pulse duration was applied to ensure a quantitative excitation of

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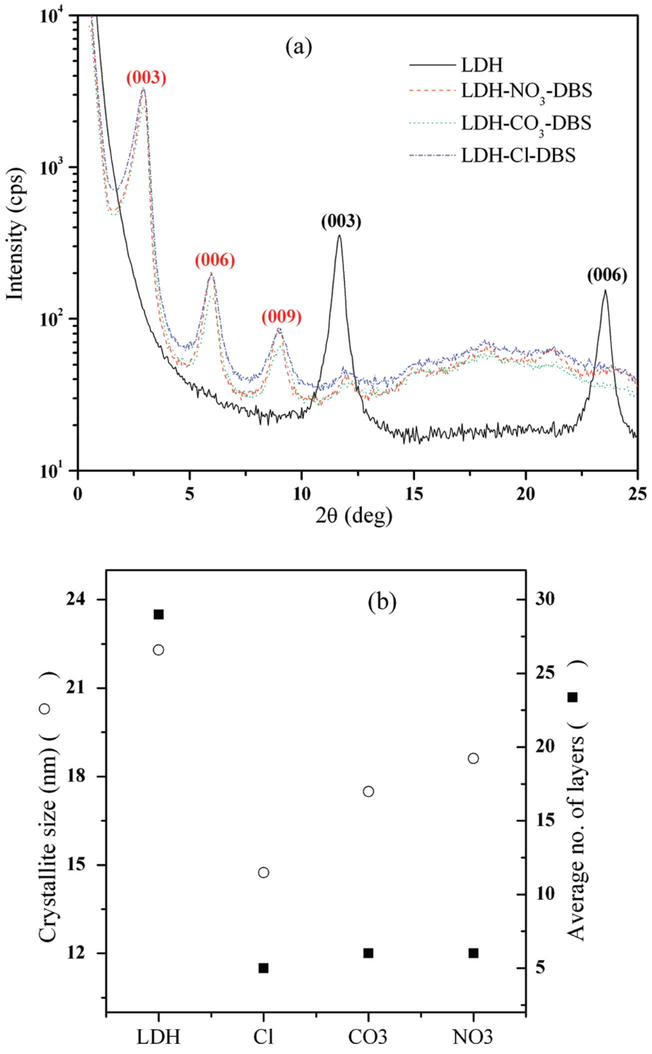

Figure 1. (a) WAXS patterns and (b) the crystallite size (thickness in the normal direction to the (00*L*) plane) for pure LDH and LDH modified by one-step synthesis.

the central transition.[22] ^{27}Al chemical shifts were referenced to 1 M AlCl$_3$ aqueous solution at 0 ppm. ^{1}H MAS NMR spectra were acquired with BL3.2 HXY 3.2 mm MAS probe-head at a spinning frequency of 20kHz and a recycle delay of 2 s employing a single 90° rf-pulse of 1.8 μs duration. ^{1}H combined rotation and multiple pulse spectroscopy (^{1}H CRAMPS) experiments were carried out employing 2.5 mm MAS probe-head and the BR-24 pulse sequence[23] at 4kHz sample spinning with a $\pi/2$-pulse duration of 1.4 μs and a cycle time of 60 μs. All ^{1}H spectra were referenced to TMS at 0 ppm using PVDF as an external reference. For quantitative analysis of NMR spectra Dmfit was used.[24]

3. Results and Discussion

3.1. Characterization of Organic LDH Synthesized by the One-Step Method. The WAXS patterns (Figure 1a) of the LDH and organo-LDH synthesized by one-step method revealed that DBS anion can be efficiently intercalated within the LDH layers by this method. In the unmodified LDH, the first basal reflection (003) at 2θ = 11.8° corresponds to an interlayer distance of 0.77 nm. The absence of any distinguishable reflection at this position in the modified LDH synthesized by the one-step method indicates that no unmodified LDH phase was formed. The reflections up to several orders in the WAXS patterns point to high crystalline order of the organo-LDH, indicating that the presence of DBS does not affect the formation of layered structure during coprecipitation of the metal ions. The WAXS patterns of organo-LDH obtained in the presence of different starting anion species, i.e. Cl$^-$, NO$_3$$^-$, and CO$_3$$^{2-}$, show the same interlayer distances proving the efficiency of the one-step method regardless of the starting material used. The possible presence of some of the anions in the interlayer region along with DBS anion does not affect the interlayer distances. This is a clear advantage of the one-step method in comparison to others, such as anion exchange, regeneration, or conventional in situ synthesis, demonstrating its universality for synthesis of organo-LDH.

