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G. M. Starukh[1], O. I. Oranska[1], S. I. Levytska[2]
[1] Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine,
17 General Naumov Str., Kyiv 03164, Ukraine
[2]Institute for Sorption and Problems of Endoecology of the National Academy of Sciences
of Ukraine, 13 General Naumov Str., Kyiv 03164, Ukraine
email: starukh_galina@ukr.net

RECONSTRUCTION OF CALCINED Zn-Al LAYERED DOUBLE HYDROXIDES DURING TETRACYCLINE ADSORPTION

Zn-Al mixed oxides containing ZnO different degree crystallinity were obtained by calcinations of Zn-Al layered double hydroxides (LDHs). The reconstruction of calcined Zn-Al LDHs has been performed under stirring in aqueous suspensions. The as-synthesized LDHs, its decomposition products, as well as the reconstructed solids upon hydration were characterized by XRD, N_2 adsorption, differential and thermal gravimetric analysis. It was found that the ability of Zn-Al LDHs to recover a layered structure under the hydration of mixed oxides depends on the degree of ZnO crystallinity. The partial reconstruction of Zn-Al layered structure occurs in tetracycline solutions irrespective to the degree of ZnO crystallinity in calcined LDHs. Calcined Zn-Al LDHs demonstrate the higher adsorption capacity to tetracycline in comparison with as-prepared Zn-Al LDHs. The adsorption of TC on calcined and uncalcined ZnAl LDHs occurs on the centers of one particular type. It is suggested that surface complexation of the A-ring ligand of TC with Al-OH centers takes place.

Keywords: Zn-Al layered double hydroxides, layered structure reconstruction, tetracycline, adsorption.

Introduction

Layered double hydroxides (LDHs) are a group of anion-intercalated inorganic functional materials which are also known as hydrotalcite-like compounds or anionic clays. LDHs composed of positively charged layers of general formula $[M^{3+}_xM^{2+}_{1-x}(OH)_2]^+$, and interlayer inorganic or organic anions compensating the positive charge, as well as hydrate water molecules. The large variety of compositions can be developed by altering the nature of the divalent (Mg^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) and trivalent (Al^{3+}, Ga^{3+}, Fe^{3+}, Cr^{3+}, etc.) cations and the interlayer anions [1, 2]. The application of LDHs in the fields of catalysis, separation science, and medicine have been well documented [3-5].

An important features of the hydrotalcite-like materials are their limited thermal stability and ease formation of mixed oxide phases. Due to the homogeneous interdispersion of constituting elements in the matrix of LDHs, the mixed oxides formed upon its thermal decomposition possess unique properties, unattainable by other preparative procedures. For this reason, LDHs gain increasing importance as extremely attractive precursors of multicomponent catalysts for many reactions of industrial interest [5].

After calcination at an appropriate temperature, the adsorption capacity of calcined hydrotalcite-like materials can be markedly enhanced over that of the original LDHs. Exposure of the as-prepared mixed oxides to an aqueous solution of an anion results in regeneration of the layered structure, with intercalation of the anion concerned [2, 6]. This phenomenon is sometimes described in the literature as the structural memory

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effect of LDHs. It is an important method of synthesizing both inorganic and organic anion-intercalated LDHs [6]. The memory effect is revealed during the preparation of intercalated systems with valuable catalytic properties [7] as well as adsorption of organic and inorganic components from aqueous media [5, 8]. The calcined samples behave as good adsorbents not only because of their ability to incorporate anions in the interlayer space, but also because they usually exhibit high specific surface areas, so they can act as adsorbing oxides [9].

Tetracycline (TC) is one of the most important antibiotics and is ranked as the second in the production in the world. A series of researches show that it is widely distributed in various waste streams [10]. Most tetracycline antibiotics enter the environment through municipal effluent, sewage sludge, solid wastes and manure applications. The continuous release of TC into the aquatic environment increases the potential for antibiotic resistance among microbial populations and the degradation by-products have been proven even more toxic than the parents [11]. Therefore, it is urgent to develop efficient and economical technologies to remove TC. There are many technologies available for TC removal including adsorption, oxidation, and photochemical degradation [12]. An adsorption, a relatively simple and inexpensive method, appears to offer the best prospects for the removal of TC from wastewater *in situ*.

