INTERCALATION OF ANIONIC SURFACTANTS INTO Zn-Al HYDROTALCITES OF VARYING COMPOSITION: PREPARATION AND CHARACTERISATION

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ABSTRACT

The synthesis and characterisation of Zn-Al hydrotalcite-like compounds intercalated with sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) have been investigated in details. The synthesis has been carried out following calcination-regeneration method. The organic modification was intended to derive hydrotalcite-like compounds appropriate for various applications such as polymer-HTlcs nanocomposite, and as scavengers of organic pollutants. The inorganic-organic hybrid materials were characterised by a range of techniques such as XRD, XRF, FT-IR, TG-DTA, and SEM. Characterisation data showed that pure phase of the series of hydrotalcites has been synthesised and cation molar ratios conform well to the expected ratios of Zn/Al cations in the different samples. Varying the ratios of the Zn^{2+}/Al^{3+} results in distinguishing properties e.g. charge density, crystallinity, amount and orientation of anions in the interlayers and morphology. TGA showed differences in the temperature at which transitions were completed.

Keywords: *Hydrotalcite-like compounds, intercalation compounds, organic-inorganic hybrid materials*

1.0 INTRODUCTION

Hydrotalcites (HTs) also referred to as layered double hydroxides (LDHs) are a group of anionic clays. They are regarded as antitype of the smectites comprised of an octahedral sheet sandwiched between two octahedral sheets. However, the structure is made up of different layers of two metal hydroxides joined together to form an octahedral sheet. Several of these sheets combine to form the hydrotalcite clay mineral. The octahedral sites of metal hydroxides share edges to form two-dimensional sheets. The crystal structure consists of brucite-like $Mg(OH)_2$ layers with Mg^{2+} ions coordinated octahedrally by hydroxide ions sharing edges to form charged neutral sheets which are stacked on top of each other held by hydrogen bonding (Rives and Ulibarri 1999). Isomorphous substitution of some of the Mg^{2+} ions in this brucite-like layers by trivalent cations like Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, Ga^{3+}, gives rise to positive charge imbalance (Cavani *et al.,* 1991). This allows for charge compensating anions and water molecules between the layers.

This group of materials were first discovered in Sweden in 1842. Manasse (1915), was the first to publish the exact formula of the hydrotalcite, $[Mg_6Al_2(OH)_{16}]CO_3.4H_2O$ and between 1930-1942, Feitknecht published a series of papers on double sheet structures (Feitknecht, 1942). This sprang up an increased interest in the hydrotalcite or layered double hydroxide chemistry. Allmann (1968) and Taylor (1969) disproved the structure that was assigned to these minerals due to their single crystal x-ray diffraction results and thus proposed that these group of mineral have layers of mixed metal hydroxides intercalated with anions and water molecules, rather than been composed of layers of one metal hydroxide intercalated with a layer of another metal hydroxide. A wide range of compositions are possible based on the general formula $[M^{2+}_{1-x}M^{3+}_{x}\ (OH)_2][A^{n-}_{x/n})].mH_2O$ where M^{2+} and M^{3+} are di- and trivalent metals in the hydroxyl sheets with x between 0.17 and 0.33 (Cavani *et al.,* 1991).

There is a possibility of a large variety of tailored-made materials for a wide range of applications such as catalysts, adsorbents, fillers, thermal and UV radiation stabilizers etc. (Cavani *et al.,* 1991; Newman and Jones, 1998). Several methods can be adopted to synthesise hydrotalcite-like compounds such as Sol-gel method, Microwave Irradiation, Steam Activation, Solvothermal method, Co-precipitation, Urea method and Combustion Synthesis. They are outstanding hosts of hybrid materials (Leroux and Besse, 2001; Iyi *et al.,* 2002).

The aim of this study is to prepare Zn-Al-CO_3 hydrotalcite-like compounds of varying layer composition and to characterize and modify them with sodium dodecylsulfate and sodium dodecylbenzenesulfonate surfactants for property optimisation. Several authors have reported different methods for this modification of HTlcs such ion exchange, regeneration, direct co-precipitation (Newman and Jones, 1998).