The interlayer distance in the organo-LDH is estimated at 2.98 nm, which resembles the value observed for DBS-modified LDH synthesized by other methods. In Figure 2, the proposed scheme suggests a monolayer arrangement of surfactant anions in the interlayer region of the modified LDH by the one-step synthesis. The interlayer distance can be calculated as

$$d_{\text{calculated}} = d_{\text{layer}} + d_{\text{inter}}$$

where d_{layer} represents the thickness of the hydrotalcite brucite-like LDH sheet, 0.49 nm,[25] and d_{inter} includes the length of intercalated species and absorptive water in the interlayer. It has been reported that in LDH-DBS the loss of the absorbed interlayer water causes 0.32 nm contraction in basal spacing.[19] Because the orientation of the molecular chain of DBS anion is proposed to be perpendicular to the layer and has a dimension of 2.14 nm,[26] the interlayer distance is estimated to be 2.95 nm, which is in agreement with the experimental result (d = 2.98 nm). The crystallite thickness (Figure 1b) is smaller in modified LDH as compared to unmodified LDH. Moreover, it has been shown that the starting anions do not have any significant influence on the growth of the LDH-DBS crystallites. The average number of layers has been estimated from the crystallite size and interlayer distances and plotted in Figure 1b as well. The obtained results show 4-fold reduction in the average number of layers in each crystallite after modification.

The FTIR spectra of the organo-LDHs reveal the presence of DBS anion in the materials (Figure 3). The characteristic vibration bands were detected for the SO$_3$ group (symmetric stretching at 1037 cm^{-1} and asymmetric at 1182 cm^{-1}), the benzene group (C−C stretching at

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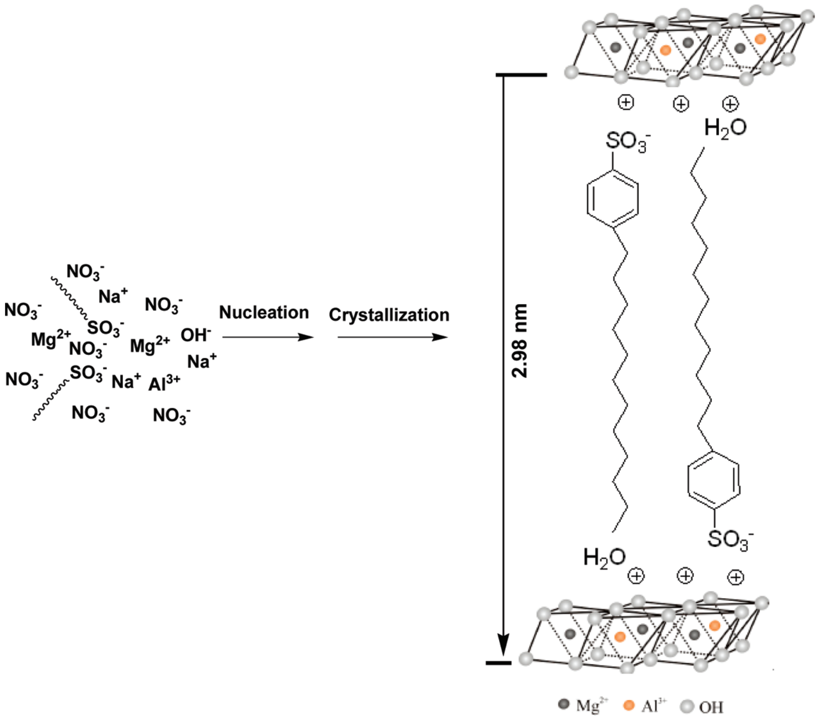


Figure 2. Schematic illustration of anion structure intercalated in the modified LDH by one-step synthesis.

