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Modification of nano-sized layered double hydroxides by long-chain organic aliphatic surfactants

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Abstract: The inter-layer anion of layered double hydroxides (LDH) with a hydrotalcite (HT)-like structure was ion-exchanged with various organic surfactants, particularly with long chain aliphatic surfactants. After the ion-exchange process, the basal spacing of the LDH was increased and the increase of the basal spacing depended on various factors, such as the intercalation capacity functionality and orientation capability of the surfactant. Of the employed surfactants, stearic acid intercalated LDH showed the highest increase of the basal spacing, which was confirmed by XRD analysis. FTIR results supported the interaction of the surfactants with the LDH. In addition, an increase in the thermal stability of the dodecanedioic acid intercalated HT was evidenced by the TGA method.

Keywords: hybrid; ion-exchange method; XRD; FTIR spectroscopy; TGA.

INTRODUCTION

Recently layered double hydroxides (LDH), synthetic clays with a hydrotalcite (HT)-like structure, have tempted both industrialists and academics due to their versatile applications as ion-exchangers, catalysts and electrolytes.[1–3] Nevertheless, their applications are limited due to their incompatibility with organic materials. In such a way their physical and chemical activities are frozen. This problem can be overcome by the introduction of a surfactant with mono- or multi-functionality into the HT structure through the ion-exchange method, with the surfactant playing the role of combatibilizer. The hydrophobicity of the HT is increased after modification with organic surfactants. Selection of the surfactant is very important because it not only increases the hydrophobicity but also increases the thermal and catalytic activities of the LDH.

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A literature search revealed a number of papers related to the present topic. You *et al.*[4] modified a HT (containing Mg and Al as the divalent and trivalent metal ions with Cl ions as the interlayer anion) using various long chain aliphatic sulfates and aromatic sulfonates. In that study, a perpendicular approach of the surfactant into the HT was proposed. LDHs with various Mg/Al ratios were synthesized in which the Cl^- ion was the interlayer anion and the obtained LDHs were ion-exchanged with stearate anions.[5] A poly(ethylene oxide) (PEO) intercalated Mg–Al LDH was reported by Wypych and co-workers.[6] A paratungstate grafted (Mg/Al = 2) LDH was reported.[7] An acrylate anion intercalated Ni-based LDH was prepared and polymerized by an *in situ* method.[8] Steven and co-workers[9] modified an LDH by the ion-exchange method with carboxylates, sulfonates, phosphonates, porphyrins and phthalocyanin for certain catalysis and electrochemical applications. Recently Narita *et al.*[10] published a calixarene-*p*-sulfonate intercalated LDH. Anbarasan *et al.*[11] communicated results on the modification of a LDH by various sulfonates. A phosphonate intercalated LDH was also prepared.[12] Mg/Al and Zn/Al LDHs were intercalated with metallic oxalato complexes and the resulting hybrids were characterized by FTIR spectroscopy and XRD analysis.[13] An L-aspartic acid intercalated LDH was prepared and characterized by various analytical techniques.[14] Intercalation of bio-molecules, such as hexose, pentose, nucleotide, deoxyribonucleic acid, amino acids and polypeptides into LDH was reported by different authors.[15–20] A tetradecanoic acid intercalated LDH was reported by Changwen *et al.*[21] A report of a 4-hydroxy-3-methoxy cinnamic acid intercalated LDH is also available in the literature.[22]

The present communication reports the modification of an Mg/Al LDH with different long-chain organic aliphatic surfactants with various structural aspects discussed. The hybrids were characterized by FTIR, XRD and TGA methods.

EXPERIMENTAL

Materials

HT (nano-sized material), an LDH with carbonate anions as the inter-layer anion (Mg/Al = = 2.1, with a layer thickness of 0.48 nm) was a gift sample from KICET (Korea) and was used as received. Dodecane-1,12-diol (DDDIOL), dodecanedioic acid (DDDA), heptadecanoic acid (HDA) and octadecanoic acid (stearic acid) (SA) (Aldrich Chemicals, Korea) were used for the purpose of modification. The employed olive oil (OO) (Junsei Chemicals Co. Ltd., Japan) consisted of 85 % oleic acid (OA) (octadec-9-enoic acid), 9 % linoleic acid and 1.5 % of linolenic acid. In this study, the activity due to OA was considered due to its high content in OO. These surfactants were purchased and used without any further purification.