2.0 MATERIAL AND EXPERIMENTAL METHODS

2.1. Materials

Zinc nitrate hexahydrate $(Zn(NO_3)_2.6H_2O$ (Sigma Aldrich, 98%), aluminium nitrate hexahydrate $Al(NO_3)_3.9H_2O$ (Sigma Aldrich, Germany 98%),

Na_2CO_3 (Sigma Aldrich, 99%), NaOH (analytical grade, 85% UK). Surfactant employed for the modification of the as-synthesised parent hydrotalcite-like compounds were sodium dodecyl sulfate (98% Sigma Aldrich) and sodium dodecyl benzenesulfonate, (Sigma Aldrich, technical grade).

2.1.1. Experimental procedure

Zn-Al HTlcs were prepared by the co-precipitation method (Miyata 1980; Reichle 1986; Xu and Braterman, 2003). 0.8M aqueous solution containing Zn^{2+} and Al^{3+} with the molar fraction ($Al^{3+}/Al^{3+}+Zn^{2+}$) between 0.20-0.33 was prepared by dissolving zinc nitrate hexahydrate and aluminium nitrate hexahydrate in 200ml deionised water. This solution and aqueous solution of NaOH/Na_2CO_3 were simultaneously added together dropwise at constant flow rate, into a Teflon bottle under vigorous stirring at ambient conditions. After the addition was complete, the mixtures were allowed to stir for a further 45mins before the resulting suspensions were aged at 110°C for 18 h (Cavani *et al.,* 1991; Costantino *et al.,* 1998) in polypropylene bottles. Thereafter, the products were separated and the precipitates washed severally with deionised water. Then, the precipitates were dried at 60°C in a drying oven for 24 h. The resultant white solids were ground and stored in sample bottles for further analysis. The material obtained was designated as $Zn(_n)$-Al-CO_3-HTlcs (where n = Zn^{2+}/Al^{3+} molar ratio). To modify the parent HTlc prepared, part of the obtained material was calcined slowly in a furnace at 350°C for 5 h, at a ramp rate of 5°C/min. The solid got was denoted $Zn(_n)$-Al-CO_3-350°C.

2.1.2. Synthesis of surfactant modified HTlcs

The as-synthesised Zn-Al-CO_3 hydrotalcite was first calcined as described above to convert it into its oxide form (denoted as calcined Zn-Al-CO_3-350°C). 0.5M solution of sodium dodecylsulfate or 0.2M aqueous sodium dodecylbenzenesulfonate solution was prepared in acidic medium. Then 1g of the Zn-Al-CO_3-350°C was added to the solution of 0.5M sodium dodecylsulfate or 0.2M aqueous sodium dodecylbenzenesulfonate solution (pH 2.06), and the reaction mixture were stirred vigorously for 24 h under nitrogen atmosphere. The obtained solids were recovered through centrifugation, washed several times with deionised water and dried at 60°C for 24 h. Finally, the obtained materials were gently powered, and denoted as $Zn(_n)$-Al-CO_3-DS and $Zn(_n)$-Al-CO_3-DBS.

2.2.3 Characterisation of the parent HTlcs and their modified forms

The parent $Zn(_n)AlCO_3$-HTlcs and their modified forms $Zn(_n)$-Al-CO_3-DS and $Zn(_n)$-Al-CO_3-DBS materials were identified by X-ray diffraction (XRD) analysis on a Bruker D8 ADVANCE X-ray diffractometer in transmission geometry and A D5005 Siemen diffractometer with CuKα radiation (λ = 1.5406 Å) in reflection geometry. The scan was performed from 5° to 70° (2θ) and 1° to 70° (2θ) respectively at a scan rate of 1° (2θ) per min. The CuKα radiation used in this XRD study was operated at 40kV and 30mA.

Fourier transform infrared (FT-IR) spectra for the parent $Zn(_n)$-Al-CO_3-HTlcs, and the SDS and SDBS treated forms were obtained using Varian 660 FT-IR spectrometer in the range of 700–4000 cm^{-1} to identify the anions in the interlayer of the various synthesised hydrotalcites. The resolution used was 4 cm^{-1} with sensitivity of 1. The attenuated total reflection (ATR) method with a diamond sample holder was used.

Thermal analysis curves of the samples were recorded with a Netzsch STA 449 FI Jupiter® apparatus, connected to a quadrupole mass spectrometer (Netzsch QMS 403 Aëolus®) analyser from 25 to 900°C under oxygen atmosphere at a heating rate of 5°C/min.

