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Layered double hydroxides intercalated by long chain anions as oil phase gelling agent

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Layered double hydroxides intercalated by long-chain anionic species were prepared and characterized by X-ray powder diffraction.The linear carboxylates are greatly disordered along the stacking direction but dimer fatty acids with planar aromatic moieties show regular X-ray patterns. Alkylarylsulfonates and petroleum sulfonates aggregated in the interlayer spaces forming bimolecular films of constant thickness, which produce integral series of basal reflections in the X-ray diagrams. Solubility and gel strength of prepared exchanged layered double hydroxides were tested in an oil base drilling fluid formulation and applications of these compounds were compared with conventional organophilic clays.

Keywords: Layered double hydroxides, Hydrotalcite, Intercalation, Long chain anion

Layered double hydroxides (LDHs), also known as hydrotalcite- like compounds have a brucite structure with general formula of $[\mathrm{M}^{\mathrm{II}}{}_{1-x}\mathrm{M}^{\mathrm{III}}{}_{x}\ (\mathrm{OH})_2]_x.\ (\mathrm{A}^{n-})_{x/n}\cdot y\mathrm{H_2O}$, where the $\mathrm{M^{II}}$ and $\mathrm{M^{III}}$ are the di- and tri-valent cations. Some of the divalent cations in LDHs can be replaced by trivalent ions to generate positively charged sheets[1,2]. A^{n-} is the interlayer anion and x can have values between 0.25 and 0.33[3]. Intercalation of anions, typically carbonate or nitrate, in the hydrated interlayer regions between the metal hydroxide layers lead to the neutrality of these anionic clays[4]. Each of two neighbor layers can be crowded by hydrogen bonding between the hydroxyl groups[5]. Besides the anionic species, water molecules are presented in the interlayer space[6].

Layered double hydroxides have been applied as catalysts, catalyst supports, selective chemical nano reactors, anion separator and scavenger[7,8]. The high anion exchange capacity of LDHs for simple inorganic species[9], polyoxometalates[10], organic anions[11], and polymers[12], make them one of the most applicable species in the solid state chemistry.

Therefore LDHs could be intercalated by organic ions such as carboxylate anions[13-15]. Due to the number of applications and interesting properties, such as different interactions between host-guest and guest-guest molecules, LDHs have attracted considerable attention in the recent years[16]. The procedure for preparing double hydroxides as suitable precursors for catalysts with controlled surface area has been described by Reichle[1] and Nunan[17]. Carlino has reviewed the main experimental methods for the intercalation of carboxylic acids into LDHs[18]. Other preparation methods for intercalating carboxylic acids into LHDs involve direct ion exchange through shaking prepared LDH in the solution of carboxylic acid[19-23], or co-precipitation of nitrate salts of di- and tri-valent cations with a basic solution of carboxylic acid under hydrothermal condition[24-26]. Two-step rehydration method consists of calcination of synthesized LDH into the oxide material (LDO) and mixing LDO with basic solution of carboxylic acid in reflux conditions[14,27,28]. Another preparation method for intercalated LDHs includes thermal reaction[29], in which LDH or LDO is mixed with carboxylic acid in solid form and heated above the melting point of the related carboxylic acid. Suzuki has been applied glycerol-effected exchange method by heating prepared LDH or LDO with carboxylic acid in glycerol[30].

Interlayered anionic species could be replaced by carboxylate anions in an ion-exchange reaction, but the exchange is often not completed specially for divalent carbonate anions that intercalate stronger than monovalent ions in the LDHs interlayer[19-22].

The most common method for intercalating organic acids into LDHs involves the calcination of LDH carbonates at 450–500°C to give mixed metaloxides. The subsequent reaction consists of adding LDH into a basic aqueous solution of carboxylate salt under nitrogen to form LDH layers with intercalated carboxylate anions[14,26,27].

Co-intercalation of carbonate ions arising from atmospheric carbon dioxide is sometimes observed, even when the reaction is carried out under nitrogen in the co-precipitation method, due to the strong basic nature of the intermediate solids. The materials are often contaminated by precursor anions from the mixed salt solution even when carbonate contamination is prevented.