Calcined LDHs have been extensively used as sorbents for the sorption of organic pollutants, such as glyphosate, 4-chloro-2-methylphenoxyacetic acid, sodium dodecylbenzenesulfonate, dicamba, and acidic pesticides [4, 13].

Recently it has been reported that the Mg-Al LDHs and its calcined forms were used as the sorbents for TC in water. Calcined Mg-Al LDHs showed markedly higher adsorption capacities for aqueous TC compared to LDHs [14]. Zn-Al LDHs, as prepared or calcined by a controlled decomposition, are often used as sorbents [15]. However, the presented in the literature results show that these solids have vast potential as photocatalysts [16, 17]. Calcined Zn-Al LDHs were active in the photocatalytic reduction of Cr (VI) and degradation of organic molecules due to presence of ZnO.

A detailed understanding of the mechanism of the transformation of mixed oxides into the LDHs is essential if the properties of the LDHs materials are to be successfully tailored for specific target applications. For the successful use of LDHs as sorbents and precursors of sorbents, catalysts and photocatalysts, it is important to understand the thermal stability of the LDHs and the ability to recover layered structure of its calcined forms under hydration in aqueous suspensions.

In this study, Zn-Al mixed oxides with defect and crystalline ZnO structures obtained upon calcinations of LDHs have been used to study the TC adsorption. The phase transformation under hydration of calcined LDHs in aqueous suspensions and in TC solutions were investigated. The influence of crystallinity of ZnO in mixed oxides and CO_2 presence in aqueous suspensions on the ability of calcined LDHs to restore layered structure has been studied.

Experimental section

ZnAl LDHs with carbonate as the interlayer anion was obtained according to the standard coprecipitation method [1] as follows. A solution containing sodium carbonate (0.5 M) and sodium hydroxide (1.5 M) was prepared. Another solution containing a mixture of zink and aluminium nitrates (total metal concentration 0.6 M, Zn/Al molar ratio 2:1) was prepared and added dropwise to the solution with sodium carbonate under stirring. Once addition was completed, the temperature was raised up to 85°C and the slurry was being kept for 6 h at this temperature under continuous stirring. Next day, the precipitate was filtered, washed with distilled water and dried at 100°C. The sample was labeled as HT. Zn-Al LDHs have been calcined at 600 °C over 1 and 2 hours and were labeled as cHT1h and cHT2h.

The calcined LDHs were hydrated by treatment with an excess of water for 24 h at room temperature under stirring. The samples were labeled as cHT1h-rehH_2O and cHT2h-rehH_2O. The hydrated samples were dried at 100°C in air. The hydration procedure was performed in aqueous TC solution without previous decarbonation. The slurries of 2 g of mixed oxides and 50 ml of aqueous $4 \cdot 10^{-3}$ M TC solution were stirred for 24 h at room temperature. These samples were labeled as cHT1h-rehTC and cHT2h-rehTC.

XRD patterns of samples were recorded with the DRON-4-07 diffractometer (CuK_α radiation). Calculation of apparent crystallite size for ZnO and LDHs has been performed by Debye-Scherrer formula $\beta(2\theta) = 0.94\lambda/(D\cos\theta°)$, using (1 0 0) reflections for ZnO and (1 1 0) reflection for LDH, employing the FWHM procedure. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using Derivatograph Q-1500 D MOM (Hungary) equipment at heating rate of $10° min^{-1}$. Nitrogen adsorption and desorption isotherms at 77K were measured on a Quantachrome Nova 2200 e Surface Area and Pore Size Analyzer. Prior to analysis, the samples were degassed in vacuum at 120°C for 20 h. Infrared spectra were obtained in the range of 4000–400 cm^{-1} on a Thermo Nicolet NEXUS FT-IR spectrophotometer (Nicollet, USA).