Morphology study was carried out on the HTlcs and their modified forms using a PhilipXL 30 Scanning Electron Microscope. The sample to be analysed was spread over a carbon tape that was placed on a silicon wafer substrate which was in turn placed on a stud and then coated slightly with gold on the surface of the particles to prevent any electron charge on the sample surface.

3.0 RESULTS AND DISCUSSIONS

The as-synthesised $Zn_{(n)}$-Al-CO_3-hydrotalcite-like compounds showed patterns characteristic of hydrotalcites (Fig. 1).

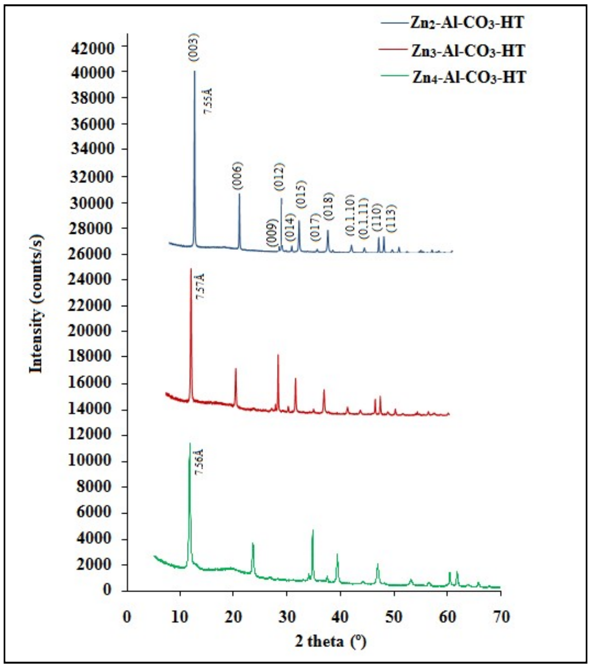

Fig. 1: Powder X-ray diffraction pattern of Zn-A-lCO₃ hydrotalcite-like compounds with different layer composition

They have a high degree of crystallinity and no impurity phase or phases were detected. A slight variation in the reflections was observed. The 003 reflection shifted towards lower angles as the Zn^{2+}/Al^{3+}

molar ratios increased, causing a slight increase in the interlayer spaces due to decreased charge density. This is ascribed to the decreasing ionic interaction between the mixed metal hydroxide layers and the interlayer carbonate anions (FT-IR confirms that the interlayer anions were carbonate anions). These materials possess high degree of crystallinity which was influenced by the Zn^{2+}/Al^{3+} molar ratios as was observed to decrease with increasing Zn^{2+}/Al^{3+} molar ratios.

Organic surfactants, sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) were intercalated into the as-synthesised parent Zn-Al-CO_3-HTlcs through calcination-regeneration method, and a high degree of intercalation was observed as compared to direct intercalation of the SDS and SDBS into the matrix of the hydrotalcite-like compounds by dispersing them into aqueous solutions of the guest SDS and SDBS anions or direct ion exchange. (Patterns are not shown, but showed phases of insoluble Mg and Al salts, with no significant intercalation). The XRD patterns of the regenerated $Zn_{(n)}$-Al-CO_3-DS and $Zn_{(n)}$-Al-CO_3-DBS) is presented in Fig. 2.

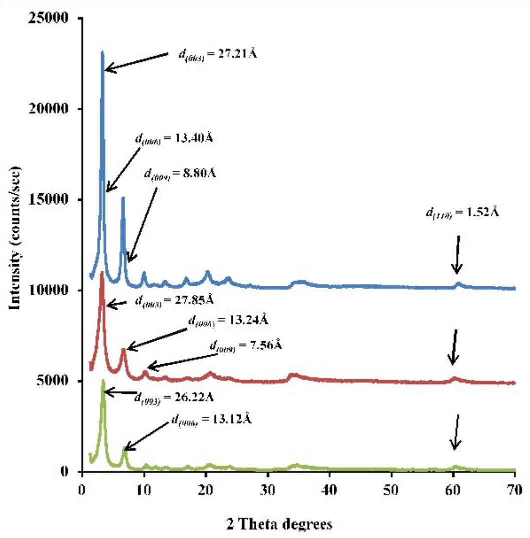

Fig. 2: Powder XRD patterns of dodecylsulfate-intercalated hydrotalcites (Zn_2AlCO_3-DS (Blue), Zn_3AlCO_3-DS (red), Zn_4AlCO_3-DS (Olive green).