In this paper we synthesized two types of LDH based on magnesium-aluminium and zinc-aluminium, and then intercalated them with several types of long-chain carboxylate and sulfonate anions by the co-precipitation method. The basal spacing of all prepared samples was extracted from their X-ray powder diffractions and the shape of intercalated anions into the LDH's interlayers was estimated. Incorporation of long-chain anions into the cationic interlayers of LDH imparts some oil solubility to the prepared solids. The prepared intercalated samples were tested in the formulation of an oil based drilling fluid as oil phase gelling agent.

Experimental Section

Reagents

All chemicals and solvents purchased from Merck chemical company and were used without further purification. Monomeric and dimeric fatty acids supplied from Croda chemical company. Sodium petroleum sulfonate (MW = 550) obtained from a domestic commercial source.

Layered double hydroxides preparation

All samples of the intercalated layered double hydroxides were synthesized by co-precipitation method in the presence of long chain anions.

Preparation of Mg/Al-Cl LDH

$MgCl_2.6H_2O$ (20 mmol) and $AlCl_3.6H_2O$ (10 mmol) were dissolved in 40 mL of distilled water. To this solution 15 mL of 30% NaOH solution was added at room temperature. The resulted mixture was stirred for 5h and its *p*H was adjusted at 9 by addition of dilute sodium hydroxide solution. The precipitate was separated by centrifuge, washed several times with water and dried over night at 100°C.

Preparation of Zn/Al-Cl LDH

In a similar manner, 20 mmol $ZnCl_2.6H_2O$ and 10 mmol $AlCl_3.6H_2O$ were dissolved in 40 mL of distilled water. To this solution 20 mL of 30% NaOH solution was added at room temperature. The resulted mixture was treated as for preparation of Mg/Al-Cl LDH.

Preparation of layered double hydroxides intercalated by long chain anions

In this study, five anionic species were selected including sodium oleate, sodium stearate, sodium dodecylbenzenesulfonate, sodium petroleum sulfonate and sodium salt of dimer oleic acid (C36).

Preparation of intercalated Mg/Al-Cl LDH

$MgCl_2.6H_2O$ (20 mmol) and $AlCl_3.6H_2O$ (10 mmol) were dissolved in 150 mL of distilled water, then 10 mmol of long chain fatty acid or sulfonate and 50 mL of 30% NaOH solution were added drop wise to this solution, and the resulting mixture was reflux overnight. The intercalated LDH was separated by filtration, washed several times with distilled water and dried in a vacuum oven.

Preparation of intercalated Zn/Al-Cl LDH

In a similar method, $ZnCl_2.6H_2O$ (20 mmol) and $AlCl_3.6H_2O$ (10 mmol) were dissolved in 150 mL of distilled water, then 10 mmol of long chain fatty acid or sulfonate and 55 mL of 30% NaOH solution were added drop wise to this solution, and the resulting mixture was reflux overnight. The intercalated LDH was separated by filtration, washed several times with distilled water and dried in a vacuum oven.

Layered double hydroxides characterization

Materials Characterization: The structure and phase purity of all synthesized samples were monitored by powder X-ray diffraction (XRD). A Bruker, D8 advance diffractometer using Cu Kα radiation was used. The scanning range of 2Θ was set between 2° and 65°. The rheological behaviors of prepared muds were measured on standard Fann® instruments packages.

Results and Discussion

Layered double hydroxides react easily with various types of organic anions because of their high surface charge density. Short and long-chain anions are rapidly exchanged for the inorganic inter layered anions. By the incorporation of large anionic molecules interlayer spacing is changed significantly. It is very important to properly introduce these long chain anions into the LDH without destroying the layered structure. Also shape and arrangement of such anionic species between the layers are very important for their physical behavior. The layered structures of the prepared samples were confirmed by powder X-ray diffraction technique. The number, size and strength of bonds between the anions and hydroxyl groups of layers affect the interlayer thickness[27,31,32]. The layer thickness of LDH is about 4.8 Å[26,33], and the basal spacing changes from 7.6 to 7.8 Å[26,28], so the interlayer distance is approximately 2.9 Å as shown in Fig. 1.