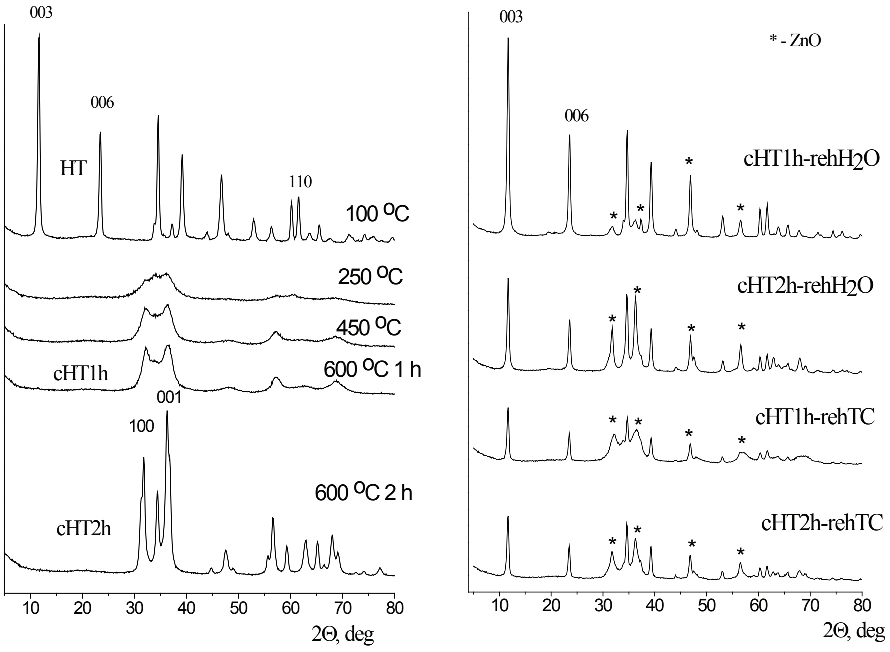
TC adsorption isotherms for the adsorbents were determined using a batch adsorption approach. At a set of an adsorbent mass and an initial concentration of the TC solutions we guided the optical density of the TC solutions after the establishing of equilibrium was in the range of 0.05 – 1 a.u. Typically, 0.05 g freshly Zn-Al mixed oxides and LDHs were introduced into 100-mL glass tubes containing 40 mL of freshly prepared aqueous TC solutions with concentrations ranging from 2×10^{-5} mol/l to 1.5×10^{-4} mol/l. About 90% of the adsorption occurred in the first hour, followed by a slow increase to the maximum over time. Based on this observation, 24 h was chosen as the equilibration time for later studies to ensure adequate time was given to reach equilibrium. Particles were removed by centrifugation at 6000 RPM, and the residual concentration of TC in the solution was determined using UV-Vis spectrometry at a detecting wavelength of 375 nm. The equilibrium adsorption amount of TC in the sample was calculated according to equation: $q_e = (C_0 - C_e)V/m$, where q_e is the amount of TC adsorbed at equilibrium, C_0 is the initial TC concentration, C_e is the equilibrium concentration of TC in solution, V is the total volume of solution, and m is the sorbent mass.

Results and discussion

The XRD pattern for as-synthesized Zn–Al LDHs is characteristic of layered materials with hydrotalcite-like structure (Fig. 1*a*). The pattern can be indexed to a hexagonal cell (a = 3.070 Å; c = 22.50 Å). A pair of basal reflections *00l* (l= 3, 6) indicating an interlayer spacing of 7.50 Å corresponding to the intercalated carbonate [1]. All the reflections are sharp indicative of an ordered material. Upon thermal treatment, it can be seen that all the reflections corresponding to the hydrotalcite have disappeared indicating a break down of the layered structure (Fig. 1*a*). The observed profiles of HT calcined at 600 °C over 1 hour are fit to defect structure of wurtzite ZnO (fig. 1*a*). A substantial improvement of the product crystallinity is achieved by elongation of calcination at

600 °C from 1 to 2 hours representing by sharper and narrower characteristic peaks of wurtzite ZnO (ICSD CC No. 44058) (fig. 1*a*). No diffraction peaks relating to the crystalline alumina modifications were observed, indicating that Al (III) cations are very well dispersed in the ZnO matrix.