There is re-appearance of the crystal structure with all characteristic reflections corresponding to the parent hydrotalcites but with broadening of the crystal reflections due to loss of some degree of crystallinity as dodecyl sulfate (DS) and dodecylbenzenesulfonate (DBS) were incorporated into the galleries of $Zn_{(n)}$-Al-CO_3-DS and $Zn_{(n)}$-Al-CO_3-DBS HTlcs. The position of the basal reflections shifted to higher d-values showing expanded interlayer distance confirming the intercalation of DS and DBS guest anions into the galleries of $Zn_{(n)}$-Al-CO_3-DS and $Zn_{(n)}$-Al-CO_3-DBS (FT-IR also confirms this), with tilt angles of 57.4° and 56.3° respectively**.** Zn_2AlCO_3-DS showed a slightly lower d-value (27.21 Å) than Zn_3AlCO_3-DS d-value of 27.85 Å). Nevertheless they both gave bilayer orientation with DS anions within the galleries while Zn_4AlCO_3-DS gave the lowest d-value of (26.22Å) with a possibility of monolayer arrangement of the DS anions within the interlayer region.

XRF analysis showed that, the molar ratio of Zn^{2+}/Al^{3+} conformed to the Zn^{2+}/Al^{3+} molar ratios of the synthesised host hydrotalcite-like compounds (Table 1) for Zn_2Al-CO_3-HTlc and its modified forms but unavailable for the others because beads breakage was encountered. This breakage of the beads may have been due to the presence of Zn, DS and DBS affecting the interlinking of the flux that stabilised the glass bead formation under supercooling conditions.

Table 1 Characteristics of hydrotalcite-like compounds (HTlcs), DS, DBS intercalated HTlcs

Hydrotalcite-like compounds	**Observed d-value (Å)**	**$Zn^{2+}/Al^{3+\ a}$**
Zn_2-Al-CO_3-HTlc	7.55	2.18:1
Zn_3-Al-CO_3- HTlc	7.57	3.75:1
Zn_4-Al-CO_3- HTlc	7.56	3.90:1
Zn_2-Al-CO_3-DS	27.2	2.34:1
Zn_3-Al-CO_3-DS	27.9	NA
Zn_4-Al-CO_3-DS	26.2	NA
$Zn_{(2)}$-Al-CO_3-DBS	39.3	3.32:1
$Zn_{(3)}$-Al-CO_3-DBS	45.6	NA
$Zn_{(4)}$-Al-CO_3-DBS	29.4	NA

[a] Determined from XRF analysis

The FT-IR spectra of the parent Zn-A-lCO_3 hydrotalcite-like compounds are presented in Fig.3. The broad absorption bands between 3384-3421 cm^{-1} are attributed to the interlayer hydrogen bond stretching of O-H group and hydrogen bonding between water and the interlayer carbonate anions. The prominent peaks located at about 1360-1361 cm^{-1} are ascribed to O-C-O stretching vibration of the CO_3^{2-} anion at the interlayer region.

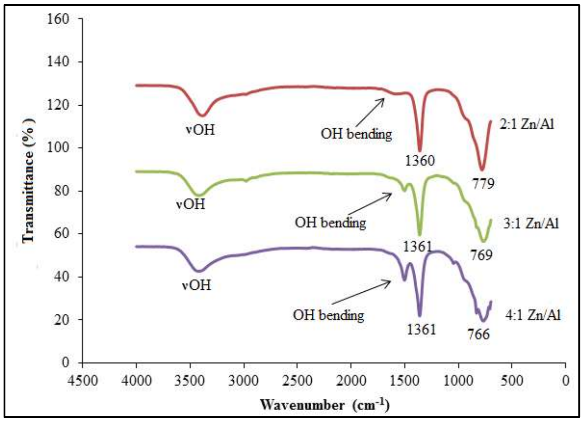

Fig. 3: FT-IR spectra of Zn-Al-CO_3 hydrotalcite-like compounds with different composition of layers.

