## **Electronic Supplementary Information (ESI)**

# Synthesis of a novel cone-shaped CaAl-Layered double hydroxide (LDH): Its potential use as a reversible oil sorbent

Kingshuk Dutta and Amitava Pramanik\*

Unilever R&D Bangalore, 64 Main Road, Whitefield, Bangalore-560066, India.

\*To whom correspondence should be addressed. E-mail: amitava.pramanik@unilever.com

Phone: +91-080-39830988. Fax: 091-080-2845-3086.

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#### **S1. Experimental section:**

#### Materials

All chemicals used in this study are of A.R. grade and were used without further purification. Calcium chloride dihydrate (CaCl<sub>2</sub>.2H<sub>2</sub>O), sodium dodecyl sulfate (SDS), aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O), sodium hydroxide (NaOH) and light liquid paraffin oil were procured from Merck, India. Aqueous solutions of the reactants (CaCl<sub>2</sub>.2H<sub>2</sub>O, SDS, Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O and NaOH) were made using distilled water with the following characteristics: pH 7.1, electrical conductance  $2 \times 10^{-6}$  S cm<sup>-1</sup>, total dissolved salt <0.5 mg/L and turbidity <0.1 NTU.

#### Hydrothermal Synthesis of CaAl-DS LDH

Calcium dodecyl sulfate (Ca(DS)<sub>2</sub>, CDS) was synthesized by a reported method via stoichiometric treatment of aqueous CaCl<sub>2</sub>.2H<sub>2</sub>O and SDS.<sup>1</sup> CaAl-LDH intercalated with DS<sup>-</sup> anions was synthesized by hydrothermal method. First, 5.71 g (0.01 mole) CDS powder was poured in a 250 mL hydrothermal bottle containing 80 mL distilled water. The mixture was heated at 85 °C for 2 h and 1.88 g (0.005 mole) Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O dissolved in 20 mL water was added to the solution at 85 °C. 3.2 mL 50 % (wt%) NaOH solution was added drop-wise to raise the pH to 13. The final mixture was subjected to hydrothermal treatment at 85 °C for different durations as mentioned in text. The precipitates formed were filtered hot through Whatman 40 filter paper, washed thoroughly with hot distilled water and dried in vacuum for 24 h.

#### Characterization

Powder X-ray diffraction pattern of all the samples were recorded on a Siemens D-5000 diffractometer using Cu K $\alpha$  ( $\lambda = 1.5406$  Å) radiation. The step size of 0.05°/s and 2 $\theta$  angle ranging from 2° to 70° were selected.

The morphology of the synthesized materials were investigated using a scanning electron microscope (SEM, Hitachi S-4700) equipped with an EDX attachment with an accelerating voltage of 20 kV. Powder samples were mounted on holey carbon tape and imaged after gold coating to make them conductive. Transmission electron microscopy (TEM) images were recorded on a Hitachi H-800 transmission electron microscope operating at 200 kV. LDH samples (from kinetic study) were dispersed in acetone and directly deposited on a carbon film supported by a copper grid. All the grids were dried for 15 min and then imaged under transmission electron microscope.

Room temperature Fourier transform IR (FT-IR) measurements were performed on a Perkin-Elmer FT-IR spectrophotometer with a resolution of 2 cm<sup>-1</sup> using the KBr pellet technique. Thermogravimetric analyses (TGA) were carried out on Perkin-Elmer Pyris1 TGA instrument with a heating rate of 5 °C min<sup>-1</sup> in N<sub>2</sub> atmosphere.



S2. EDX pattern for synthesized CaAl-DS LDH sample (24 h):

**Fig I.** EDX pattern for synthesized CaAl-DS LDH sample (24 h); The presence of Au and Si is due to Au coating of LDH sample pasted on glass slide prior to EDX.



#### S3. PXRD patterns for time-variant CaAl-DS LDH samples:

**Fig. II.** PXRD patterns for time-variant CaAl-DS LDH samples; '0 h' means excluding the 15 min filtration and washing time after mixing the reagents at 85 °C.

#### **S4. FT-IR spectroscopy:**

Fourier transform IR (FT-IR) spectra of CDS, SDS surfactants and CaAl-DS LDH are shown in Fig. III below. The presence of surfactant in the interlayer region is confirmed from the spectrum of LDH sample. The IR spectra for all exhibit broad absorptions bands in the range of 3700–3000 cm<sup>-1</sup>. The large and strong band centered at 3479 cm<sup>-1</sup> can be assigned to O-H stretching vibration of interlayer water molecules and of OH groups.<sup>2</sup> In all cases, characteristic –CH<sub>3</sub> asymmetric stretching band was observed at 2956 cm<sup>-1</sup> and two –CH<sub>2</sub> stretching vibrations appeared at 2919 (asymmetric stretching vibration) and 2850 cm<sup>-1</sup>. Absorption band at 1632 cm<sup>-1</sup> is assigned to bending vibrations of the interlayer co-intercalated water molecules. The



