

# Synthesis of Li/Al layered double hydroxide-guest composites under mild acid conditions

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**ABSTRACT:** Layered double hydroxides (LDHs) are known as ‘anionic clays’. They comprise a class of material with positively charged octahedral double hydroxyl layers and exchangeable anions. The Li/Al LDH term includes a group of LDHs with Li/Al octahedral double hydroxyl layers. We have demonstrated a modified method, using Li/Al LDH-OH (OH<sup>-</sup> as interlayer anions) as the starting material, for preparing Li/Al LDH-X (X represents interlayer anions, including dioctyl sulphosuccinate (DOSS), dodecyl sulphate (DDS), mercaptoacetate (MA), EDTA, Tiron and dichromate) under mild acid conditions (pH in the range 4 to 5). However, in the case of acid-sensitive anions, Fe(CN)<sub>6</sub><sup>4-</sup>, Li/Al LDH-Fe(CN)<sub>6</sub><sup>4-</sup> can be prepared by a two-step procedure using Li/Al LDH-DOSS or similar compounds as intermediates to react with acid-sensitive anions under mild alkaline conditions (pH ≈ 9).

**KEYWORDS:** layered double hydroxide, LDH, anionic clay, intercalation, organic anion, oxometallic anion, organometallic anion.

Layered double hydroxides (LDHs), the so-called anionic clays, consist of a class of materials including naturally occurring minerals and synthetic compounds, with positively charged octahedral double hydroxyl layers and exchangeable interlayer anions. The lamellar structure and anion exchange capacity of LDHs allow inorganic or organic anions into interlayers between octahedral layers and give rise to a wide range of anion-exchanged derivatives. Some have found widespread applications as heterogeneous catalysts in the oxidation of secondary amines (Choudary *et al.*, 2002), as nonviral vectors (Choy *et al.*, 2000) or biosensors (de Melo *et al.*, 2002), as sorbents for organic pollutants (Barriga *et al.*, 2002; You *et al.*, 2002; Dutta & Robins, 1994a), as a chromatographic

stationary phase (Jakupca & Dutta, 1995), as photochemical materials (Robins & Dutta, 1996; Cooper & Dutta, 1990), and as precursors of nanoscale systems (Isupov *et al.*, 1997) or other compounds (Yang & Wang, 2003; Feng *et al.*, 1999).

The best known group of LDHs is represented by the formula  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]A_{x/n}^{n-} \cdot m\text{H}_2\text{O}$  (You *et al.*, 2002; Newman & Jones, 1998).  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations, respectively, with an ionic radius similar to that of Mg<sup>2+</sup> (Newman & Jones, 1998). Li/Al LDHs consist of Li-Al octahedral layers with a generalized formula  $[\text{LiAl}_2(\text{OH})_6]^+A^- \cdot m\text{H}_2\text{O}$  (designated as Li/Al LDH-A) (Newman & Jones, 1998; Besserguenev *et al.*, 1997; Serna *et al.*, 1977, 1982).

The  $M^{2+}/M^{3+}$  LDHs were discovered in the mid-19<sup>th</sup> century (Khan & O’Hare, 2002), but Li/Al LDHs were first prepared only in 1977 (Serna *et al.*, 1977, 1982). As analogous materials to

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$M^{2+}/M^{3+}$  LDHs, Li/Al LDHs have attracted much attention since their discovery. Studies related to their anion-exchanged derivatives, including organic anion-exchanged Li/Al LDH (Fogg *et al.*, 1998, 2002; Dutta & Robins, 1994b; Cooper & Dutta, 1990; Sissoko *et al.*, 1985), oxometalate-exchanged Li/Al LDH (Twu & Dutta, 1989) and organometallic anion-exchanged Li/Al LDH, are numerous. Because the exchange of anions is in the order  $\text{CO}_3^{2-} \gg \text{SO}_4^{2-} \gg \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$  (Newman & Jones, 1998; Carlino, 1997), all anion-exchanged Li/Al LDHs were derived from Li/Al LDH-Cl or Li/Al LDH- $\text{ClO}_4^-$  (Fogg *et al.*, 2002; Dutta & Robins, 1994b; Cooper & Dutta, 1990; Dutta & Puri, 1989). It was suggested that the system should exclude  $\text{CO}_2$  during synthesis and exchange reaction (Twu & Dutta, 1989).