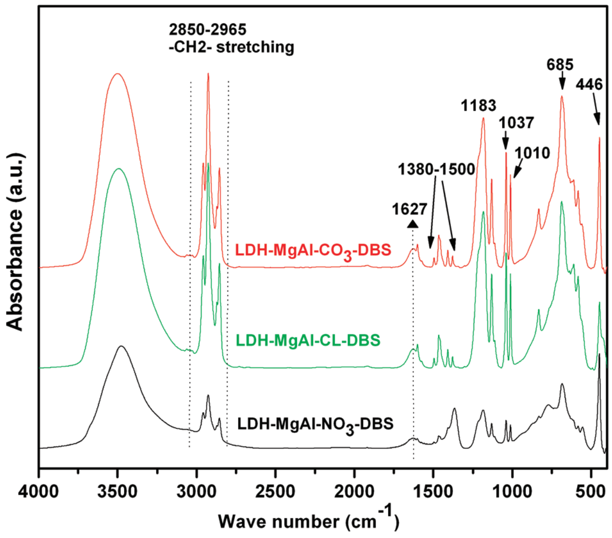
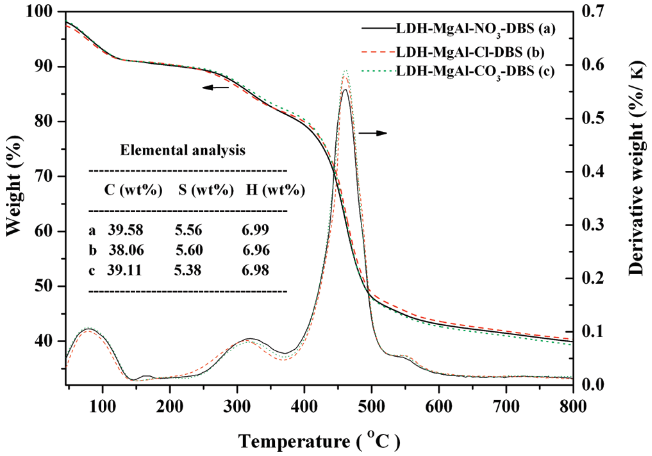


Figure 3. FTIR spectra of LDH modified by one-step synthesis.



Elemental analysis

	C (wt%)	S (wt%)	H (wt%)
a	39.58	5.56	6.99
b	38.06	5.60	6.96
c	39.11	5.38	6.98

Figure 4. TGA and elemental analysis of LDH modified by one-step synthesis.

1496 and 1602 cm^{-1}, C$-$H in plane bending at 1011 and 1131 cm^{-1}) and alkyl group (asymmetric stretching of CH_3 and CH_2 at 2958 and 2926 cm^{-1} respectively, symmetric stretching of CH_3 and CH_2 at 2872 and 2855 cm^{-1}, respectively, and CH_2 scissoring at 1466 cm^{-1}). The bands recorded below 800 cm^{-1}, especially the sharp and strong characteristic band around 450 cm^{-1}, arise because of the vibration of metal$-$oxygen bond in the brucite-like lattice. These results indicate the presence of DBS molecules in all the modified LDH and were consistent with the results of WAXS.

The elemental analysis of organo-LDH obtained by the one-step method along with their thermograms is showed in Figure 4. The results exhibit a 2:1 Mg:Al ratio and very high (nearly 100%) intercalation of the DBS anions within LDH layers. The similar contents of C, H and S in organo-LDH obtained from different starting materials indicate their similar chemical composition. These findings obviously establish the fact that the presence of nitrogen atmosphere is not always a necessary condition to incorporate DBS anion within LDH layer. The thermograms presented in Figure 4 reveal the similar thermal decomposition behavior for the organo-LDH materials synthesized by the one-step method that results from similarity of their chemical compositions identified by the elemental analysis. The characteristic features of these thermograms corresponding to the low temperature weight loss (roughly below 250 °C) and the thermal decomposition indicate similar amounts of interlayer water and the same Mg:Al ratio in all samples investigated, respectively.