Hydration of calcined hydrotalcite cHT1h leads to the reconstruction of its original layered structure (fig. 1*b*). Zn-Al LDHs with high crystalline structure was obtained. The hydration of Zn-Al LDHs calcined at 600 °C over 2 hours (sample cHT2h) causes to partial reconstitution of layered structure (fig. 1*b*).



a b

Fig. 1. X-ray diffraction patterns of as prepared and calcined Zn-Al LDHs – *a*; calcined Zn-Al LDHs after hydration – *b*.

The partial reconstruction of Zn-Al layered structure occurs under hydration of calcined cHT1h and cHT2h in TC aqueous solution (fig. 1*b*). In presented work, TC adsorption study was conducted at pH 7.0 when aqueous TC consists of about 70 % zwitterionic species and 30 % anionic species [18]. It is well known that interlayer distance in LDHs depends on kind of anion of interlayer space [5]. The value of the distance between layers of rehydrated LDHs was calculated from the first basal reflection d_{003}. The interlayer distance of cHT1h-rehTC and cHT2h-rehTC was similar to that of cHT1h-rehH$_2$O and cHT2h-rehH$_2$O, that is, 2.80 Å. Zn-Al HT surface has a positive charge due to the isomorphic substitution of Zn^{2+} ions by Al^{3+} ions. The positive charge-balancing anions are located in the interlayer space of LDHs. Therefore, negatively charged form of TC can be integrated into interlayer space as charge compensating anions.

TC is an amphoteric molecule having multiple ionizable functional groups (fig. 2). Two conformations were generally accepted for TC [18].

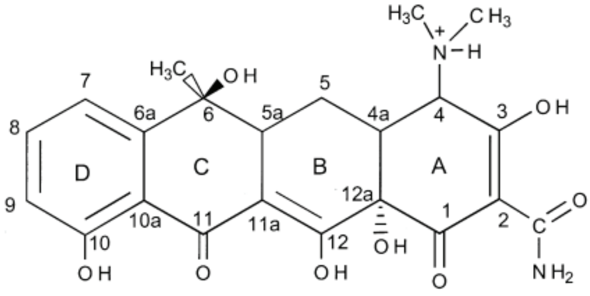


Fig. 2. Chemical structure of tetracycline

In basic solution TC has extended conformation when the dimethylamino group lies below the plane spanned by the ring system and in acidic to neutral solutions TC has twisted conformation when the dimethylamino group lies above the ring system TC. In the twisted form TC was 12.9 Å long, 7.5 Å wide, and 6.2 Å high [19]. Therefore, the interlayer distance of Zn-Al LDHs of hydrated samples is smaller than the sizes of the TC molecule and no intercalation of TC into Zn-Al LDHs occurs. There is no other peak in XRD patterns evidenced the expansion of interlayer space.

Thermoanalytical measurements were recorded to investigate the phase transformations during the calcination of ZnAl LDHs and its hydrated derivatives. The TG curves are characterized by a continuous weight loss without well-defined plateau between the decomposition steps. In order to study the contribution of water and CO_2, weight losses were divided in three intervals: 60–190, 190–300 and 300–500 °C (Table 1). In the literature, three events have been assigned to these ranges: in the first one, the weight loss is attributed to the removal of water loss from internal gallery surfaces and the external non-gallery surface; in the second interval, the loss is ascribed to the dehydroxylation of the brucite-like sheets and removal of interlayer anions, in this case, carbonate; in the last one the weight loss is recognized as the total dehydroxylation, and collapse of the structure due to the removal of the remaining interlayer anions [5]. The small weight loss observed in interval 500 – 700 °C can be ascribed to the loss of some carbonate anions strongly adsorbed on the mixed oxides crystallites.

The highest weight loss was observed at 190-300 °C for all samples due to intensive processes of dehydroxylation and decarboxylation. The endothermic peak at 250 °C was observed at DTG patterns of HT and its rehydrated derivatives that corresponded to the collapse of the double layer structure of HT. Accordingly, the XRD pattern of Zn-Al hydrotalcite calcined at 250 °C refers to the defect zink oxide phase (fig. 1, a).