The variations in band positions of these materials were attributed to possible differences in order/disorder in the stacking of the layers due to varying Zn^{2+}/Al^{3+} molar ratios. The bands between 1502- 1579 were assigned to the bending vibration (δH_2O) of interlayer water and the intensity increases slightly with increasing Zn^{2+}/Al^{3+} ratio. The band appearing between 766-779 cm^{-1} is the flexural vibration of CO_3^{2-} anion.

The modification of $Zn_{(n)}$-Al-CO_3-HTlcs by intercalating DS and DBS surfactants into the hydrotalcite galleries is confirmed by FT-IR spectra. Illustrating with $Zn_{(2)}$-Al-CO_3-HTlcs, Fig. 4 presents the FT-IR spectra of the host $Zn_{(2)}$-Al-CO_3-HTlcs, $Zn_{(2)}$-Al-CO_3-DS and $Zn_{(2)}$-Al-CO_3-DBS HTlcs.

The appearance of the CH_2 and OSO_3^- band is seen at 2849, 2912 and 1198, 1058cm^{-1} respectively. For the SDBS derivative, bands ascribed to C-H, C-H aromatic, C=C aromatic and SO_3^- are apparent at 1492 cm^{-1}; 1127, 1059cm^{-1}; 1465, 1059 cm^{-1} and 1193, 1035, 1059, 1008cm^{-1} respectively. This demonstrates the intercalation of dodecylsulfate and dodecylbenzenesulfonate anions into the host Zn_2AlCO_3 hydrotalcite interlayer. The peaks with wavenumber of 700 - 1000cm^{-1} are assigned to metal–oxygen vibrations and this is common to all of them suggesting that the DS and DBS modified hydrotalcites maintained the hydrotalcite structure. These results are in agreement with reports of previous researchers (Wang *et al.,* 2005, Anbarasan *et al.,* 2005) who observed similar vibration bands.

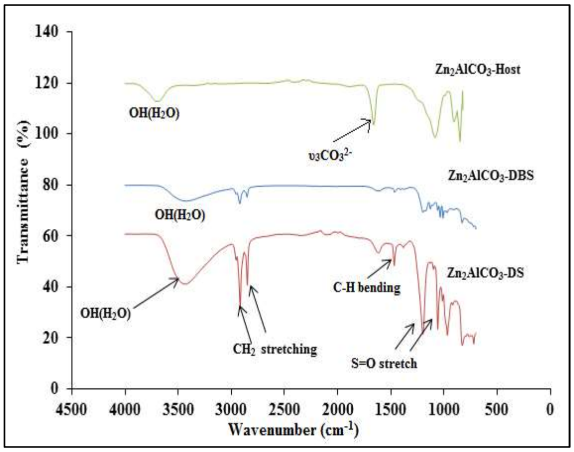

Fig. 4: FT-IR spectra of Zn_2AlCO_3 hydrotalcite (Host HT-CO_3), Zn_2AlCO_3-SDS (dodecylsulfate-intercalated hydrotalcite) and Zn_2AlCO_3-SDBS (dodecylbenzenesulfonate-intercalted hydrotalcite)

The thermal behaviours of $ZnAlCO_3$ HTlcs with different molar ratios are shown in Fig. 5. The hydrotalcites exhibited thermal behaviour characterised by two transition stages. These stages or steps are not clearly resolved on the TG curves for these hydrotalcite-like series.