The thickness of interlayer spacing of LDH as a host was increased by intercalation of anions. In this case, the basal spacing depends on the size and nature of inter layered anions[18]. The XRD reflection peak with the greatest d-spacing value is related to basal spacing of the LDH intercalation and is attributed to the (003) plane. Generally, the XRD pattern of carboxylate-intercalated LDHs consists of three major reflection including the greatest basal spacing d_{003}, the half-height harmonic d_{006} which is equivalent to half $d_{003}$and the d_{009} reflection which is equivalent to one third d_{003}[18]. Carboxylate ions can be intercalated into the LDHs interlayers in three forms of flat stacks, monolayers and bilayers. Monocarboxylate ions commonly form more complicated structures than dicarboxylates with two terminal carboxylate functional groups[28,34]. Aromatic anions form the structure with the pendant groups from the layers[35]. The d-spacing of intercalated LDHs could be calculated by Eq 1 and Eq 2 for mono and bilayer intercalated structures, respectively[15, 18].

$$d_L = d_0 + 1.27\, n \cos\alpha + d_1 \qquad \ldots (1)$$

$$d_L = d_0 + 2.54\, n \cos\alpha + d_2 \qquad \ldots (2)$$

where "n" is the number of carbon atoms of the carboxylate ion, d_L = basal spacing, d_0 = distance between the terminal ionized carboxyl group and the center of Mg/Al-$(OH)_x$(4.4 Å), d_1 = distance between the terminal methyl group and the center of layer(7.2 Å), d_2 = distance between the two facing terminal methyl groups (3 Å) and α = the slant angel of the carbon chain from the normal of the layers. XRD patterns of all prepared intercalated LDHs were shown in Fig. 2 and Fig. 3.

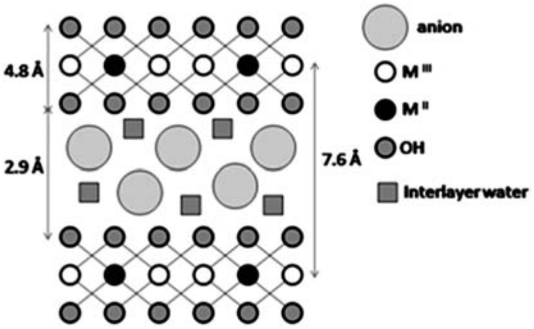

Fig. 1 — A schematic view of basal spacing, interlayer distance and thickness of layer in the host LDH

All the three major reflections and their related d-spacing for intercalated Mg/Al-LDHs and Zn/Al-LDHs were summarized in Table 1 and the basal spacing is related to $d_{(003)}$ planes are highlighted in it.

The basal spacing of host LDHs from XRD is 7.67 and 7.91 Å for Mg/Al-Cl LDH and Zn/Al-Cl LDH,