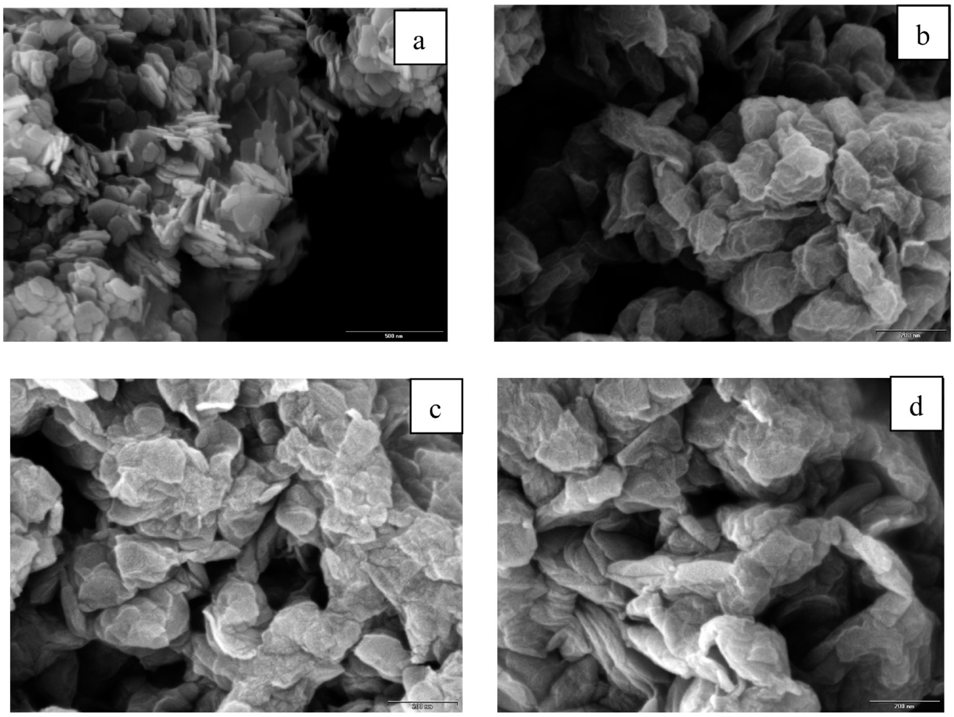


Figure 5. SEM micrographs showing the particle morphology of the LDH samples obtained by one-step synthesis: (a) MgAl21-CO_3 LDH, (b) MgAl21-Cl LDH-DBS, (c) MgAl21-CO_3 LDH-DBS, and (d) MgAl21-NO_3 LDH-DBS.

The morphological analysis of the modified LDHs obtained from different starting materials is shown in Figure 5. The unmodified LDH has platelike morphology with sharp edges, but no defined shape. Although some particles are crystallized in hexagonal shape, in most cases the formation of well-defined hexagonal plate was not complete. All the modified LDHs obtained by the one-step method show unambiguously similar particle morphology. The primary particles are found to be platelike without any defined shape; the edges are more irregular than in unmodified LDH, indicating that the growth of the crystal was not uniform on all the particle edges.

3.2. Comparison of the One-Step Method with the Regeneration and Anion Exchange Methods. In the previous section, it has been established that the one-step method is indeed a universal method for synthesizing organo-LDH and has not been affected by the presence of other common anions, like Cl^-, CO_3^{2-}, NO_3^-, etc. In this section, we report the comparison of this method with other conventional methods in terms of crystallinity, morphology, chemical composition of the modified LDH, and the efficiency of the modification process. For this purpose, such methods as anion exchange at room temperature and under reflux and the regeneration method have been considered. The samples obtained from these methods are designated accordingly as LDH-DBS (anion exchange-RT), LDH-DBS (anion exchange-reflux), and LDH-DBS (regeneration). The starting anion was CO_3^{2-}, which is known to have very high affinity for LDH layers.

3.2.1. WAXS Analysis of the Organo-LDH Synthesized by Different Methods. Figure 6 shows the WAXS pattern of unmodified LDH and the organo-LDH synthesized by anion exchange method at room temperature and under reflux condition, regeneration method, and one-step route. It is obvious that DBS ions do not undergo any ion-exchange reaction with the carbonate-based LDH at room temperature. But, under reflux conditions, evidence of a partial exchange reaction has been observed as some distinct diffraction maxima appear at lower 2θ values that correspond to an interlayer distance of 2.98 nm. However, a strong diffraction maximum at the original (003) position indicates that a large fraction of the LDH remains unaffected, which proves the inhomogeneity of

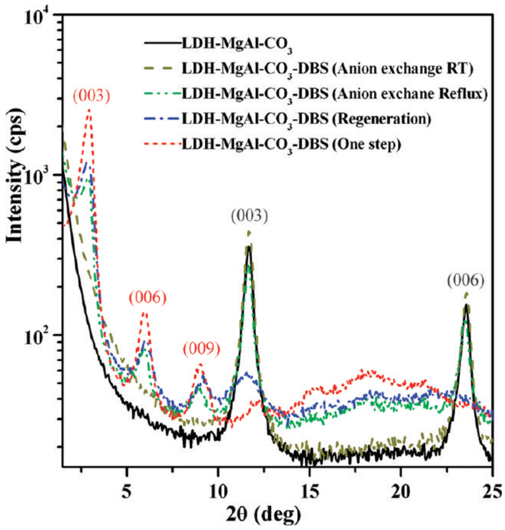


Figure 6. WAXS pattern of the organo-LDH synthesized by anion exchange method at room temperature and under reflux condition, regeneration method, and one-step route.