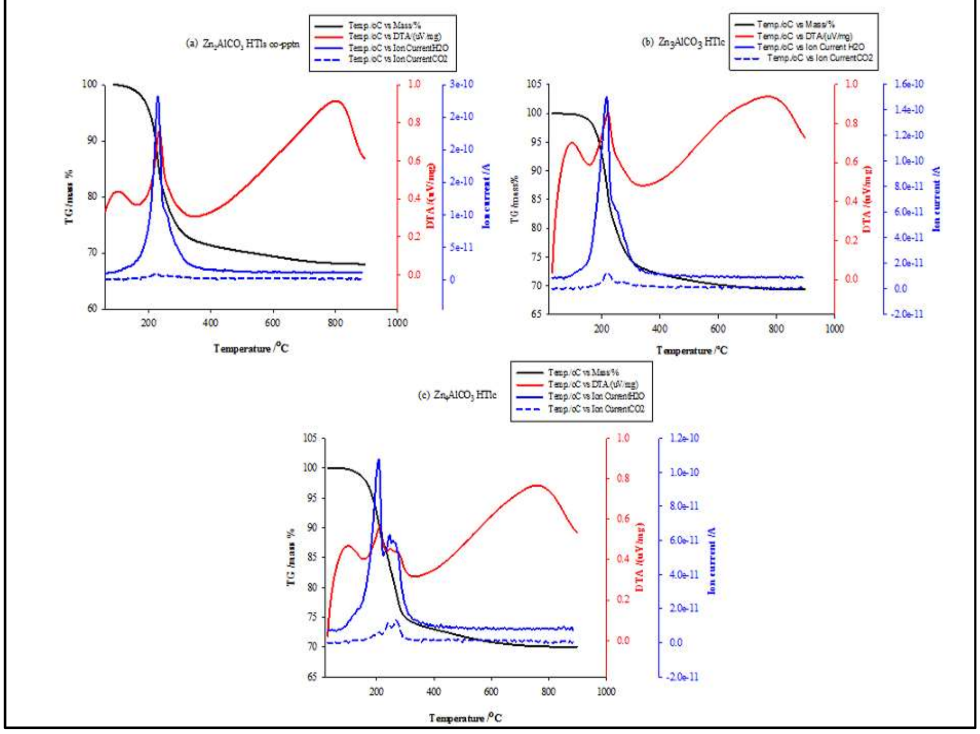

Fig. 5: TG, DTA and gas evolution ion current curves of $Zn_{(n)}AlCO_3$ HTlcs (n=Zn/Al molar ratios)

There appeared to be series of overlapping processes (Velu *et al.,* 1997) during the decomposition of these samples. However, the DTA clearly show three endothermic peaks in all three samples. The first change that occurs during thermal analysis of this type of sample is associated with the removal of water physically adsorbed on the surfaces of the hydrotalcites and from the interior surfaces of the galleries and it usually occurs at low temperature. For these samples, this may have happened around 90-140°C (Fig. 5), followed by the second step involving simultaneous abstraction of water from the layers and carbonate from the internal galleries leading to the collapsed of the structure (XRD and FT-IR data not shown). This step and the former may have overlapped and is represented on the DTA by the endothermic peak centered at 235°C for Zn_2-Al-CO_3 HTlc, 222°C for Zn_3-Al-CO_3 HT and at 212°C for Zn_4-Al-CO_3 HTlc. The mass spectrometry analysis showed the evolution of H_2O in a single step at 231°C and CO_2 at 225°C for Zn_2-Al-CO_3 HTlc, H_2O at 216°C and CO_2 at 218°C for Zn_3-Al-CO_3 HTlc and for Zn_4-Al-CO_3 HTlc, H_2O was released in 2 steps at 200°C and 246°C while CO_2 is released at 268°C. By 350°C, evolution was complete for these samples. The strong endothermic peaks around 740°C - 800°C may be due to heat absorbed during the formation into the spinel phase, $ZnAl_2O_4$ (Guimarães *et al*., 2000; Padmasri, *et al.,* 2002). Total weight losses of 32, 31 and 30% respectively were derived.

The thermal behaviour of the regenerated $Zn_{(n)}$-Al-CO_3 HTlcs is similar to those of the hosts from which they were derived and an illustration with the 2:1 form of Zn_2-Al-CO-HTlc intercalated with DS and DBS is presented in Fig. 6.