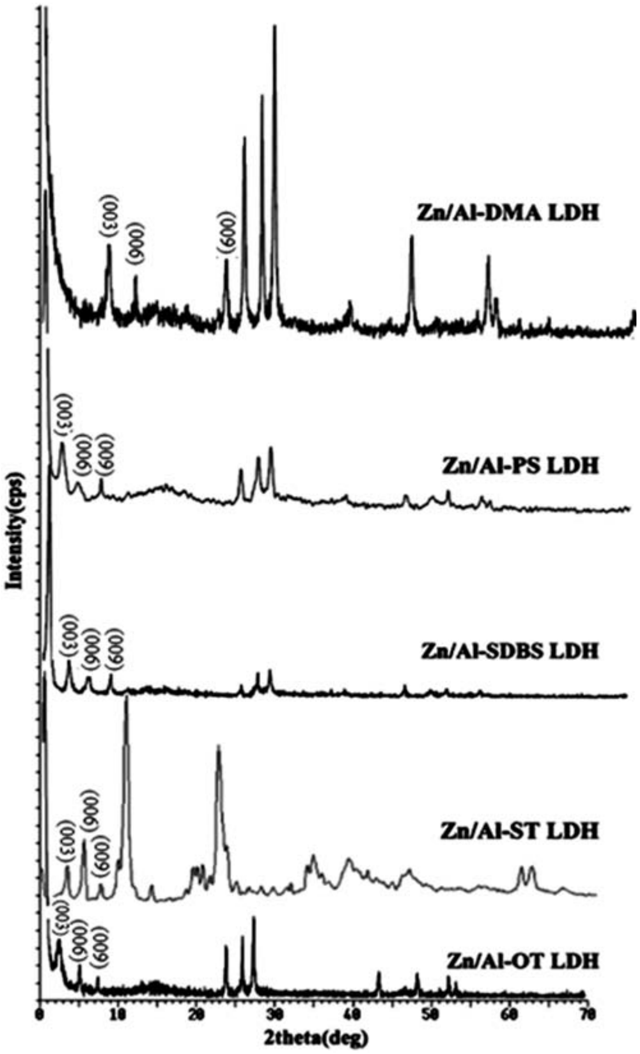

Fig. 2 — XRD patterns for carboxylate intercalated Zn/Al-LDHs and Mg/Al-LDHs. OT= Oleate, ST=Stearate, SDBS= Dodecyl benzene sulfonate, PS= Petroleum sufonate and DMA= Dimer oleic acid

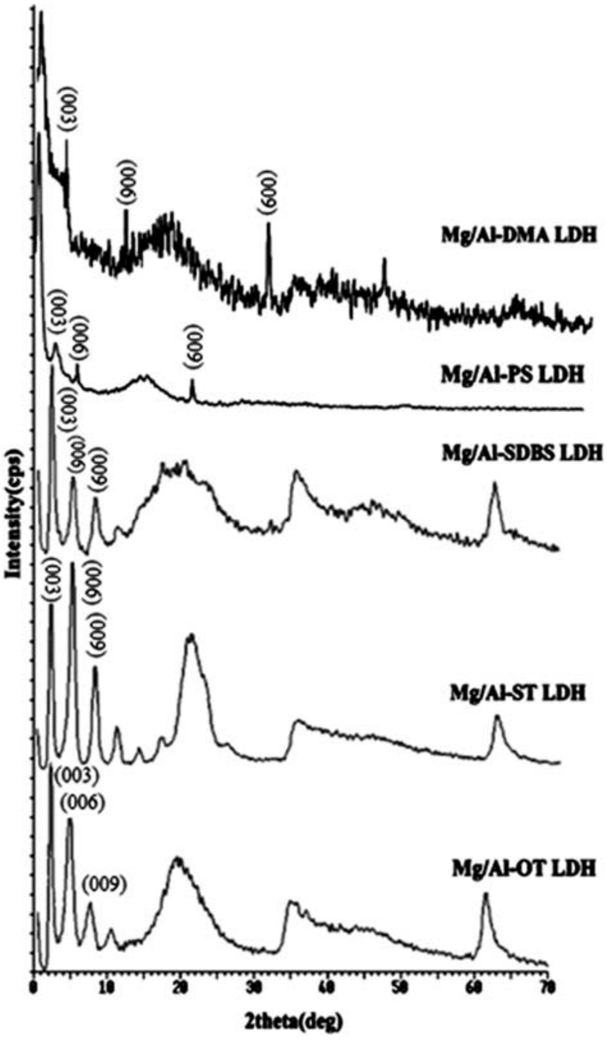

Fig. 3 — XRD patterns for carboxylate intercalated Mg/Al-LDHs. OT= Oleate, ST=Stearate, SDBS= Dodecyl benzene sulfonate, PS= Petroleum sufonate and DMA= Dimer oleic acid

respectively. This interlayer spacing was increased by intercalation of the anions into an LDH as shown in Table 1.

Resulted basal spacing in the Table 1, was suggested different mono and bilayer structures for the prepared carboxylate intercalated LDH. The observed basal spacing from XRD confirmed that for oleate intercalated LDH, two isomers of *cis* and *trans* exist in the interlayer space of Mg/Al-LDH and Zn/Al-LDH. Oleic acid in the *trans* conformation could be intercalated in the interlayer structure of LDHs in the either monolayer or bilayer form. Slant angel of the carbon chain from the normal of the layers was calculated from the Eq 1 and Eq 2. The observed basal spacing is compatible with monolayer and bilayer intercalated structure for Mg/Al-LDH with slant angel 14° and 61.5°, respectively, whereas for Zn/Al-LDHonly bilayer form with slant angel 44° was existed.