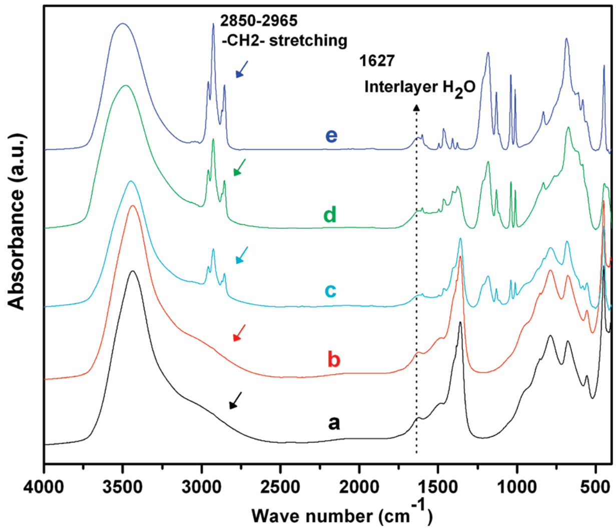
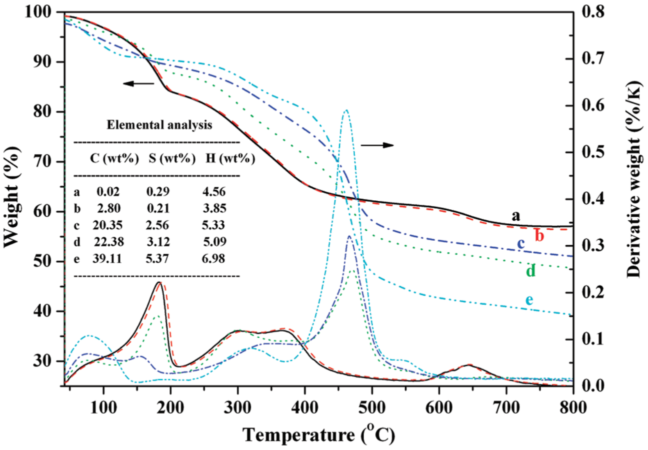


Figure 7. FTIR spectra of LDH materials: (a) MgAl21-CO_3 LDH, (b) MgAl21-CO_3LDH-DBS (anion exchange at room temperature), (c) MgAl21-CO_3 LDH-DBS (anion exchange under reflux condition), (d) MgAl21-CO_3 LDH-DBS synthesized by regeneration method, (e) MgAl21-CO_3 LDH-DBS synthesized by one-step synthesis.

the material. The regeneration is a very efficient method to synthesize organo-LDH from a carbonate-based precursor. Although a high degree of intercalation of DBS anion after regeneration has been observed in the present work, formation of some unmodified LDH fraction is still unavoidable, as indicated by the presence of a broad diffraction maximum at original (003) position. The LDH-DBS obtained by the one-step method appears to be the most homogeneous materials according to its WAXS pattern, which show significantly sharper diffraction maxima than commonly observed in DBS intercalated LDH. Moreover, no maximum corresponding to the unmodified phase is detected, translating the formation of a single-crystalline phase in organo-LDH obtained by the one-step method.

3.2.2. *FTIR Analysis.* The FTIR analysis presented in Figure 7 further proves that the ion-exchange reaction at room temperature does not cause any intercalation of DBS anion when carbonate-based LDH is used as precursor, because its spectrum exactly reproduces that of unmodified LDH. When anion exchange has been carried out under more aggressive condition, i.e., under reflux conditions, a partial intercalation of DBS within LDH has occurred, which is also detected in the FTIR spectra of the material. The presence of CH_2 and CH_3 stretching bands in range 2850−2970 cm^{-1} and a strong band at around 1357 cm^{-1} in this material indicate that both DBS and CO_3^{2-} are simultaneously present in the material. The modified LDH obtained by the regeneration method also show a broad, but strong band characteristic of CO_3^{2-} vibration, indicating that some CO_3^{2-} is still present in the final material. In contrast, the one-step method provides organo-LDH without any trace of CO_3^{2-} in the interlayer region because no characteristic bands have been detected in its FTIR spectrum. The largest differentiation between the organo-LDHs synthesized by the one-step method and the regeneration method is observed in the region below 500 cm^{-1}, which is responsible for stretching bands due to M-O bonding. That is, the sharp and strong 450 cm^{-1} band in the one-step LDH indicates the formation of the metal−oxygen framework similar to that in unmodified LDH, whereas a slight shift and a deformed shape of this band in the regenerated LDH point to the fact that some structural changes might have occurred in metal hydroxide layers during regeneration process. The detailed study of the structure of metal−oxygen framework is provided by solid-state ^{27}Al NMR and discussed in section 3.2.4.1.