Because of the exchange order of anions, Li/Al LDH-OH is not an ideal starting material for synthesizing anion-exchanged Li/Al LDH. Nevertheless, it can be prepared easily, so in this study, we used Li/Al LDH-OH to prepare new anion-exchanged Li/Al LDH with  $\text{CO}_2$  not excluded.

#### LI/AL LDH-OH

Our synthesis procedure for Li/Al LDH-OH is modified from the reported method (Dutta & Puri, 1989; Twu & Dutta, 1989; Serna *et al.*, 1982). An Al chip (10.8 g) was dissolved in 500 ml of boiling 2 M lithium hydroxide. The Li/Al LDH-OH thus formed was adjusted to pH 6 and washed with deionized distilled water (DDW). The suspension was filtered, dried and kept for exchange experiments.

#### One-step procedure for preparing Li/Al LDH-X

Six species of anion-exchanged derivatives of Li/Al LDH-OH, Li/Al LDH-X, were prepared. The X represents dioctyl sulphosuccinate (DOSS), dodecyl sulphate (DDS), mercaptoacetate (MA), EDTA, Tiron or dichromate. Intercalation into Li/Al LDH-OH (5 g of powder) was carried out with a 0.5 M aqueous solution of guest anions at 373 K, with stirring at a rate of 400 rpm for 3 h. The initial pH of the suspension was adjusted in the range 4 to 5 with LiOH and HCl solutions. After the exchange period, solids were filtered and washed extensively with DDW, dried in an oven at 323 K for 24 h, and stored in sample bottles.

#### Two-step procedure for preparing Li/Al LDH- $\text{Fe}(\text{CN})_6^{4-}$

Li/Al LDH- $\text{Fe}(\text{CN})_6^{4-}$  cannot be prepared in the same way as other Li/Al LDH-X because  $\text{Fe}(\text{CN})_6^{4-}$  ions are not stable and may release toxic HCN gas in acid media. Thus, we adopted a two-step procedure for preparing Li/Al LDH- $\text{Fe}(\text{CN})_6^{4-}$ . The first step is to prepare the intermediate of Li/Al LDH-DOSS, using the one-step procedure. An exchange reaction between  $\text{Fe}(\text{CN})_6^{4-}$  in solution and DOSS in interlayers is as follows: 2 g of Li/Al LDH-DOSS were suspended in 50 ml of 0.5 M  $\text{Fe}(\text{CN})_6^{4-}$  at 373 K with a stirring rate of 400 rpm for 3 h. The initial pH of suspension was in the range 8 to 9, close to the pH of 0.5 M  $\text{K}_4\text{Fe}(\text{CN})_6$ . After the exchange reaction, solids were filtered and washed extensively with DDW, dried in an oven at 323 K for 24 h, and stored in sample bottles.

#### X-RAY DIFFRACTION

In order to check whether intercalation of guest anions occurs or not, oriented thin-film samples, supported on pieces of filter membrane (0.45  $\mu\text{m}$ , 25 mm diameter), were scanned by X-ray diffraction (XRD) analysis from 3 to 30° or 5 to 30°(2 $\theta$ ) at a rate of 2° min<sup>-1</sup> with a Rigaku Miniflex X-ray diffractometer. The Cu-K $\alpha$  radiation was used in the XRD studies of these oriented samples at 30 kV and 10 mA.

#### FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier Transform infrared (FTIR) spectra were obtained from KBr disks containing 200 mg of KBr and 1 mg of sample. The transparent disks were scanned using a Thermo Nicolet Nexus spectrometer equipped with an MCT-B detector. Each spectrum was collected by co-addition of 512 individual scans ranged from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

#### SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs (SEM) were taken using an Hitachi S-800 Field Emission Scanning Electron Microscope, which was equipped with Kevex Delta 80000 EDS. The samples were coated