**Fig. III.** FT-IR spectrum for (a) CDS, (b) SDS and (c) CaAl-DS LDH powder (24 h sample). bands at 1467, 1417 and 1378 cm<sup>-1</sup> are assigned to CH<sub>2</sub> scissoring, asymmetric bending and symmetric bending.<sup>3</sup> While the symmetric vibration of S=O is shifted from 1084 (for SDS) to1063 cm<sup>-1</sup> (for LDH), similar to the free SDS, the asymmetric vibration of the S=O was at 1223cm<sup>-1</sup>. Absence of absorption peaks at 1368 and 1384 cm<sup>-1</sup> confirms the absence of  $CO_3^{2-}$  and  $NO_3^{-}$  anions respectively in the inter-layer region as impurity phases.

#### S5. Thermogravimetric analysis (TGA):

CaAl-DS LDH powder was subjected to TGA in order to study its primary decomposition profile at elevated temperatures (Fig. IV). Generally, the thermal evolution of LDH is characterized by four main steps of weight loss: (a) desorption of physically adsorbed water, (b) dehydration of interlamellar water, (c) loss/decomposition of interlayer anions and (d) dehydroxylation of the LDH layers, in which the some of the steps may overlap.<sup>4</sup> Initially, physically adsorbed water



Fig. IV. TGA pattern of CaAl-DS LDH sample (24 h).

and cointercalated water molecules are lost at temperatures up to 150 °C. This is then followed by the dehydroxylation of the metal hydroxide layers and loss of  $SO_x$  from the intercalated DS anion (150 °C - 350 °C). The final steps, from around ~350 °C onwards, is a combination of the further decomposition of the guest and the dehydration of the hydroxide layers, resulting in a final product that is a mixture of calcium aluminium oxides.

## S6. Elemental Analysis of CaAl-DS LDH (24 h sample):

| Elemental analysis of CaAl-LDH intercalated with DS (in wt%) |      |       |      |   |
|--|------|-------|------|---|
| Ca   | Al   | С     | Н    | Comments                                |
| 12.8   | 4.35 | 27.29 | 6.92 | Observed                                |
| 14.65  | 4.95 | 26.37 | 7.14 | Calculated for $Ca_2Al(OH)_6(DS).4H_2O$ |



S7. SEM and TEM images of CaAl-DS LDH samples at different time-interval:

Fig. V(a). SEM images of CaAl-DS LDH samples at different time-interval.



Fig. V(b). TEM images of CaAl-DS LDH samples at different time-interval.

## **S8.** Measurement of contact angle:

Contact angle measurements of the samples were done by following a procedure reported elsewhere.<sup>5</sup> The substrate was prepared by sticking a double sided adhesive tape on a glass slide. LDH particles were uniformly spread on the surface of the adhesive tape with a spatula and gently pressed with a glass cover. The slide was then flushed with air to remove the free loose

LDH particles. This process of spreading the powder on the tape, pressing, and flushing with air was repeated several times until the adhesive tape was completely covered by the LDH particles so that it forms a homogeneous coating.

Water contact angle of the LDH modified tape was measured with a Krűss G10 Drop Shape Analyzer Goniometer using the sessile drop technique. 10  $\mu$ L of distilled water was gently dropped onto the surface of the adhesive tape coated with LDH sample. A photo of the water drop on the surface was taken by the camera of the instrument. Contact angle was determined by drawing a tangent at the droplet-substrate contact point (using ImageJ software – Drop-Snake method).<sup>6</sup> Three consecutive contact angle measurements were performed at three different places on the substrate and then averaged to get final contact angle value.



**Fig. VI.** Contact angles for (a) water, (b) LLPO and (c-e) water with pH 2, 7 and 13; (f) Variation of contact angle with pH (enlarged version of Fig. 4).

#### **S9.** Study of selective absorption of oil from oil-water mixture:

a. *Qualitative study to demonstrate selective oil adsorption*: To study the oil absorption capacity of the synthesized superhydrophobic LDH sample, light liquid paraffin oil

(LLPO, Merck, India) was chosen to prepare the oil–water mixture. Two different studies were done to establish the oil absorption efficacy of the LDH powder. In one case, 1 g of the oil was placed on 20 g of water in a 50 mL beaker. Trace quantity of oil soluble dye (Macrolex Violet B) was mixed with the oil previously in order to make it coloured so as to make a clear, visible distinction of the oil on water. LDH powder sample was gradually sprinkled on top of the floating oil. The oleophilic LDH powder rapidly absorbed the oil while remaining non-wet with water. At the end of the adsorption process, which took about 30 s, the solid mass containing oil and LDH powder was easily removed with a spatula leaving clear water in the beaker.