At 700 °C, a total weight loss for HT was the highest in comparison with hydrated samples (table 1).

The smaller total weight loss of hydrated samples is determined by the fact that the layered structure was not fully restored by hydration of cHT1h and cHT2h. So, the hydrated sample contained fewer hydroxides and carbonate ions in comparison with as prepared HT. As shown by XRD analysis, the traces of ZnO remain in the pattern of cHT1h-rehH_2O (fig. 1*b*).

Table 1

The thermal decomposition stages of Zn-Al LDHs

Samples	Temperature intervals, °C				Total weight loss, %
	60-190	190 – 300	300 – 500	500 – 700	
HT	4.8	20.4	4.5	1.7	31.4
cHT1h-rehH_2O	3.9	17.6	4.0	1.3	26.8
cHT2h-rehH_2O	3.9	11.9	2.6	0.9	19.3
HT-TC	5.4	22.7	7.7	1.1	36.9
cHT1h-rehTC	5.9	10.6	5.8	0.6	22.9
cHT2h-rehTC	6.2	8.1	6.2	0.6	21.1

The thermal behavior of the samples with adsorbed TC is shown at Fig.4. The total weight loss of HT-TC is higher in comparison with HT (Table 1). The additional endothermic peak is observed in the range between 300 and 500 °C which corresponds to the thermal decomposition of TC. According to the literature [20] tetracycline hydrochloride undergoes decomposition in three steps in the temperature ranges 233-260, 260-286 and 386- 570 °C. The weight loss at the first step points to the elimination of H_2O and HCl. The anhydrotetracycline is formed in the second step after losing the radical •$N(CH_3)_2$ The third step corresponds to the total decomposition of TC molecule.

The total weight loss for cHT1h-rehTC and cHT2h-rehTC differs insignificantly (Table 1). The samples that were hydrated in suspensions of TC solutions have shown the lower weight loss in the range between 190 and 300 °C in comparison with the samples hydrated in aqueous suspensions at the same conditions. As was shown by XRD the restoration of the layered structure under hydration of mixed oxides in TC solution was not as intense as in aqueous suspensions without previous decarbonation in spite of TC solutions containing carbon dioxide. So, we can conclude that TC adsorption on the surface of mixed oxides prevents the formation of hydrotalcite structure. That is why for the samples cHT1h-rehTC and cHT2h-rehTC the decarboxylation processes at 190-300 °C are less intensive than for cHT1h-rehH_2O and cHT2h-rehH_2O. The most intensive weight lost between 300 and 500 °C for the samples with adsorbed TC is explained by decomposition of TC molecules.

The nitrogen adsorption/desorption isotherms of as-prepared LDHs and its calcined forms show an uptake at intermediate relative pressures, typical for mesoporous materials (Fig. 3). The shape of the hysteresis loops can be explained by the presence of slit-shaped pores or plate-like particles. Upon calcination of HT for 1 h at 600°C, the porosity of obtained samples is increased, probably due to the increase in surface area from 31 to 61 m^2/g. Such a behavior has been reported for hydrotalcites and assigned to the formation of craters through the layers due to the evolution of carbon dioxide and water [21]. The prolongation of calcination to 2 h causes to further increasing of BET surface area to 94 m^2/g. As is seen, cHT2h has the highest pore volume (0.92 cm^3/g) compared to cHT1h and as-prepared HT (0.19 and 0.26 cm^3/g correspondingly).

