



Platelets to rings: Influence of sodium dodecyl sulfate on Zn–Al layered double hydroxide morphology

Ceren Yilmaz^a, Ugur Unal^{a,b,c}, Havva Yagci Acar^{a,b,c,*}

^a Graduate School of Science and Engineering, Koc University, Rumelifeneri Yolu, Sariyer 34450, Istanbul, Turkey

^b Koc University, Chemistry Department, Rumelifeneri yolu, Sariyer 34450, Istanbul, Turkey

^c Koc University, Surface Science and Technology Center, KUYTAM, Rumelifeneri yolu, Sariyer 34450, Istanbul, Turkey

ARTICLE INFO

Article history:

Received 8 October 2011

Received in revised form

14 January 2012

Accepted 23 January 2012

Available online 30 January 2012

Keywords:

Intercalation

Sodium dodecylsulfate

Layered double hydroxide

Ring morphology

Template assisted synthesis

Urea hydrolysis

ABSTRACT

In the current study, influence of sodium dodecyl sulfate (SDS) on the crystallization of Zn–Al layered double hydroxide (LDH) was investigated. Depending on the SDS concentration coral-like and for the first time ring-like morphologies were obtained in a urea-hydrolysis method. It was revealed that the surfactant level in the starting solution plays an important role in the morphology. Concentration of surfactant equal to or above the anion exchange capacity of the LDH is influential in creating different morphologies. Another important parameter was the critical micelle concentration (CMC) of the surfactant. Surfactant concentrations well above CMC value resulted in ring-like structures. The crystallization mechanism was discussed.

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1. Introduction

There is a great interest in obtaining advanced materials with altered morphologies, since often shape and size dictates the properties and applications [1–3]. Layered double hydroxides (LDH) have received considerable interest due to their wide range of application areas [4,5]. LDHs have a brucite-like lamellar structure with a general formula of “[M_{1-2x}²⁺M_x³⁺(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·yH₂O”. M²⁺ and M³⁺ are divalent and trivalent metal ions giving a net positive charge to the sheets, Aⁿ⁻ is hydrated anion balancing the charge of the sheets. Ability to change all three components of the formula provides a quite rich portfolio of LDHs suitable for many applications from sensors to drug delivery.

Conventional co-precipitation technique in the presence of NaOH [6] or even urea hydrolysis method [7] may give rise to hexagonal platelet LDHs. These hexagonal platelets tend to form ‘rosette’ aggregates, especially in relatively low urea or hexamethylenetetramine (HMT) concentrations [8]. However, morphology of the materials can be modified by templates formed by self-assembled structures. Recently, there is a growing trend in the

template-assisted synthesis of the layered double hydroxides using surfactants.

Surfactants usually have low solubility in water and they spontaneously form aggregates of well-defined structures such as spherical micelles, cylinders, bilayers, inverted micelles and even liquid crystal phases, etc. above a critical micelle concentration (CMC) [9,10]. The shape of the micelle and the type of the aggregate structure formed depend on many factors such as the structure of the surfactant, concentration, presence of electrolytes and the critical packing constant as proposed by Israelachvili et al. given by the equation $P_c = V/a_0l_c$, where V is the volume of the hydrophobic part of the surfactant, a_0 is the effective area per head group, l_c is the length of the hydrocarbon chain [11]. In general, at $P_c \leq 1/3$ spherical micelles, at $1/3 < P_c \leq 1/2$ cylindrical (rod-like) micelles and at $1/2 < P_c \leq 1$ bilayers are formed. SDS with a single hydrocarbon chain and a sulfate head group has a P_c value of 0.37 which indicates a tendency to form spherical micelles in water at the critical micelle concentration [9]. However, the effective head group area, a_0 varies depending on the repulsion interactions between head groups and hydrophobic attraction. P_c increases with increasing surfactant concentration due to the decrease in bound water [10]. Hence at high concentrations, micelles might combine into cylindrical forms, elongated ‘worm-like’ structures and convert into lamellar sheets which might be of various lengths [12]. Furthermore, addition of the electrolytes into surfactant solutions increases the screening of

* Corresponding author at: Koc University, Chemistry Department, Graduate School of Science and Engineering, Rumelifeneri Yolu, Sariyer 34450, Istanbul, Turkey. Fax: +90 2123381559.

E-mail address: fyagci@ku.edu.tr (H. Yagci Acar).

the electrostatic repulsion of the head groups giving rise to an increase in P_c but a decrease in CMC. Structure of the aggregates hence changes also upon addition of electrolytes. It is reported that SDS forms 'prolate spherocylindrical' micelles far from CMC, at high [SDS], high [salt], and low temperature conditions [13].

M^{2+}/Al^{3+} (Mg^{2+} , Zn^{2+} , Co^{2+}) LDHs usually form plate like structures. There is a significant amount of work on template-assisted synthesis especially for widely studied Mg–Al LDHs. Li et al. have seen bent structures and sand rose aggregates for Mg–Al LDHs synthesized with SDS [14]. Gunawan et al. have coral like microspheres of SDS/ethyleneglycol intercalated Mg–Al LDH [15]. Braterman et al. observed bar like particles as well as curved and platy Mg–Al LDH from dodecylbenzenesulfonate [16]. Ogawa et al. use hydrothermal method with gibbsite and brucite as starting materials to construct 'curved platy' particles of deoxycholate intercalated Mg–Al LDH. In all of these studies surfactants approximately 20 times the ion exchange capacity have been used at most. No different morphologies than these have been reported in the literature for LDHs to the best of our knowledge.

