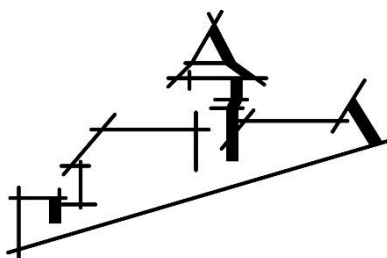# PROGRESSIVE TRENDS IN COORDINATION, BIOINORGANIC, AND APPLIED INORGANIC CHEMISTRY

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Intercalation and oxidation of cysteinate between the layers of Ca₂Al-layered double hydroxide

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Nowadays, the environmental as well as the laboratory syntheses concentrate on using the principles of green chemistry in designing products and processes to minimize the amount of the useless and occasionally hazardous by-products. Applying materials with confined environment like layered double hydroxides (LDHs) as nano-reactors may be useful in this respect, since in it, the chance of side reactions may decrease. In a nanoreactor like this, the position of one or more reactants are fixed in anionic forms due to the anion-exchange property of the LDH. In this work, the oxidation of cysteinate fixed in CaAl-LDH nanoreactor was studied. Structural features of the LDH was obtained by X-ray diffractometry, and the reaction was followed by Raman spectroscopy.

INTRODUCTION

Layered double hydroxides (abbreviated as LDHs) are anionic clay materials with the $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{m-}_{x/m} \cdot nH_2O)]^{x-}$ general formula, where M^{2+} and M^{3+} stand for the di- and trivalent metal ions, A^{m-} represents the interlayer anions with charge m, and $x = M^{3+}/[M^{2+}+M^{3+}]$ with the common value between 0.1 and 0.33 [1]. They brucite-like layers (brucite is layered $Mg(OH)_2$), in which the metal cations are octahedrally surrounded by hydroxide ions and trivalent metal ions substitute isomorphously part of the divalent cations. The frequently occurring combinations consist of Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+}, Al^{3+}, Cr^{3+} ions, while the variety of interlayer exchangeable anions are huge, among others quite often nitrate, carbonate, sulfate or chloride anions [2].

CaAl-LDH belongs to the hydrocalumite subgroup, its structure is derived from portlandite $[Ca(OH)_2]$ [3]. The Ca^{2+} ions are partially replaced by Al^{3+} ions forming a layered structure with the formula of $[Ca_2Al(OH)_6]^{x+}[A \cdot nH_2O]^{x-}$. In hydrocalumites, the calcium to aluminium ratio is fixed at 2:1 owing to the heptahedral coordination sphere of calcium, due to its larger size than the octahedrally coordinated Mg^{2+}. This arrangement results in an extra coordination site occupied by an interlamellar anion or water molecule, and thus, the calcium-based LDHs have increased ion-exchange capabilities [4, 5].

One of the most advantageous features of LDHs stems from the versatility of tailoring their structures to specific needs by modifying the ratio and the quality of metal ions in the layers and/or the bulkiness of the interlayer anions. The latter allows the control of the basal spacing (sum of the thickness of a layer and the interlayer distance) in the angstrom-scale. Furthermore, they have relatively high specific surface areas with enhanced anion-exchange capabilities, and thus, remarkable potential as efficient adsorbers [6, 7]. They can be utilized as flame retardant polymer composites [8, 9], in health care, as

transporters of medically important molecules or novel antacids [10] or as models of supramolecular systems [11, 12]. Finally, their as-prepared and heat-treated states are frequently applied as catalysts in base-catalyzed [13-15] or hydrogenolysis reactions [16] or the synthesis of chiral complexes [17].

LDH can also be applied as nanoreactor [18-20], where one or more reactants are fixed in it, and the confined environment allows to suppress side-reactions, thus minimizing the amount of hazardous and environmentally dangerous by-products.

Cysteine is a sulfur-containing essential amino acid, which is easily oxidized to cystine [21]. The oxidation of cysteine has two directions: one way is the transformation of cysteine to cystine, and the other possibility is the oxidation to cysteic acid [22, 23].

In the experimental work leading to this contribution, the role of Ca_2Al-LDH and the reaction conditions were studied in the oxidation reaction of cysteinate in the LDH on using various oxidant types. The results of this work are communicated in the followings.

EXPERIMENTAL PART

Reagents

L-cysteine, $Ca(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, hydrogen peroxide, peracetic acid, methanol and NaOH were purchased from Sigma Aldrich.