If the intercalated oleate adapts to the *cis* form, as in Fig. 4, the calculated basal spacing (31Å) is matched with the observed basal spacing only for Mg/Al-LDH (32.5 Å).

As it is shown in Fig. 5, Stearate anion could be intercalated by Mg/Al-LDH and Zn/Al-LDH in two monolayer and bilayer forms. The calculated slant angels in the monolayer are 22.8° and 62.2° in Mg/Al-LDH and Zn/Al-LDH, respectively. These angels in bilayer intercalation are 62.8° and 76.8° in Mg/Al-LDH and Zn/Al-LDH, respectively.

The interlayer spacing for intercalated dodecyl benzene sulfonate in Mg/Al-LDH and Zn/Al-LDH is 31.5 and 30.5 Å, and for petroleum sulfonate is 31.9

Table 1 — Observed XRD data for carboxylate intercalated Mg/Al-LDHs and Zn/Al-LDHs. OT= Oleate, ST=Stearate, SDBS= Dodecyl benzene sulfonate, PS= Petroleum sufonate and DMA= Dimer oleic acid.

Sample	hkl	2θ/deg	d(Å)	Sample	hkl	2θ/deg	d(Å)
Mg/Al-OT LDH	d_{003}	2.17	32.57	Zn/Al-OT LDH	d_{003}	2.91	38.82
	d_{006}	5.28	16.72		d_{006}	5.00	19.34
	d_{009}	7.97	11.08		d_{009}	7.34	12.27
Mg/Al-ST LDH	d_{003}	2.82	31.30	Zn/Al-ST LDH	d_{003}	4.09	21.56
	d_{006}	5.81	15.18		d_{006}	6.21	14.22
	d_{009}	8.56	10.31		d_{009}	8.24	10.71
Mg/Al-SDBS LDH	d_{003}	2.79	31.58	Zn/Al-SDBS LDH	d_{003}	3.10	30.60
	d_{006}	5.58	15.82		d_{006}	5.92	15.11
	d_{009}	8.48	10.41		d_{009}	9/00	9.99
Mg/Al-PS LDH	d_{003}	3.21	31.91	Zn/Al-PS LDH	d_{003}	2.82	35.03
	d_{006}	5.98	16.27		d_{006}	5.11	17.84
	d_{009}	20.12	4.53		d_{009}	7.86	11.97
Mg/Al-DMA LDH	d_{003}	4.50	19.19	Zn/Al-DMA LDH	d_{003}	8.40	10.67
	d_{006}	12.82	7.82		d_{006}	11.98	7.59
	d_{009}	20.92	4.41		d_{009}	23.91	3.78

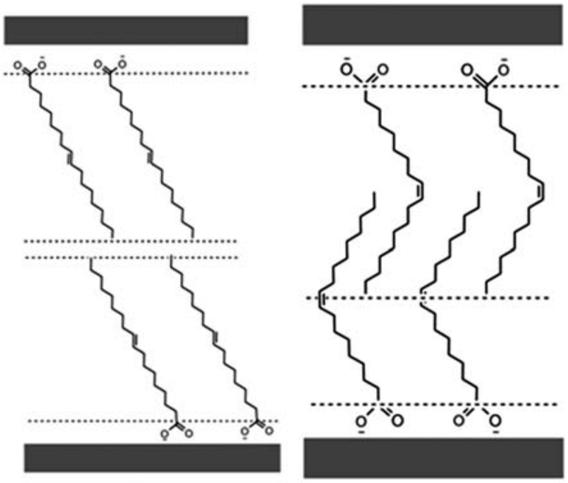

Fig. 4 — Interlamellar arrangement of oleate anion in bilayer conformation in the cis (right) and trans (left) forms