Zn–Al LDH are valuable materials for applications including fire resistance, sensors, absorbers, and drug carriers. For example, Zn–Al LDH has already been proved as a nontoxic drug carrier [17,18] and Zn^{2+} replacing Mg^{2+} in LDH results in a product with higher thermal stability and transparency [19]. A significantly different morphology for Zn–Al LDH other than the irregularities has not been reported to the best of our knowledge. Therefore, in this study, the influence of the surfactant and surfactant concentration as well as the reaction time on the Zn–Al LDH morphology was investigated. Zn–Al LDHs were synthesized via urea hydrolysis method in the presence of sodium dodecyl sulfate at concentrations which are below and above the critical micelle concentration of the SDS.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), urea (CH_4N_2O), dodecyl sulfate sodium salt (SDS) were purchased from Merck and Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was from LaCheMa. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

2.2. Synthesis of LDHs

In a typical synthesis, 10 mM Zn^{2+} and 5 mM Al^{3+} salts were dissolved in distilled and decarbonated water under Ar in a 4-necked round bottom flask fitted with a mechanical stirrer. Desired amount of SDS (5, 15, 100 mM) was added into the above solution. Finally, the ammonia releasing agent (urea) was added at urea/ Zn^{2+} = 3.5 mol ratio and the mixture was stirred at 90 °C for several hours. A control sample with no surfactant was prepared under identical conditions. LDH in the form of a white precipitate was removed through centrifugation at 4000 rpm for 30 min and it was washed with a copious amount of decarbonated water and dried under vacuum before analysis.

2.3. Characterization

The crystal structure and crystallinity of the samples were analyzed on XRD Rigaku MiniFlexII using Cu- K_α radiation. Zn/Al ratio was detected by Bruker Energy Dispersive Spectrometer (EDX) attached to a ZEISS Ultra Plus Field Emission Scanning Electron Microscope (FE-SEM). Samples were prepared by drying

a small amount of sample dispersed in ethyl alcohol dropped on SEM specimen mounts. Samples were coated with carbon before the analysis. The FT-IR spectra were recorded on JASCO FT-IR-600 PLUS spectrometer using KBr pellets. Thermogravimetric Analysis (Shimadzu TGA 50H) was performed on dried powders to analyze the surfactant and water content. The morphology of the powders was examined with a Leo Supra 35VP Field emission scanning electron microscope, and Leo 32 electron dispersive spectrometer software was used for images and analysis. Imaging was generally done at 2–5 keV accelerating voltage, using the secondary electron detector.

3. Results and discussion

SDS (Sodium dodecylsulfate) intercalated Zn–Al layered materials were synthesized by the urea hydrolysis method [20]. The crystallinity of the Zn–Al- CO_3 and SDS intercalated LDHs that were synthesized under identical conditions, was verified by the XRD analysis of powders (Fig. S1 and Fig. 1). The sharpness of the peaks suggests ordered and regular stacking of the sheets. XRD of the Zn–Al- CO_3 (Fig. 1) displays $d_{003}(11.49^\circ)$, $d_{006}(23.39^\circ)$, $d_{009}(37.30^\circ)$, $d_{012}(34.62^\circ)$, $d_{015}(39.24^\circ)$, $d_{018}(46.78^\circ)$, $d_{110}(60.36^\circ)$, $d_{113}(61.72^\circ)$ crystal planes with the basal spacing of 0.769 nm. The appearance of the (0 1 2), (0 1 5) and (0 1 8) reflections indicate $3R_1$ polytype with rhombohedral symmetry which is believed to be the structure of the most carbonated LDH [5]. Basal spacing, calculated from the Bragg's equation accounts for the interlayer gallery distance since it is equal to the thickness of one brucite-like layer plus one interlayer [21]. Intercalation of the anionic surfactants depending on their size, functional group and alkyl chain length might result in a change in the interlayer gallery distance. XRD patterns of the SDS intercalated samples in Fig. 1 show (0 0 3), (0 0 6), (0 0 9) crystal planes as expected. The characteristic intense basal reflection peaks together with the appearance of higher order peaks indicate intercalated LDH structure highly oriented in c-direction for all samples. Significant increase in the basal spacing with respect to Zn–Al- CO_3 (0.769 nm) indicates SDS intercalation within the galleries, as expected. Basal spacing is in the range of 2.505–2.627 nm as given in Table 1. Accepting the full length of SDS molecule as 2.08 nm, SDS molecules should form a tilted interdigitated bilayer between the Zn–Al sheets. The reported basal spacing values for SDS intercalated LDHs vary in a considerable range due to the arrangement of the surfactant inside the layers. These differences are attributed to the presence of adsorbed water [22], identity of the metals [23], M^{2+}/Al^{3+} ratio [24], intercalation pH and the method of synthesis [25].

The packing of the hydrocarbon chains in between the LDH layers has been of considerable controversy. Guo et al. envisions

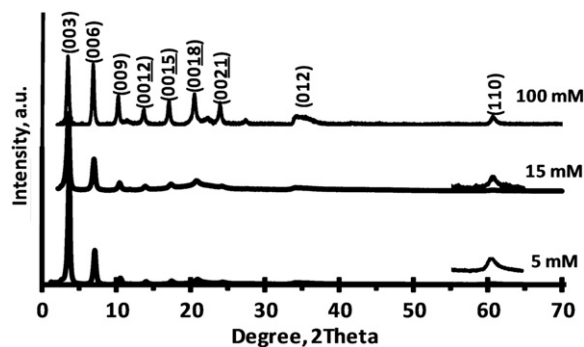


Fig. 1. Powder XRD patterns of Zn–Al LDH with different SDS concentrations: 5 mM, 15 mM and 100.

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