Method

HT (5 g) was placed in a 500 ml three-necked round-bottomed flask containing 250 ml of de-ionized water. The middle neck was used to attach a stirrer and the other two were used as the nitrogen inlet and outlet. Surfactant (10 g) was added under vigorous stirring to the content of the flask under inert atmosphere at 70 °C. Stirring in the alkaline medium was continued for 48 h. The ratio of carbonate to surfactant must be 1:2 because the divalent carbonate anions were ion-exchanged by the monovalent surfactant. After 48 h, the content of the flask was filtered and the precipitate was washed several times with de-ionized water to remove the sodium carbonate formed during the ion-exchange reaction and dried at room temperature overnight. The thus obtained white solid was ground and stored in a vial bottle.

Characterization

The HT powder before and after the ion-exchange reaction was characterized by XRD analysis using a Rigaku Rint 2000 (Japan) diffractometer at room temperature with CuKα1 radiation, in the 2θ angle range from 2 to 70° and by FTIR spectroscopy (KBr pellet technique) using a Nicolet 760 magna FTIR spectrometer. The thermal stability of the HT before and after modification was checked by thermogravimetric analysis (TGA), performed under a dynamic air atmosphere at a heating rate of 10 °C min^{-1} using an SDT 2960 TGA instrument.

The basal spacing (d) (from the Bragg equation), the inclined angle (ϕ) and the gallery height (L) can be calculated from Eqs. (1), (2) and (3), respectively.

$$d = \frac{\lambda}{2\sin\theta} \tag{1}$$

$$\sin\phi = \frac{\text{Basal spacing of } d_{003} \text{ plane} - \text{Thickness of layer}}{\text{Length of the organic anionic surfactant}} \tag{2}$$

$$L = d - \text{Thickness of layer} \tag{3}$$

where d is the basal spacing, θ the diffraction angle, λ the wavelength, ϕ the contact angle and L is the gallery height. The chain lengths of the organic aliphatic surfactants were calculated based on Isupov's[23] semi-empirical formula.

RESULTS AND DISCUSSION

The FTIR spectrum of pure HT is shown in Fig. 1 (curve a). It exhibited four peaks: *i.e.*, a peak at 3500 cm^{-1}, due to OH stretching (from interlayer water molecules); a bending vibration of water at 1641 cm^{-1}; carbonate stretching at 1377 cm^{-1}, as a sharp peak, and metal–hydroxide stretching at 679 cm^{-1}. The FTIR spectrum of HT–DDDIOL is shown in Fig. 1(curve b), from which it can be seen that some new peaks are present in addition to the HT peaks, *i.e.*, a twin peak at 2924 and 2836 cm^{-1}, due to C−H antisymmetric and symmetric stretching, peaks at 1453, 1044 and 990 cm^{-1}, due to CH_2 bending, alcoholic C−O antisymmetric stretching and chain folding, respectively. The appearance of the new peaks confirms the interaction between HT and DDDIOL. The FTIR spectra of HT–DDDA, HT–HDA, HT–SA, and HT–OO are shown in Fig. 1 (curves c–f, respectively). The same peaks as mentioned above were also present in these spectra. These FTIR spectra are, however, not sufficient to prove the existence of interaction between HT and surfactants and they cannot clearly explain the type of interaction. A peak due to carbonyl stretching of the long chain carboxyl group (≈ 1730 cm^{-1}) is not visible in Fig. 1 (curves c–e). Normally, FTIR spectra for long chain carboxyl compounds do not show the carbonyl peak clearly. In the case of HT–OO (Fig. 1, curve f), a peak at 1742 cm^{-1} due to carbonyl stretching of the unsaturated long-chain aliphatic carboxylic acid can be seen. This is an entirely new peak and different from the other long chain carboxylic acids. The reason for this will be discussed in detail in the following XRD and TGA section. Nevertheless, in all the FTIR spectra, including HT–OO, one can observe a peak at ≈ 1365 cm^{-1} due to carbonate stretching. This indicates that even after modification of HT with the organic surfactants, complete removal of carbonate anion from the gallery space was not possible. This is because of the high charge density of the HT layer and the rapid uptake of CO_2 from the atmosphere by the water molecules and very fast re-substitution reactions.