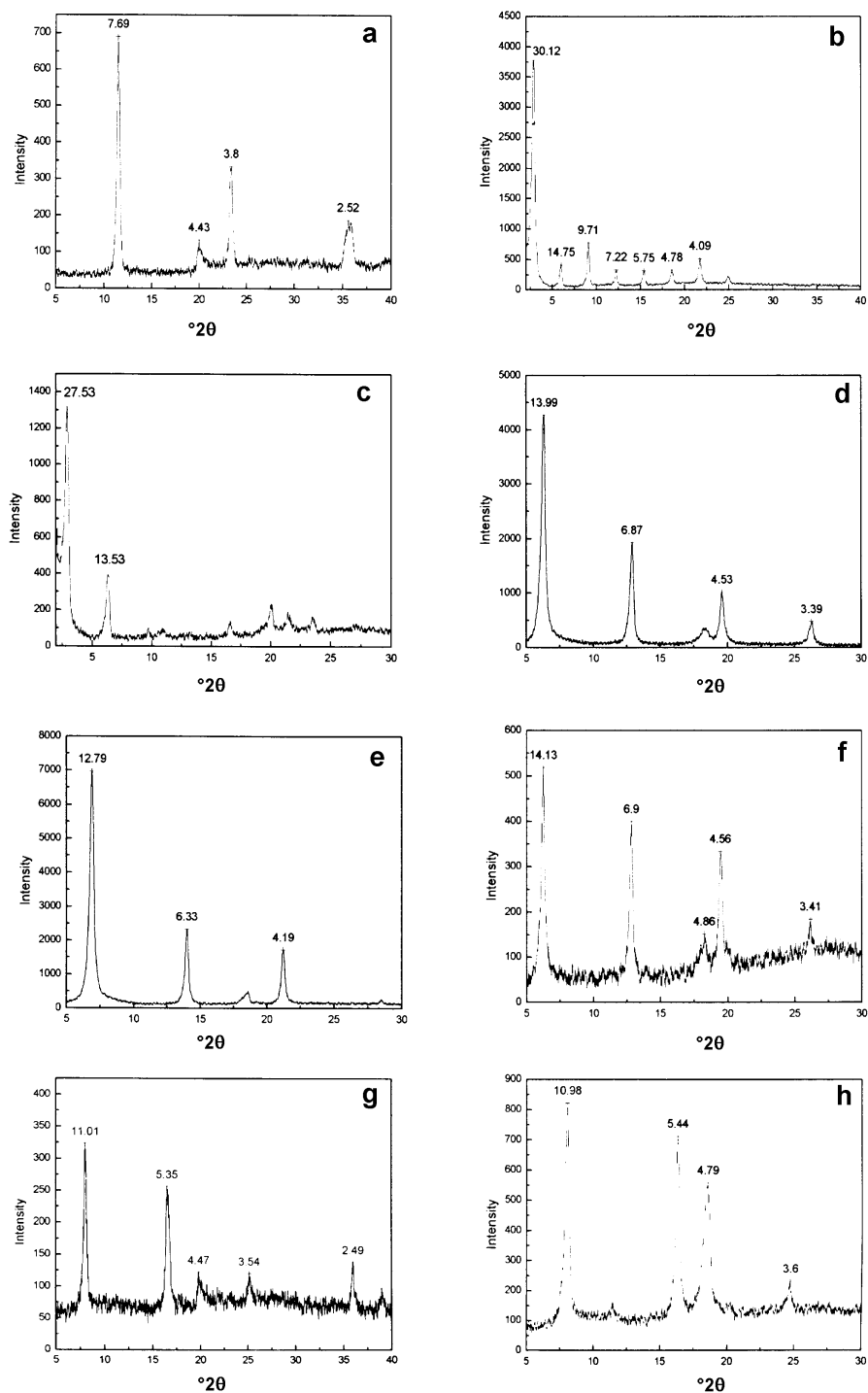


FIG. 1. XRD patterns of oriented samples of Li/Al LDH-X of (a) Li/Al LDH-OH; (b) Li/Al LDH-dioctyl sulphosuccinate; (c) Li/Al LDH-dodecyl sulphate; (d) Li/Al LDH-mercaptopacetate; (e) Li/Al LDH-EDTA; (f) Li/Al LDH-Tiron; (g) Li/Al LDH-dichromate; and (h) Li/Al LDH- $\text{Fe}(\text{CN})_6^{4-}$ .

with gold and SEM analysis was then conducted at an operating voltage of 20 kV.