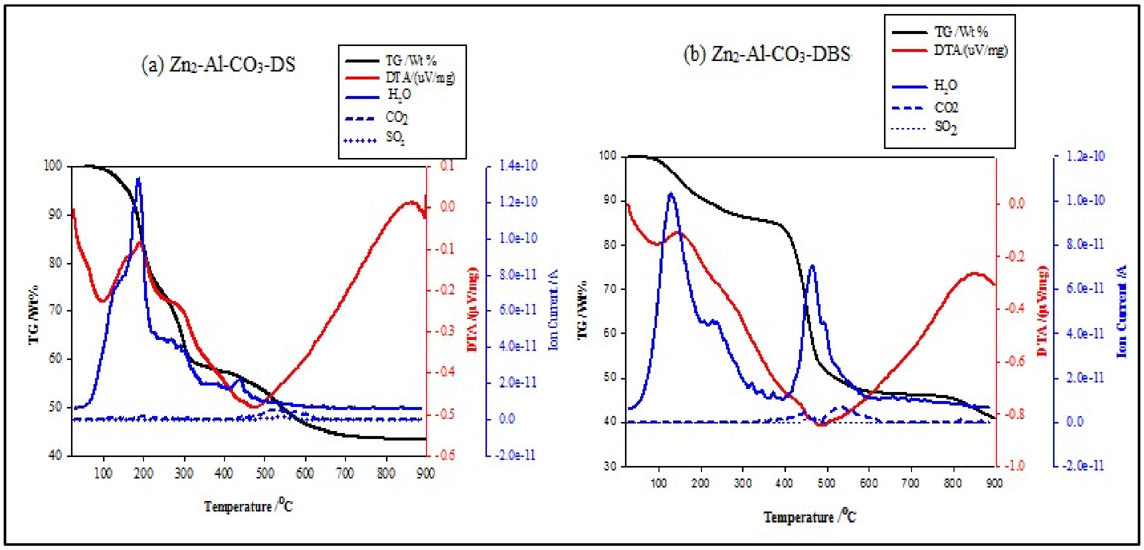

Fig. 6: TGA-DTA of (a) Zn_2AlCO_3-DS (Zn_2Al-CO_3 hydrotalcite intercalated with sodium dodecylsulfate anion) and (b) Zn_2AlCO_3-DBS (Zn_2Al-CO_3 hydrotalcite intercalated with sodium dodecylbenzenesulfonate anion).

The TGA, DTA and ion current plots showed additional endothermic and exothermic peaks and water loss in the temperature range of 200-500°C for 6(a) and 200-600°C for 6(b). The two materials showed thermal transitions with variations in the temperatures associated with the transition steps and the weight changes. This may be due to the strength of interaction between the surfactant anions and the Zn_2AlOH layers, and the most likely the breakdown and combustion of the dodecylsulfate and dodecylbenzenesulfonate anions. The total weight loss at 900ºC is 57% in Zn_2AlCO_3-DS and 59% in Zn_2AlCO_3-DBS.

SEM images of the Zn-Al-CO_3-HTlcs and modified forms are shown in Figs 7. It can be seen that the host hydrotalcites (Fig. 7a, d and g) have thick hexagonal plate-like crystals with non-homogenous crystals. The sizes are not uniform and they possess sharp edges. The modified counterparts show the same morphology as the host precursors, but many of the particles have been broken down into smaller pieces, as a result of both the dehydration/dehydroxylation pre-treatment and regeneration with organic anions. The shape of the particles of the Zn-Al-CO_3-DS and Zn-Al-CO_3- DBS HTlcs became more irregular with rougher crystal surfaces when compared to the host Zn-Al-CO_3-HTlcs. The DS and DBS intercalated samples also show particle surfaces that are floppy in appearance and showing secondary growth of further smaller layers.

4. CONCLUSION

Hydrotalcite-like compounds with Zn^{2+}/Al^{3+} cations in the layers at different mole ratios were synthesised. They were characterised by a range of techniques. The influence of layer cations influenced the crystallinity which in turn affected the properties of the hydrotalcite-like materials.

Dodecylsulfate (DS) and dodecylbenzenesulfonate (DBS) anions were intercalated successfully into the galleries and characterisation studies by the same technique that were used for the parent hydrotalcites showed that the hydrotalcites structure was maintained and the interlayer space expanded, suggesting that intercalation of other organic compounds or other surfactants may be possible. The intercalated dodecylsulfate and dodecylbenzenesulfonate anions arranged themselves in monolayer and bilayer configuration in the interlayer. These modified hydrotalcites have well-ordered layered structures, Zn^{2+}/Al^{3+} mole ratios that are close to those of the host precursors. SEM images show that the modification with DS and DBS led to many of the particles being broken down into smaller pieces due to thermal pre-treatment and regeneration with organic anions, but overall morphology was maintained as the host. They show thermal transitions that were comparable to the host, exhibiting transition steps in which there were changes in the temperature at which weight losses were completed.