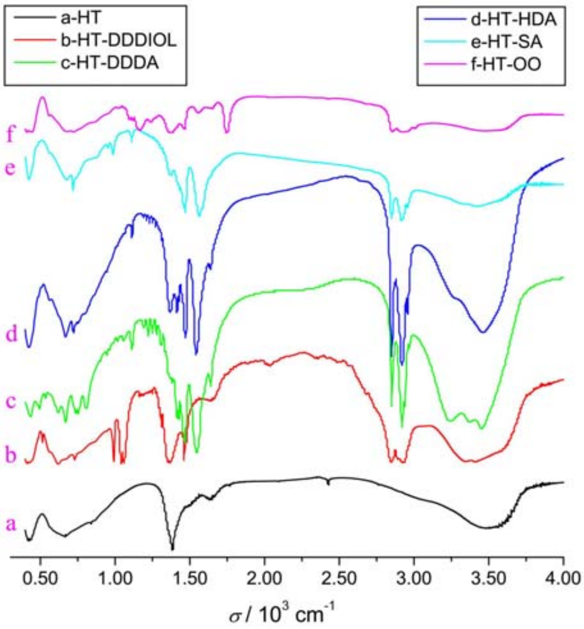


Fig. 1. FTIR spectrum of a) HT, b) HT–DDDIOL, c) HT–DDDA, d) HT–HDA, e) HT–SA and f) HT–OO.

The XRD profiles of HT before and after modification are shown in Fig. 2 and the data given in Table I. The crystalline peaks of HT are represented in Fig. 2 (curve a), in which the d_{003}, d_{006}, d_{012}, d_{015}, d_{018}, d_{110} and d_{113} plane peaks are visible. The original HT showed a gallery height of 0.289 nm, corresponding to the length of the carbonate anion. After modification with DDDIOL (Fig. 2, curve b), the gallery height was increased to 1.176 nm. This can be confirmed by the appearance of a small peak at the 2θ value of 7.21°, with the corresponding basal spacing of 1.224 nm. DDDIOL approached the hydroxyl layer of HT at 21° (parallel approach), with the formation of a mono-layer structure. It is possible to form a bi-layer structure because DDDIOL has an OH group at both ends of its molecule. However, the XRD results showed no formation of a bi-layer structure (*i.e.*, no pillar-like structural arrangement). The intensity (normalized intensity) of the d_{006} plane peak was greatly enhanced due to the presence of DDDIOL. The other small peaks are due to crystalline peaks of DDDIOL. The important point noted here is the maintenance of the layered arrangement even after the modification with long chain aliphatic surfactant. The XRD pattern of HT–DDDA is shown in Fig. 2, curve c (normalized intensity), with a gallery height of 1.544 nm with a monolayer structure. The orientation angle was calculated as 39°. Two new peaks appeared at low 2θ values, *i.e.*, at 4.36 and 6.86°, which correspond to the d_{001} and d_{002} planes, respectively. Other small shoulders which appeared in the XRD pattern are due to DDDA. DDDA has a better intercalation capacity than DDDIOL. In the case of organic–inorganic hybrids, the length of a surfactant is an important factor. In the present system, both DDDIOL, and DDDA have very similar chain lengths but their intercalation capacity is different due to their different functionalities. DDDA form a mono-layer structure with HT (Scheme 1). Hence, the alignment of the surfactant in the gallery space is also of primary importance. However, sometimes the layered structure may be delaminated due to improper alignment of the surfactant molecules in the interlayer space of HT. Moreover, both are bi-functional in nature but their intercalation capacities and orientation capabilities are different. This is because of the nature of the functional groups, which tend to form ionic structures.