## RESULTS AND DISCUSSION

X-ray diffraction patterns of the Li/Al LDH-OH and its derivatives are shown in Fig. 1. The XRD pattern of the starting material, Li/Al LDH-OH, is shown in Fig. 1a. The  $d$  spacing of its first reflection is 7.69 Å, similar to that in previous reports (Fogg *et al.*, 2002). The first reflections for Li/Al LDH-DOSS, Li/Al LDH-DDS, Li/Al LDH-MA, Li/Al LDH-EDTA, Li/Al LDH-Tiron, Li/Al LDH-dichromate and Li/Al LDH-Fe(CN) $_6^{4-}$  were found at 30.12, 27.53, 13.99, 12.79, 14.13, 11.01 and 10.98 Å, respectively (Fig. 1b–h). Apparently, the Li/Al LDH-OH is resistant to other anions, undergoes anion-exchange reactions with guest anions, and gives rise to a variety of Li/Al LDH-guest anion derivatives with their own XRD patterns. Scanning electron micrographs of Li/Al LDH-OH and its derivatives (except Li/Al LDH-Fe(CN) $_6^{4-}$ ) are shown in Fig. 2 (a) Li/Al LDH-OH; (b) Li/Al LDH-DOSS; (c) Li/Al LDH-DDS; (d) Li/Al LDH-MA; (e) Li/Al LDH-EDTA; (f) Li/Al LDH-Tiron; (g) Li/Al LDH-dichromate). Although particle sizes may vary, the platy morphology of crystallites of the Li/Al LDH, inherited from the Li/Al LDH-OH, can be identified in Fig. 2.

The FTIR spectra of Li/Al LDHs are shown in Fig. 3. There are five major bands at 3457, 1376, 1004, 745 and 537  $\text{cm}^{-1}$ . The band at 3457  $\text{cm}^{-1}$  is due to OH stretches of the hydroxide layers and interlayer water. The band at 1376  $\text{cm}^{-1}$  is caused by the stretching vibrations of carbonate, in interlayers or adsorbed on the surfaces of the Li/Al LDH-OH. The bands at 1004 and 745  $\text{cm}^{-1}$  are assigned to OH deformation. Al–O stretches are indicated by the band at 537  $\text{cm}^{-1}$ . In addition to the bands observed in the Li/Al LDH-OH, some bands are seen in the region around 2900  $\text{cm}^{-1}$  (Fig. 3b,c) and in the region between 1600 and 1000  $\text{cm}^{-1}$ . The bands observed around 2900  $\text{cm}^{-1}$  are attributed to the stretches of  $-\text{CH}_2$ . The bands found in the range between 1600 and 1000  $\text{cm}^{-1}$  are  $\text{COO}^-$  vibrations as well, OH-deformation bands from both host and guest OH groups.

Our results reveal that exchange reactions between Li/Al LDH-OH and guest anions can occur as readily as Li/Al LDH-Cl does under mild acid conditions (pH range of 4 to 5). If the pH is

>7, carbonate and the stability of interlayer  $\text{OH}^-$  may inhibit anion-exchange reaction. The ease of anion exchange is of the order  $\text{CO}_3^{2-} \gg \text{SO}_4^{2-} \gg \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$  (Newman & Jones, 1998; Carlino, 1997). The affinity of carbonate to LDH is very strong and may inhibit any anion-exchange reaction. The starting material of Li/Al LDH-OH was prepared in strong alkaline conditions. Under such conditions, the concentration of carbonate in NaOH solution can reach a level that merits attention. Therefore, carbonate may occupy exchangeable sites on LDH surfaces, or even in interlayers. The anion-exchange feasibility of Li/Al LDH-OH is thus reduced. If exchange reactions were conducted in solution of pH >7, the solubility of carbonate would again reduce the feasibility of anion-exchange reactions. In addition, interlayer  $\text{OH}^-$  anions are stable at pH >7. This increases the resistance to exchange interlayer  $\text{OH}^-$ .