Preparation of cysteinate-intercalated CaAl-LDH

The cysteinate-intercalated system was prepared by the method of co-precipitation. Aqueous solutions of $Ca(NO_3)_2 \cdot 4H_2O$ (0.03 mol), $Al(NO_3)_2 \cdot 9H_2O$ (0.015 mol), NaOH (3M) and L-cysteine (0.0062 mol in 65 ml methanol) were mixed under nitrogen atmosphere. The reaction mixture was stirred for 3 days at 65°C, filtered, washed and dried at 50°C.

Interlayer oxidation of cysteine

In the experiments, peracetic acid was oxidant (60 μl or 100 μl), the solvent was methanol, and the reaction time was 60 min. The quantity of Cys-LDH (0.1 g), the volume of the solvent (8.4 cm³) and the reaction temperature (298 K) were kept constant.

Instrumental methods to characterize the LDH samples and to follow the reactions

The solid samples were characterized by X-ray diffractometry (XRD). It was used to study the as-prepared, the intercalated LDHs and the changes in the structure of LDH samples occurred during the oxidation reactions. The X-ray diffractograms were recorded on a Rigaku XRD-6000 diffractometer, using $Cu_{K\alpha}$ radiation ($\alpha = 0.15418$ nm) at 40 kV and 30 mA. In order to follow the oxidation reactions, the Raman spectra of the solid samples were recorded on a Thermo Scientific DXR confocal Raman microscope using a 780 nm laser source.

RESULTS AND DISCUSSION

Preparation of the cysteinate-intercalated CaAl-LDH (Cys–CaAl-LDH)

The cysteinate anion was intercalated among the layers of CaAl-LDH by the co-precipitation method. The X-ray diffractograms of the pristine and the intercalated samples (Fig. 1) verify that the intercalation was successful, since in the diffractogram of the intercalated sample (Fig. 1, trace B), the 003 reflection

shifted towards lower 2Θ values compared to those of the pristine CaAl-LDH (Fig. 1, trace A), *i.e.*, the basal distance increased from 0.361 nm to 0.415 nm.

The Raman spectra of L-cysteine, CaAl-LDH and the cysteinate-intercalated LDH are showed in Fig 2. The spectrum of CaAl-LDH displays characteristic bands at 534 cm^{-1} and 1054 cm^{-1} (Fig. 2, trace A) belonging to Al–O–Al skeletal stretch and surface-adsorbed carbonate, respectively. The other bands belonging to L-cysteine are as follows: C–H at 2968 cm^{-1}, S–H vibration at 2554 cm^{-1} and 944 cm^{-1}, asymmetric and symmetric carboxylate at 1405 cm^{-1} and 1355 cm^{-1}, respectively, C–S at 694 cm^{-1} and 641 cm^{-1} and finally, C–C–N at 445 cm^{-1} (Fig. 2, trace B) [24-26]. The Raman spectrum of the cysteinate-intercalated LDH (Fig. 2, trace C) only shows the characteristic vibrations of CaAl-LDH.
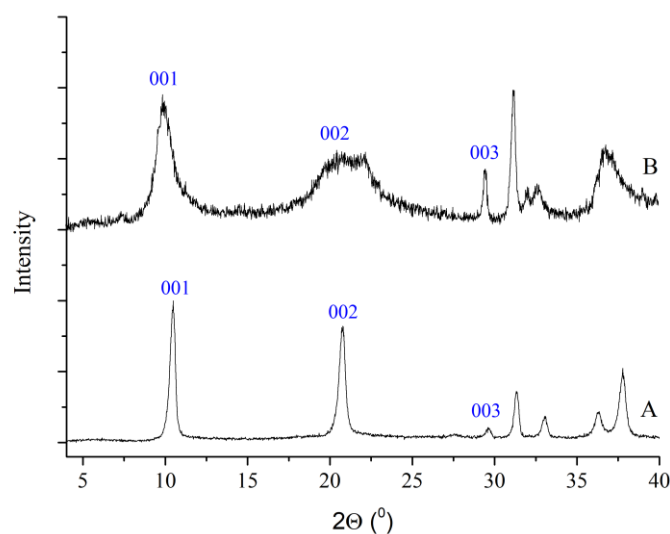