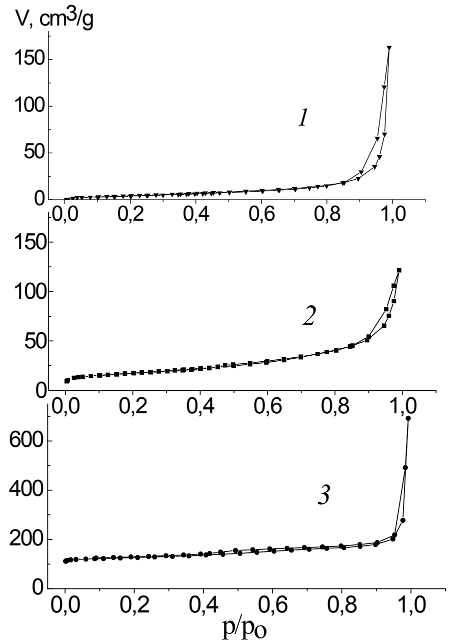


Fig. 3. The N_2 adsorption/desorption isotherms of: HT – 1, cHT1h – 2, cHT2h – 3.

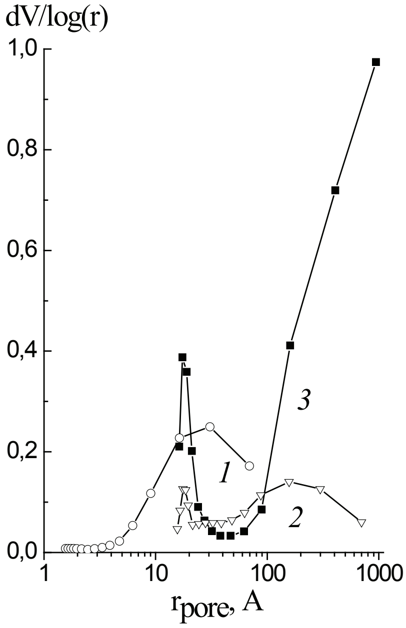


Fig. 4. BJH pore radius distributions of: HT – 1, cHT1h – 2, cHT2h – 3

Pore size distributions were obtained by the Barrett-Joyner-Halenda (BJH) method. HT presented a one-mode distribution with the most frequent pore radius in the 40 to 700 Å range (fig. 4; curve 1). In contrast, two-mode distributions were observed for calcined LDHs (fig. 4; curves 2,*3*). cHT1h presented narrow pore distribution with maximum at 18 Å and broad pore size distribution with pore radius in the 50 to 700 Å range. cHT2h contained the increased quantity of pores of two modes distribution.

The adsorption of TC from aqueous solutions on Zn-Al LDHs and its derivatives was studied using a batch adsorption approach. The isotherms of TC adsorption are presented at fig. 5.

The adsorption capacity of Zn-Al LDHs was lower in comparison with it calcined forms. We explain this by the restriction of access of adsorbate to sorption centers of LDHs matrix. As was written above, Zn-Al LDHs are presented as brucite-type octahedral layers, in which Al^{3+} cations substitute partially for Zn^{2+} cations. The positive charge resulting from this substitution is balanced by carbonate ions and water molecules arranged in interlayers. In addition, LDHs adsorb CO_2 from the air due to its high basic properties [8]. All these facts confirm our assumption about carbonate ions blocking of TC molecules access to Al^{3+} ions of the LDHs surface.

The adsorption capacity of cHT1h and cHT2h was 97 and 95 m^2/g, correspondingly.

The strong metal-binding tendency of TC to Al^{3+} ions plays an important role in contributing to their strong interactions with mineral surfaces [22, 23]. We suggest the preference of Al species as sorption centers TC molecules. The formation of soluble TC complexes with Al^{3+} ions derived from the LDHs matrix after contact of Zn-Al mixed oxides with TC solution was observed in the study [23]. There was shown the similarity of absorption spectra of TC solutions and the absorption spectra of TC-Al^{3+} complexes with TC:Al^{3+} ratio 1:1. The same picture we observed for our systems.

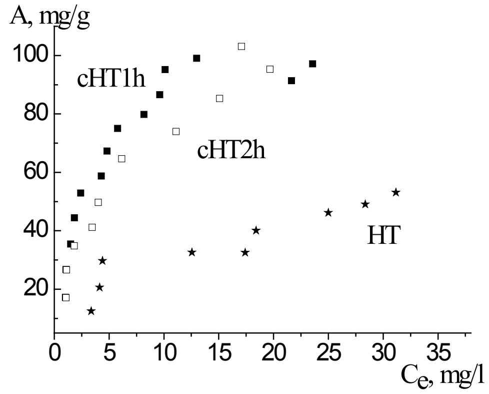


Fig. 5. Adsorption isotherms of Tetracycline on HT, cHT1h and cHT2h.