On the contrary, the solubility of carbonate is greatly decreased in mild acid conditions. The adverse effect of carbonate in anion-exchange reactions does not exist. On the other hand, carbonate adsorbed on surfaces of Li/Al LDH-OH will react with  $\text{H}^+$  and release  $\text{CO}_2$ . We observed bubbles at the time of acid solutions being mixed with Li/Al LDH-OH. It is believed that guest anions are easier to intercalate into interlayers of Li/Al LDH-OH with carbonate-free surfaces. Moreover, the existence of  $\text{H}^+$  cations reduces the stability of interlayer  $\text{OH}^-$  anions. An exchange reaction between anions in solution and OH in Li/Al LDH-OH becomes more feasible in mild acid conditions.

Li/Al LDH-Fe(CN) $_6^{4-}$  is the only exception. Owing to its acid-sensitivity, it cannot be prepared by the one-step procedure under acid conditions as were other anions in this study. The  $\text{Fe(CN)}_6^{4-}$  anions become unstable and may release toxic cyanide gas in acid conditions. In order to prepare this organometallic Li/Al-LDH, we adopted a two-step procedure, using Li/Al LDH-DOSS which was prepared from the one-step procedure as an intermediate to react with  $\text{Fe(CN)}_6^{4-}$  solution at pH  $\approx$  9.

## CONCLUSIONS

Li/Al LDH- $X$  was prepared using a modified method. The known exchange-resistant Li/Al LDH-OH undergoes exchange reactions with organic and oxometallic anions to form Li/Al