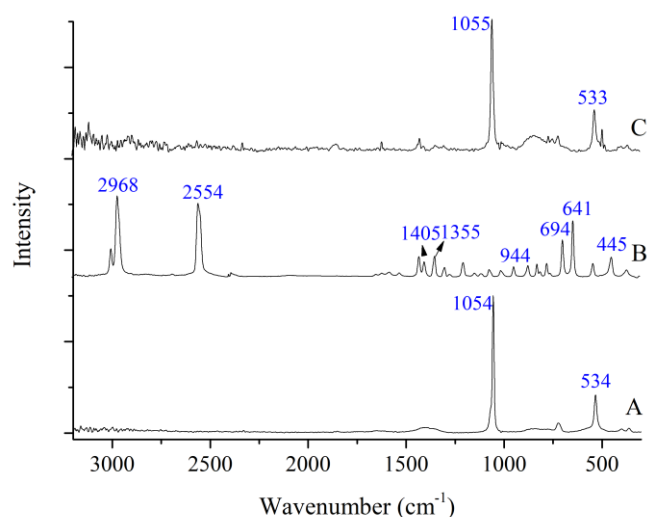Figure 1. X-ray diffractograms of A: pristine CaAl-LDH, B: cysteinate-intercalated LDH.

Figure 2. Raman spectra of A: pristine CaAl-LDH, B: L-cysteine and C: L-cysteinate-intercalated LDH.

Interlayer oxidation of the cysteinate ion

When the amount of peracetic acid was 60 µl (Cys–Ca$_2$Al-LDH:oxidant = 1:2), after 60 min reaction time, the X-ray diffractogram showed that the 001 reflection shifted towards larger 2Θ values compared to that of Cys–CaAl-LDH (Fig. 3, trace A, B). The basal spacing decreased from 0.415 nm to 0.364 nm (Fig. 3, trace B), which means that the product left the interlayer space and adsorbed on the outer surface of the LDH. After 60 min reaction time The Raman spectrum (Fig. 4, trace B) revealed bands of cysteinate vibrations and the characteristic bands of CaAl-LDH. New bands appeared at 664 cm^{-1} and 954 cm^{-1} belonging to the C–S bond and S(=O)O group 2934 cm^{-1} and 2843 cm^{-1} assigned to C–H stretches [27]. These results indicate that the reaction started, but did not proceed to completion. To our surprise, the oxidation reaction did not produce the expected cystine or cysteic acid, but cysteine sulfinic acid was formed.
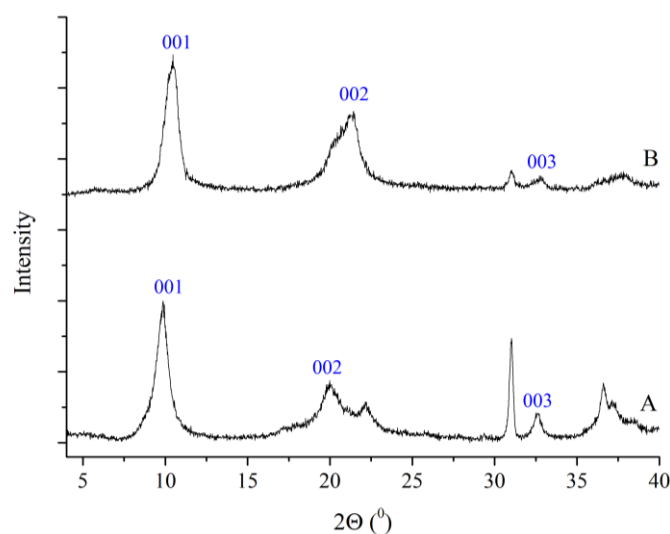

Figure 3. X-ray diffractograms of the solid samples. A: Cys–CaAl-LDH, B: CaAl-LDH after the oxidation reaction with 60 µl of peracetic acid.
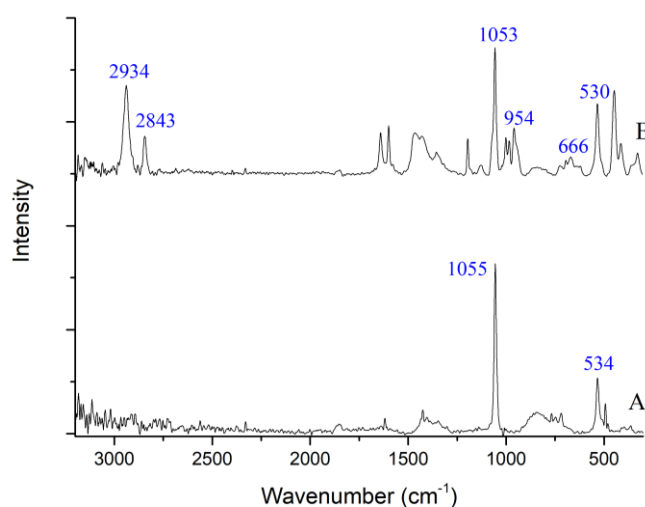

Figure 4. Raman spectra of the solid samples. A: Cys–CaAl-LDH and B: CaAl-LDH after the oxidation reaction with 60 µl of peracetic acid.