Elemental analysis

	C (wt%)	S (wt%)	H (wt%)
a	0.02	0.29	4.56
b	2.80	0.21	3.85
c	20.35	2.56	5.33
d	22.38	3.12	5.09
e	39.11	5.37	6.98

Figure 8. TGA and elemental analysis of LDH and modified LDH by different methods.

3.2.3. *Thermal Analysis.* Thermogravimetric analyses (TGA) of the organo-LDH synthesized by different methods (Figure 8) show different thermal decomposition behavior resulted from different chemical compositions. The weight loss below about 225 °C is mainly due to loss of interlayer water and carbonate ions. The unmodified LDH and the LDH-DBS (anion exchange-RT) show the highest amount of weight loss in this region, whereas it is significantly smaller in other modified sample and is minimal in LDH-DBS synthesized by one-step method. Besides, the low-temperature weight loss in LDH-DBS (one-step) occurred up to about 125 °C, above which there is nearly no weight loss until about 250 °C. This indicates the presence of a very small amount of weakly bound interlayer water in LDH-DBS (one-step). The thermal stability is found to increase in the order of LDH-DBS (anion exchange-reflux), LDH-DBS (regeneration), LDH-DBS (one-step). This result correlates with the elemental analysis (the insert in Figure 8), which shows an increase in the amount of intercalated DBS in the same sequence. Our observation confirms the previously reported result that the intercalated surfactant improves the thermal stability of metal hydroxide layer in LDH.[27] The different extents of intercalated DBS in the modified LDH have been also reflected in the residue obtained, as LDH-DBS (one step) containing the highest amount of intercalated DBS yield the lowest amount of residue.

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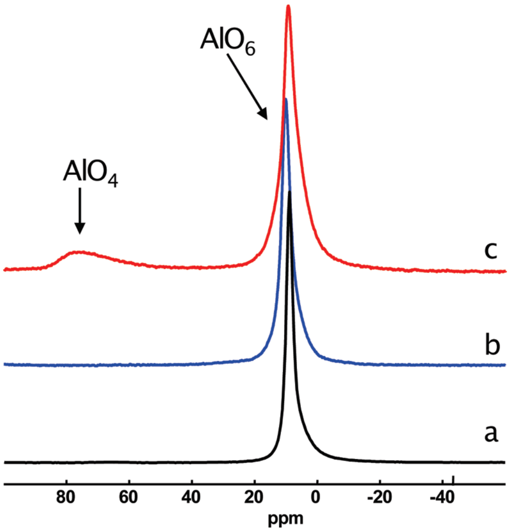

Figure 9. ^{27}Al MAS NMR spectra of (a) unmodified LDH, (b) LDH−DBS produced by one-step route, and (c) LDH−DBS produced by the regeneration method.

3.2.4. NMR Analysis. 3.2.4.1. ^{27}Al NMR. Figure 9 depicts the ^{27}Al MAS NMR spectra of one unmodified and two LDH−DBS samples produced by the regeneration method and by the one-step route, respectively. All spectra show an intense signal centered at ca. 10 ppm, which is unambiguously attributed to octahedral Al (or six-coordinated AlO_6) sites. This observation supports the fact that the structure of LDH is composed of Al cations that are coordinated by six OH groups (hydroxide) forming octahedral sheets. LDH formed by either route is composed of octahedral aluminum, proving the equivalence of the synthetic routes (though the one-step route is simpler to implement). Deconvolution of the AlO_6 signals (not shown here) reveals coexistence of two nonequivalent aluminum sites regardless of the processing route. Their relative peak area ratios coincide within an error margin ± 5% in pure LDH and one-step route produced LDH−DBS that abundantly evidence the similarity in their local structures. In the ^{27}Al spectrum of regenerated LDH, a signal centered at 70 ppm is also observed that is a signature of tetrahedral aluminum (or four-coordinated AlO_4). A quantitative analysis reveals that 15% of the four-coordinated aluminum is present in the regenerated LDH, which is thought to be the product of calcination involved in the regeneration procedure. Partial transformation of six-coordinated aluminum to the four-coordinated aluminum has been recently observed in BEHP-modified LDH also prepared by the regeneration method.[28]