These clay based materials are perceived as promising materials for technological applications such as, precursors to other materials like cement, as catalyst and catalyst supports, as anion exchangers and adsorbents; and in chemical process industry.

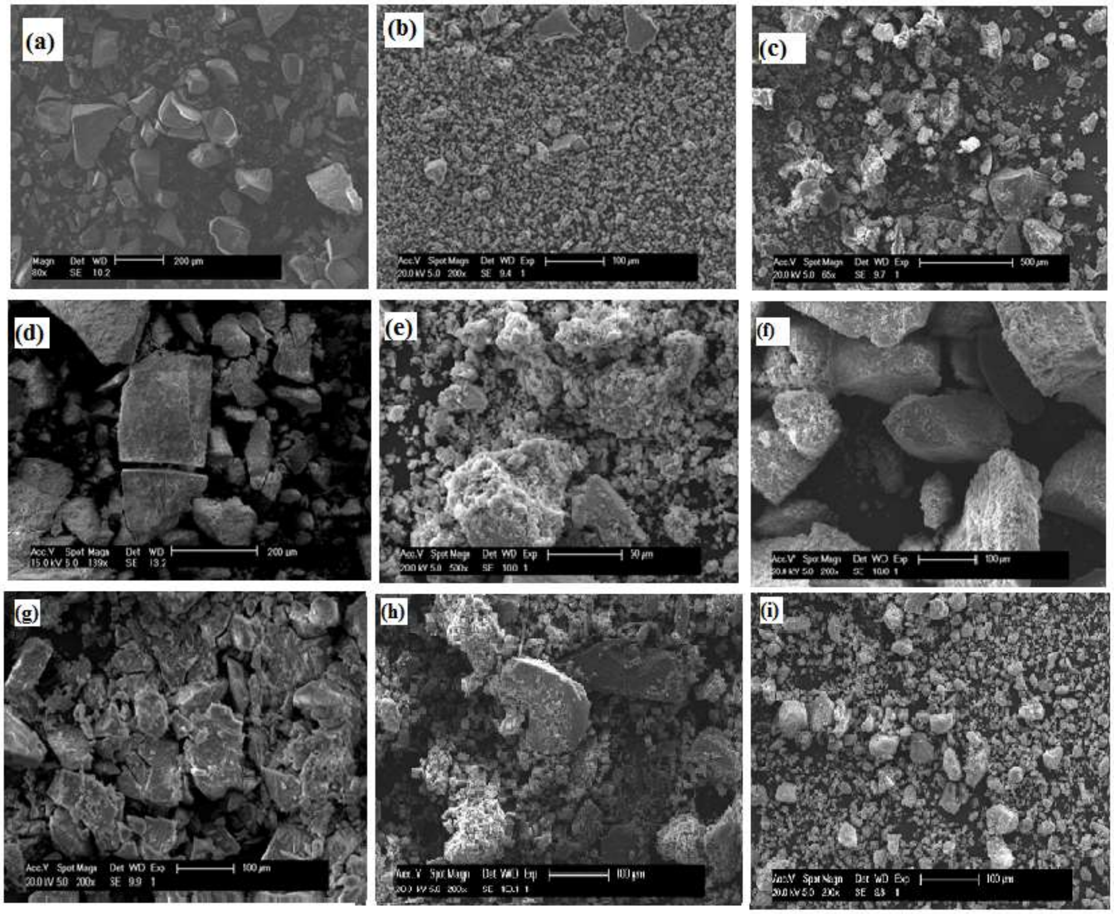

Fig.7: SEM micrograpghs of parent and modified hydrotalcite-like compounds. (a) Zn_2-Al-CO_3- HTlc, (b) Zn_2-Al-CO_3- DS, (c) Zn_2-Al-CO_3- DBS, (d) Zn_3-Al-CO_3- HTlc, (e) Zn_3-Al-CO_3- DS, (f) Zn_3-Al-CO_3- DBS, (g) Zn_4-Al-CO_3- HTlc, (i) Zn_4-Al-CO_3- DS, (J) Zn_4-Al-CO_3- DBS

5. ACKNOWLEDGEMENTS

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