On applying 100 µl of the oxidant, the layered structure was destroyed, the reflections of the LDH disappeared from the diffractogram (Fig. 5, trace B) and complete amorphization took place. The Raman spectra (Fig. 6) confirm the destruction of LDH: the vibration of Al–O–Al bond disappeared, but the carbonate band could be detected at 1054 cm^{-1}, together with the bands belonging to the C–S bond at 666 cm^{-1}, the S(=O)O group at 955 cm^{-1} and the CH stretches at 2935 cm^{-1} and 2839 cm^{-1}. The X-ray diffractogram and the Raman spectra prove that the crystallinity of the CaAl-LDH sample was lost, the oxidation reaction proceeded towards the formation of cysteine sulfinic acid, and the relative cleanliness of the Raman spectrum indicates that the transformation was close to being complete.
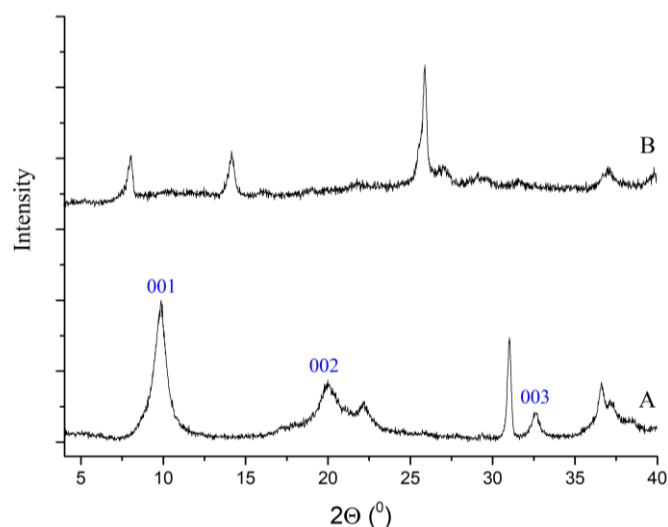

Figure 5. X-ray diffractograms of the solid samples. A: Cys–CaAl-LDH; B: CaAl-LDH after the oxidation with 100 µl of peracetic acid.
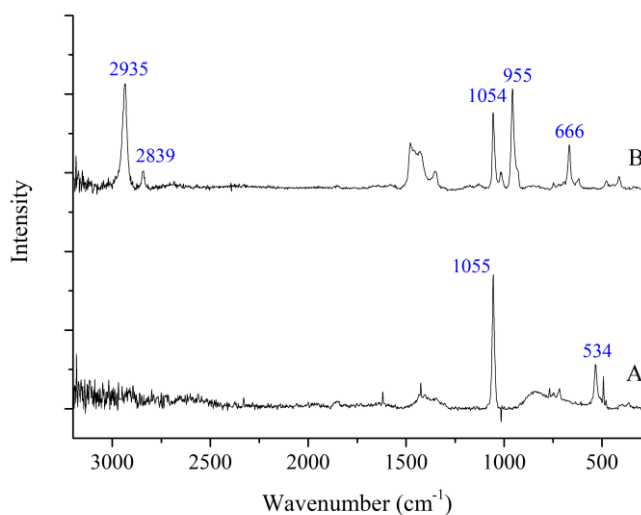

Figure 6. Raman spectra of the solid samples. A: Cys–CaAl-LDH, B: CaAl-LDH after the oxidation with 100 µl of peracetic acid.

CONCLUSIONS

The effects of CaAl-LDH was studied in the oxidation reaction of intercalated cysteinate. It was found that on using small amount of peracetic acid, the cysteinate to cysteine sulfinic acid transformation started. On increasing the amount of peracetic acid, the reaction became more complete; however, the crystallinity of the CaAl-LDH disappeared, and it became completely amorphous, thus, it could not be reused any more.

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