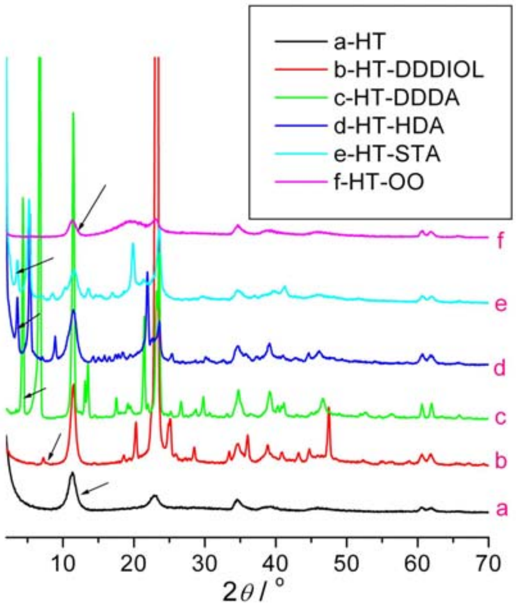
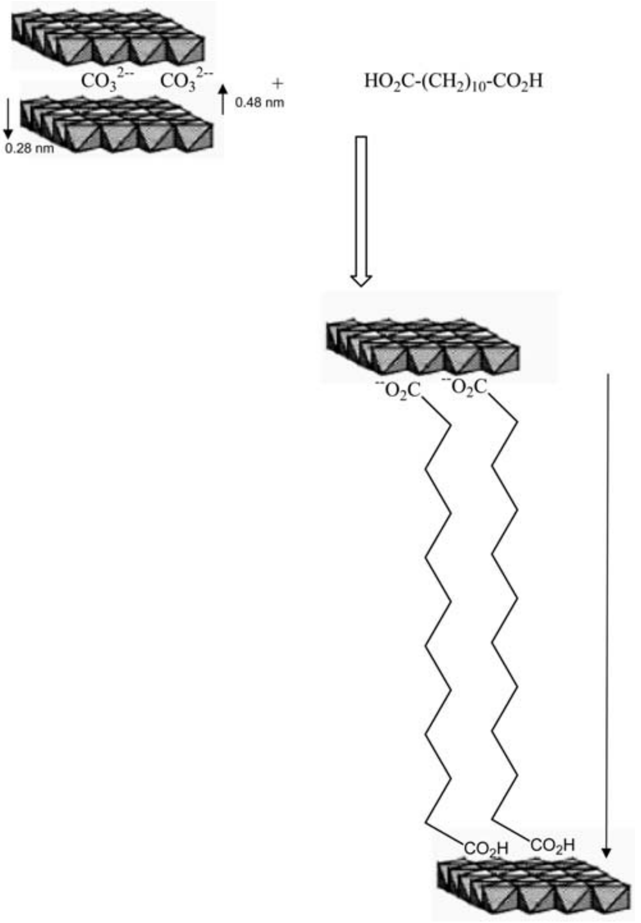


Fig. 2. XRD Pattern of a) HT, b) HT––DDDIOL, c) HT–DDDA, d) HT–HDA, e) HT–SA and f) HT–OO.

The XRD patterns of HT–HDA and HT–SA are shown in Fig. 2 (curves d and e), with gallery heights of 1.987 nm and 2.192 nm, respectively. These surfactants differ by only one $-CH_2-$ group. Their orientation angle increases from 44° for HDA to 54° for SA. However, their chemical activities coincide by forming a mono-layer structure because they have only one functional group at their chain ends. Comparing their intercalation capacities, SA exhibited a better intercalation capacity by increasing the basal spacing than HDA, DDDIOL or DDDA. The XRD results indicated that with increasing chain length of the surfactant, the basal spacing and orientation angle are also increased. The highest basal spacing exhibited by the HT–SA system indicated that SA had the best intercalation capacity of the four above-mentioned surfactants.

TABLE I. XRD analysis of HT before and after modification with various surfactants

System	2θ / °	Basal spacing nm	Orientation angle ϕ / °	Layer structure	Gallery height nm
HT	11.49	0.769	–	–	0.289
HT–DDDIOL	7.21	1.224	21	Monolayer	1.176
HT–DDDA	4.36	2.024	39	Monolayer	1.544
HT–HDA	3.57	2.467	44	Monolayer	1.987
HT–SA	3.30	2.672	54	Monolayer	2.192
HT–OO(OA)	11.49	0.769	–	–	0.289



Scheme 1.

In the case of the HT–OO system (Fig. 2, curve f), the gallery height was not increased even after the ion-exchange process with OO. This indicates that OO was not intercalated into the HT structure. On the contrary, the FTIR spectrum showed a possible interaction between HT and OO. This controversy can be explained as follows. The FTIR results of the HT–OO system inferred the presence of carbonyl stretching but the XRD indicated a zero increase in the gallery height. As mentioned in the experimental part, OO contains different compounds with different chain lengths and different numbers of double bonds. The ion-exchange process was carried out at 70 °C under a nitrogen atmosphere with vigorous stirring. Under these experimental conditions, polymerization, oligomerization or at least dimerization could be thermally initiated as a result of which the size and chain length of the surfactants were increased and hence unable to intercalate into the HT gallery space. In OO, polymerization occurred in two different ways, *i.e.*, homo and copolymerization, because OO consists of 85 % OA (containing one double bond), 9 % linoleic acid (containing two double bonds) and 1.5 % linolenic acid. OA leads to homopolymerization because of its higher content in OO. Simultaneously, it is possible to form copolymers with other double bond-containing compounds. In this case, intercalation and polymerization are competitive reactions. The XRD results confirmed that polymerization was the dominant reaction through the zero increase in the basal spacing of HT. Polymer, either homo or copolymer, formed in the reaction medium may restrict the interaction between HT and the single linear double bond containing surfactants by increasing the viscosity of the reaction medium. Formation of polymer or oligomer during the ion-exchange process could be visually seen by the gel-like appearance of the hybrid. Secondly, the FTIR spectrum did not show a peak due to C=C around 1680 cm^{-1}. Hence, the FTIR and XRD results combined led to the proposal of interaction *via* the hydrogen bonding mechanism, *i.e.*, OO interacts with HT through the only possible way of hydrogen bonding. There is no other chemical force between them.