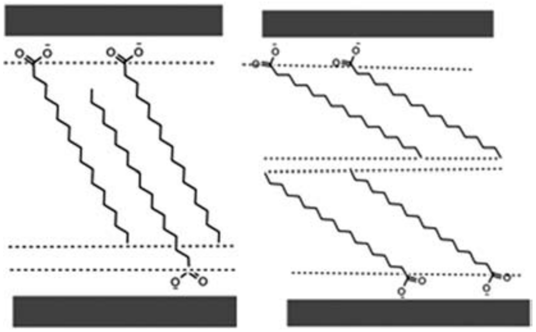

Fig. 5 — Interlamellar arrangement of stearate anion in two momolayer (left) and bilayer (right) forms

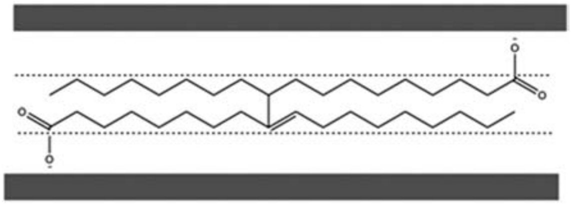

Fig. 6 — The flat stack of dicarboxylate anion in the Zn/Al-LDH

and 37.7 Å, respectively that is in good agreement with the value estimated from an anti-parallel packing model[36,37].

The flat stack form was confirmed with the basal spacing of 10.6 Å for dimeric oleate dicarboxylate anion in the interlayer space of Zn/Al-LDH (Fig. 6). The basal spacing was increased to 19.1 Å and the dianion adapted a slant angel of 61° in Mg/Al-LDH.

Because the presence of long-chain anionic species between the inorganic layers make LDHs oil wet, we tested these modified LDHs in the formulation of drilling fluid as oil phase gelling agent. In Table 2 a typical formulation of oil base drilling fluid is shown.

Table 2 — Typical oil based drilling mud formulation

	1	2	3	4
Oil/Water ratio	60/40	80/20	60/40	80/20
Weight, PCF	64	90	64	90
Gas oil , mL	187.5	181.5	187.5	181.5
Versamul, mL	10.5	10.5	10.5	10.5
Lime, g	12	8	12	8
Versatrol, g	13	10	13	10
Sat. NaCl , mL	140	57	-	-
Sat. $CaCl_2$, mL	-	-	140	57
Viscosifier, g	0.5	0.5	0.5	0.5
Versacoat, mL	3.5	3.5	3.5	3.5
Limestone, g	-	245	-	238

Versamul and Versacoatare primary and secondary emulsifier from MI SWACO.
Versatrol is fluid loss controller from MI SWACO.

Table 3 — Plastic viscosity and yield point of hot rolled muds.

Sample No	Plastic viscosity	Yield point	Settling
Mg/Al-OT LDH	47	14	no
Zn/Al-OT LDH	38	12	no
Mg/Al-ST LDH	43	11	no
Zn/Al-ST LDH	34	10	no
Mg/Al-SDBS LDH	41	8	settling
Zn/Al-SDBS LDH	29	6	settling
Mg/Al-PS LDH	35	14	no
Zn/Al-PS LDH	18	7	settling
Mg/Al-DMA LDH	28	18	no
Zn/Al-DMA LDH	17	14	no
Organophilic clay "Benton 910"	30	17	no
Blank	18	2	settling

Prepared muds were rolled in a roller oven at 200°F for 4 h and their rheology was measured at 140°F. The plastic viscosity and yield point of hot rolled muds in Table 3 are shown that at least Mg/Al-DMA has similar rheological properties to Benton 910 as the commercial organophilic clay.

Conclusion

Long-chain anionic species intercalated between layered double hydroxides adopted different shapes and slant angels. The linear carboxylates are greatly disordered along the stacking direction whereas more complex dimer fatty acids with planar aromatic moieties show regular X-ray patterns. Alkyl arylsulfonates and petroleum sulfonates aggregate in the interlayer space of LDHs forming bimolecular films of constant thickness, which produce integral series of basal reflections in the X-ray diagrams. Solubility and gel strength of the prepared anion-exchanged LDHs were tested in an oil based drilling fluid formulation and applicability of these compounds were compared to conventional organophilic clays.

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