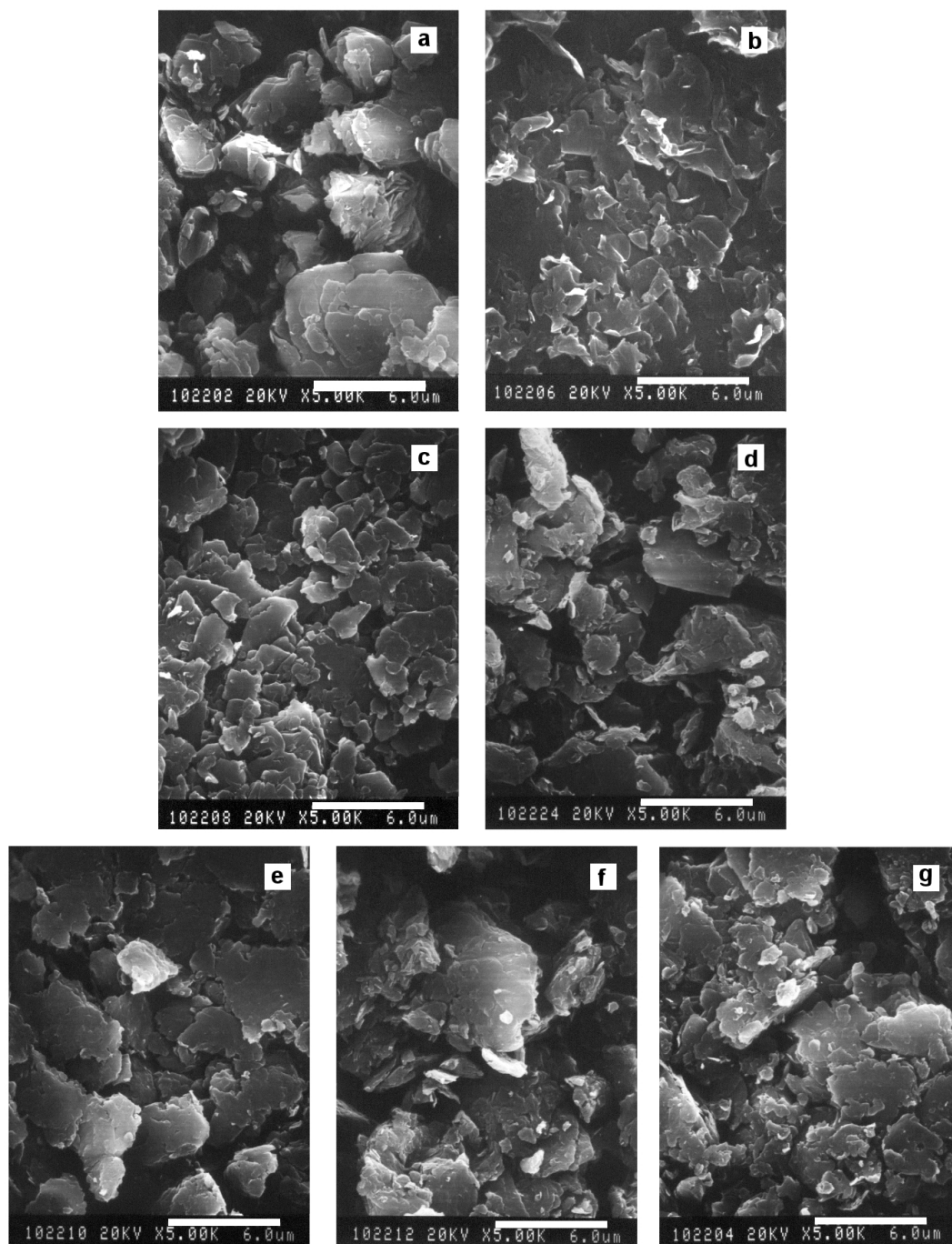


FIG. 2. SEM images of Li/Al LDH-*X* of (a) Li/Al LDH-OH; (b) Li/Al LDH-dioctyl sulposuccinate; (c) Li/Al LDH-dodecyl sulphate; (d) Li/Al LDH-mercaptoacetate; (e) Li/Al LDH-EDTA; (f) Li/Al LDH-Tiron; and (g) Li/Al LDH-dichromate.

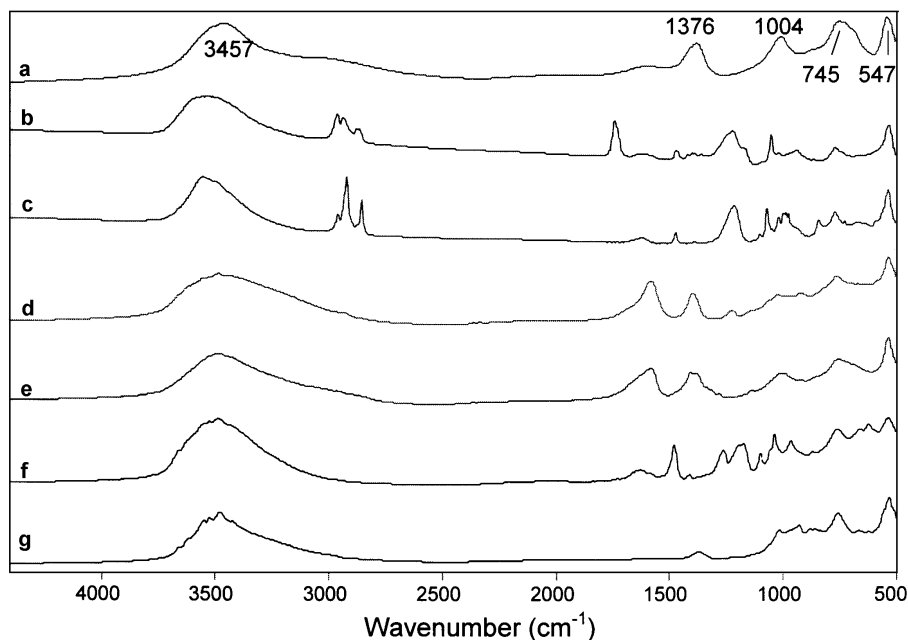


FIG. 3. FTIR spectra of Li/Al LDH-*X* of (a) Li/Al LDH-OH; (b) Li/Al LDH-dioctyl sulphosuccinate; (c) Li/Al LDH-dodecyl sulphate; (d) Li/Al LDH-mercaptoacetate; (e) Li/Al LDH-EDTA; (f) Li/Al LDH-Tiron; (g) Li/Al LDH-dichromate.

LDH-*X* under mild acid conditions. However, acid-sensitive anions, such as  $\text{Fe}(\text{CN})_6^{4-}$  can be successfully intercalated into interlayers of Li/Al-LDH by a two-step procedure, using Li/Al LDH-DOSS or similar compounds as intermediates to react with acid-sensitive anions under mild alkaline conditions.

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