The XRD results of the hybrids indicated on comparing all that SA acts as a better intercalating agent than the other surfactants, even though it is a mono-functional compound, as the basal spacing of HT increased without layer degradation. All intercalants, except OO, interacted with HT through ionic bonding. OO prefers hydrogen bonding because polymerization or oligomerization led to a bulky size and very long chain length. Recently, the hydrogen bonding mechanism was proposed for the HT–hydroxyethanesulfonic acid hybrid system.[10]

The thermal stabilities of HT and its hybrids are presented and compared in Fig. 3 and Table II. Nominally, HT showed a four-step degradation mechanism (Fig. 3, curve a). The first and second steps corresponded to the removal of physisorbed and interlayer water molecules, respectively. The major and important step is the removal of water molecules through the dehydroxylation process. The last minor step was the degradation of carbonate inter-layer anions. Up to 400 °C, HT showed a mass loss of 29.63 % (Table II). The residual mass at 700 °C was 56.95 %. In the case of the HT–DDDIOL hybrid system (Fig. 3, curve b), a two-step degradation process was evidenced. The first major degradation step corresponds to the degradation of DDDIOL from the HT, followed by a dehydroxylation process. The second minor step was the dehydroxylation process alone. For pure HT, the dehydroxylation occurred at around 350 °C. However, in the present system (HT–DDDIOL), dehydroxylation occurred at ≈ 250 °C. This is due to the poor intercalation capacity of DDDIOL. Once the DDDIOL had been removed, dehydroxylation immediately occurred. At 400 °C, it showed a 22.52 % mass loss. The residual mass at 700 °C was 19.45 %, due to the formation of mixed metal oxides.

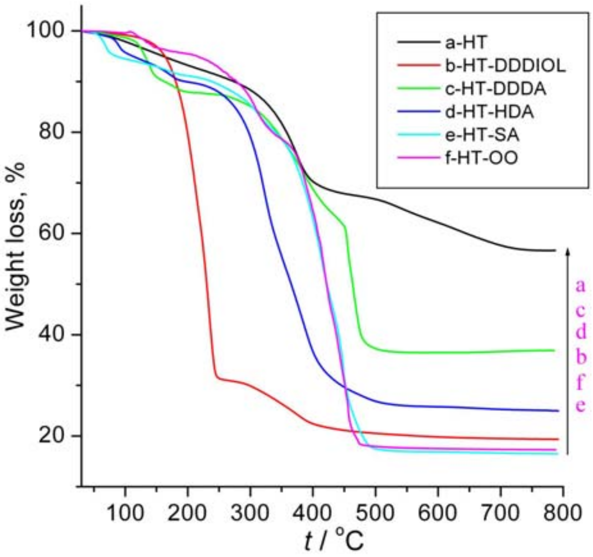


Fig. 3. TGA of a) HT, b) HT–DDDIOL, c) HT–DDDA, d) HT–HDA, e) HT–SA and f) HT–OO.