Additional information can be extracted analyzing the line shape of the quadrupolar ^{27}Al spectrum, in which the strength and distribution of quadrupolar interactions point to the symmetry and ordering in local aluminum environment. Thus the narrower and rather symmetric AlO_6 signal observed in LDH−DBS prepared by the one-step route in contrast to the regenerated LDH−DBS indicates lower quadrupolar coupling and its lower distributions translating more ordered and symmetric octahedral Al positions. It means that LDH−DBS obtained from the one-step route has formed a relative single-crystalline phase that is consistent with the result of WAXS.

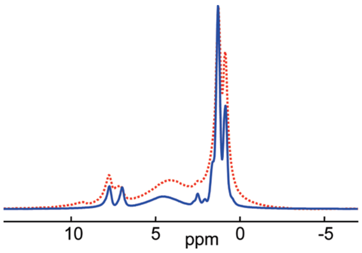

Figure 10. ^{1}H MAS NMR spectra of LDH-DBS produced by the regeneration method (red dashed line) and by one-step route (blue solid line).

3.2.4.2. ^{1}H MAS NMR and ^{1}H CRAMPS. The ^{1}H MAS NMR spectra of LDH−DBS prepared by the regeneration and the one-step method are presented in Figure 10. The peak positions in both spectra are identical, whereas those widths are significantly different. A group of narrow and intense signals between 0.8 and 2.5 ppm arise from aliphatic hydrocarbon chain protons of DBS; the benzene ring protons show the signals at 7.0−7.8 ppm. The broad resonances in both spectra centered at 4.0−4.5 ppm are attributed to superposition of physically adsorbed water and metal bound OH groups. Strong residual dipolar interactions due to restricted mobility of interlayer water molecules as well as diversity of the local environment of individual hydroxyl sites within an LDH layer[29] cause significant broadening of this signal.

Comparing the line widths of both ^{1}H MAS spectra, one can note that the signals of the regeneration-produced LDH are considerably broader than those from one-step-route-synthesized LDH. This broadening can originate either from structural disorder resulted in distribution of isotropic chemical shifts or from the strong homo- or heteronuclear dipolar coupling. ^{1}H CRAMPS (not shown here) unambiguously evidence that structural disorder is responsible for the line broadening in the case of regenerated LDH, because dipolar coupling is averaged out by CRAMPS and thus does not contribute to the line width. The possible explanation for disorder can be on the one hand the smaller LDH-platelet sizes, and on the other hand the presence of calcination products, e.g., tetrahedral aluminum, which is clearly visible in the ^{27}Al NMR spectrum.

4. Conclusion

The objective of the present investigation has been achieved successfully through developing a novel single-step method to synthesize organo-modified LDH. The starting point was based on the most difficult system, where the interfering anion CO_3^{2-} is known to have a very

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strong affinity for LDH layers. A critical control of the pH value of the system during the addition of surfactant solution was the pivotal aspect of this synthesis process. The intercalation behavior and structure of organo-LDH synthesized by the one-step method have been characterized by WAXS, FTIR, SEM, TGA, ^{27}Al NMR, and ^{1}H MAS NMR and compared with those obtained by the common modified methods such as regeneration and ion exchange.

The reported one-step method has been indeed proven to provide very efficient intercalation of anionic surfactant in LDH irrespective of starting counteranions of the metal ions. Although the cointercalation of CO_3^{2-} could not be avoided completely, it was kept at very low level as compared to other methods. The modified LDH obtained by the one-step method shows the high degree of crystallinity and homogeneity in composition. In comparison to the regeneration method, the most commonly used for organic modification of CO_3^{2-}-based LDH, the proposed one-step method provides improved quality of the modified LDH in terms of crystallinity, extent of intercalation, thermal stability not affecting the local structure of metal−oxygen framework. Thus, the experimental characterization of the one-step prepared LDH and detailed comparison with those obtained by other methods deliver solid evidence that the one-step synthesis is the superior method to synthesize organically modified LDH under ambient conditions and without requirement of carbonate free condition.

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