b. *Qualitative study on selective oil adsorption of the LDH loaded on a porous substrate*: A dilute polystyrene solution (0.1%) was prepared in toluene. 15 mL of this solution was taken in a centrifuge tube and 0.1 g of synthesized CaAl-DS LDH powder was added to it. The mixture was sonicated for 15 min to make a homogeneous dispersion. A porous polyurethane sponge of  $2\times2\times1$  cm<sup>3</sup> size (mass 64 mg) and 50-100 µm pore diameters was placed in the mixture and shaken @400 rpm in a shaker bath for 30 min. The liquid dispersion was soaked by the sponge by capillary action. After that it was kept open overnight for the solvent to evaporate slowly. The dried sponge thus had LDH particles dispersed into its pores. Instead of sprinkling LDH powder, this sponge was then used to scavenge oil floated on water, as mentioned in S9(a). In this case, 30 g of water was taken in a petridish on which 1 g of LLPO (dyed with trace Orange OT) was floated. The dried sponge was then placed on this oil-water mixture. It was seen to selectively mop-up the oil phase completely in 30 s, while floating on water. After taking out of the sponge from

the petridish, gentle squeezing of the sponge lead to recovery of a large part of the absorbed (and coloured) oil phase with no water present in it.

c. Capacity and kinetics of oil-absorption by CaAl-DS LDH treated sponge: To study the kinetics of oil-absorption process, a porous polyurethane sponge of 2×2×0.5 cm<sup>3</sup> size (mass 32 mg) and 50-100 µm pore diameters was placed in 7.5 mL 0.1% polystyrene solution containing 0.1 g CaAl-DS LDH suspended in it. After that it was shaken @400 rpm in a shaker bath for 30 min and then kept open overnight for the solvent to evaporate. The LDH incorporated sponge was placed over the oil-water mixture (30 g water containing 2 g LLPO oil) and the mass variation of the sponge was checked at different time interval. This was repeated with an untreated sponge (without having any CaAl-DS LDH loaded in it) as well. As shown in Fig. VII, the adsorption of liquid (measured by



Fig. VII. Adsorption of liquid by CaAl-DS LDH-loaded sponge and control sponge with time.

mass gain of the sponge) is very fast for the LDH-loaded case, reaching maximum at <10 s, whereas the same for the control sponge was gradual. After reaching a constant mass gain at 60 s, both LDH-loaded and control sponges were examined for water content analysis by a moisture balance. Total mass gain for LDH-loaded sponge and the rate at which the mass was gained was significantly different from those with the unloaded sponge. At the same time, LDH-loaded sponge adsorbed almost only the floated oil [water content of the sponge was found to be  $(0.4\pm0.05)$  % post adsorption], whereas the unloaded sponge adsorbed oil-water mixture [water content (60±2) %], proving the former to be quite specific towards oil uptake. The amount of oil adsorbed by the LDH treated sponge was found to be ~10 times that of the sponge's mass (oil-absorption capacity, C=M<sub>max</sub>/M<sub>sponge</sub>= 9.9±1.33, where M<sub>max</sub>= maximum adsorbed oil amount in sponge's volume, and M<sub>sponge</sub>= mass of the sponge).

#### S10. Images of untreated and treated sponges:



**Fig. VIII.** (a) Unmodified polyurethane sponge, (b-c-d) LDH modified sponge at different magnification; insets are the digital photographs of the corresponding sponges.

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- <sup>3</sup> C. Yilmaz, U. Unal, H. Y. Acar, J. Solid State Chem., 2012, **187**, 295.
- <sup>4</sup> C. Li, L. Wang, D. G. Evans and X. Duan, Ind. Eng. Chem. Res., 2009, 48, 2162; G-J. Cui, X-
- Y. Xu, Y-J. Lin, D.G. Evans and D-Q. Li, Ind. Eng. Chem. Res., 2010, 49, 448.
- <sup>5</sup> Z. Hu and Y. Deng, *Ind. Eng. Chem. Res.*, 2010, **49**, 5625.
- <sup>6</sup> A. F. Stalder, G. Kulik, D. Sage, L. Barbieri and P. Hoffmann, *Colloids Surf.*, A, 2006, **286**, 92.

<sup>&</sup>lt;sup>1</sup>Q. Shen, L. Wang, Y. Huang, J. Sun, H. Wang, Y. Zhou and D. Wang, *J. Phys. Chem. B*, 2006, **110**, 23148.

<sup>&</sup>lt;sup>2</sup> A. Wongariyakawee, F. Schäeffel, J. H. Warner and D. O'Hare, *J. Mater. Chem.*, 2012, **22**, 7751.