TABLE II. TG Analysis of HT before and after modification with various surfactants

System	Weight loss at 200 °C, %	Weight loss at 400 °C, %	Weight loss at 500 °C, %	Weight loss at 600 °C, %	Residual mass %
HT	93.01	70.37	66.80	61.97	56.95
HT–DDDIOL	80.42	22.52	20.62	19.92	19.45
HT–DDDA	87.67	69.04	37.21	36.53	36.53
HT–HDA	89.99	36.76	26.78	25.77	25.34
HT–SA	91.08	63.46	17.44	16.76	16.57
HT–OO(OA)	95.34	64.80	17.78	17.40	17.08

In the case of HT–DDDA (Fig. 3, curve c), the first and second steps were as usual the removal of physisorbed and interlayer water molecules. Third step at 385 °C was due to the degradation of DDDA. The fourth major mass loss was due to the dehydroxylation process (at 457 °C). At 400 °C, it showed only 30.96 % mass loss (Table II). Above 700 °C, the residual mass was 36.53 %. Comparing the thermal stability of HT, HT–DDDIOL and HT–DDDA, the last one exhibited the highest thermal stability. This may be due to the strong intercalation capacity of the bi-functional DDDA. The increase in thermal stability confirms the existence of strong ionic forces between HT and DDDA. The TG curve of HT–HDA is shown at Fig. 3 (curve d). In this hybrid system, dehydroxylation occurred at temperatures between those of pure HT and HT–DDDIOL. The residual mass above 700 °C was 25.34 %. The thermal degradation stability of HT–SA is shown in Fig. 3 (curve e). In this case, dehydroxylation occurred around 425 °C, which is higher than that of pristine HT. At 400 °C, it exhibited a mass loss of 36.54 %. The residue above 700 °C was 16.57 %. Comparing the thermal stability of HT–HDA and HT–SA, it can be seen that the latter hybrid showed a higher thermal stability, although the surfactants have a very similar chain length with structural identity. It showed the second highest thermal stability after the HT–DDDA hybrid system.

The TG curve of HT–OO is shown in Fig. 3 (curve f). At 400 °C, a 35.20 % mass loss was observed while the residue above 700 °C was 17.08 % (Table II). The dehydroxylation of HT–OO occurred at 416 °C. This system showed higher thermal stability for the dehydroxylation process than the pristine HT, HT–DDDIOL and HT–HDA systems. As mentioned earlier, only hydrogen bonding exists between HT and OO, but nevertheless this system showed a slightly higher thermal stability. This may be due to the following reason, *i.e.*, at 350 °C, it showed an initial dehydroxylation process but immediately the free carboxyl groups of the polymerized or oligomerized OO interacted with the HT through ionic linkage. Hence, the dehydroxylation temperature was increased. The dissociation of HT–OO linkages and dehydroxylation could be simultaneous processes.

In an overall discussion of the TGA results it should be mentioned that separate decomposition step due to carbonate decomposition in the modified HT was not evidenced, although the FTIR spectra confirmed the presence of carbonate anions in the hybrids. From these two results, it can be concluded that carbonate ions may be present only in trace amounts, which may not be sufficient to appear on the TG curves. Secondly, the long chain diol is not suitable for hybrid preparation because of its lower thermal stability. Finally, the mono-functional acid surfactants with similar structures showed different thermal stabilities.

CONCLUSIONS

Organic–inorganic hybrids were prepared *via* the ion-exchange method with various long chain organic aliphatic surfactants. FTIR spectroscopy supported the presence of the long chain anionic aliphatic surfactants in the LDH structure. The XRD results showed that the mono-carboxylic (SA) surfactant exhibited a higher basal spacing than the dicarboxylic acid surfactants and the diol surfactant without degradation of the layer structure. OO interacted with HT through hydrogen bonding whereas the diol and other surfactants interacted with LDH through ionic linkage. XRD analysis also confirmed that no pillar-like structure was formed during the modification. TGA results revealed that the di-carboxylic acid containing surfactant DDDA showed a higher thermal stability than the alcohol and mono-carboxylic acid containing surfactants.

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ИЗВОД

МОДИФИКАЦИЈА НАНОДИМЕНЗИОНИХ ДВОСТРУКИХ СЛОЈЕВИТИХ ХИДРОКСИДА ДУГОЛАНЧАНИМ ПОВРШИНСКИ АКТИВНИМ СУПСТАНЦАМА

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Међуслојни анјон у структури двоструког слојевитог хидроксида (LDH) типа хидро-талка (HT) је јонском изменом замењен различитим дуголанчаним алифатичним површински активним супстанцама. После јонске измене базално међуслојно растојање (LDH) је расло у зависности од интеркалационе способности, оријентације и функционалних група коришћених површински активних супстанци. Резултати XRD потврђују да се највеће повећање базалног растојања постиже интеркалацијом стеаринске киселине. Резултати FTIR потврђују интеракцију површински активних супстанци са LDH. TGA анализа је потврдила да се термална стабилност HT повећава интеркалацијом додекан-дикиселине.

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