FT-IR was used to determine a possible coordination of tetracycline on the surface of the evaluated solids (fig. 6). The FT-IR spectra of as-prepared HT, cHT2h-rehH_2O and cHT2h-rehTC show a wide band placed between 3600 and 3200 cm^{-1}, that is attributed to OH^- stretching vibration of the surface and from interlayer water molecules [1].

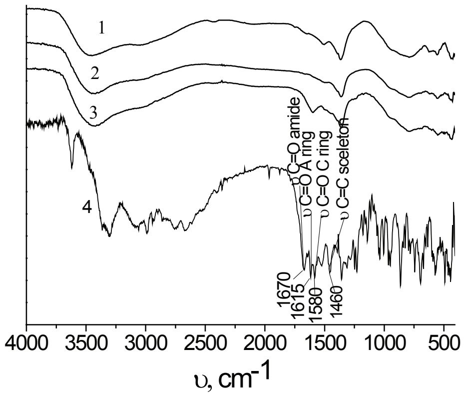


Fig. 6. FT-IR spectra of HT – 1*;* cHT2h-rehH_2O – 2; cHT2h-rehTC– 3, crystalline tetracycline – 4.

The broad shoulder close to 3000 cm^{-1} (fig. 6, *1-3*) has been attributed to hydrogen bonding between water and carbonate anions in the interlayer galleries of three samples [1]. The narrow band at 1360 cm^{-1} corresponds to the v_3 stretching mode of the interlayer carbonate anions in a symmetric environment was observed for all samples (fig. 6, *1- 3*).

These results indicate that the carbonate ions in the interlayers of reconstructed LDHs were not replaced by TC molecules. The bands in the low-frequency region correspond to the lattice vibration modes such as the translation vibrations of Zn-OH (612 cm^{-1}), Al-OH (785, 558 cm^{-1}) and deformation vibrations of HO-Zn-Al-OH (436 см$^{-1}$) and Al-OH (around 937 см$^{-1}$) [24].

The difference between as-prepared HT and TC-adsorbed LDHs was a minute. The major difference was the appearance of the vibration band at 1600 cm^{-1} due to the interaction of TC with Zn-Al LDHs. The most characteristic region of the TC IR spectrum has been observed in the range of 1700-1500 cm^{-1} [25]. The tricarbonylamide system of the A ring is responsible for this region [25]. The bands at 1670, 1615 and 1580 cm^{-1} can be assigned to amide I, the C = O stretching at ring A, and the C = O stretching at ring C, respectively. The vibration bands at 1600 cm^{-1} evidenced of the involvement of the A-ring ligand of TC in surface complexation with Zn-Al LDHs. The large shift to lower frequency of the amide vibrations C = O at 1665 cm^{-1} evidenced of the participation of the A-ring ligand of TC in complexation with hydroxyapatite [25]. A shift of ketone carbonyl vibrations to lower frequency when organic compounds are adsorbed by clay was observed in cases where the carbonyl group was directly coordinated with the interlayer cations or when the carbonyl group hydrogen bonded with hydroxyl groups of the water coordinated to the interlayer cation [26]. We suggest that Al^{3+} ions of LDHs coordinate with carbonyl or/and tricarbonylamide groups of adsorbed TC. Gu and Karthikeyan [22] indicated that TC complexation with hydrous Al oxide and hydrous Fe oxide could be occurring at the tricarbonylamide and carbonyl functional groups.

From the results of this study the following conclusions can be drawn:

1. Calcined ZnAl LDHs with defect structure of ZnO are able to restore hydrotalcite structure under hydration in aqueous suspensions. Calcined ZnAl LDHs with well crystalline ZnO structure partially restore the lamellar structure in aqueous suspension due to the presence of carbon dioxide.
2. In aqueous suspensions of TC and calcined LDHs the lamellar structure was partially restored, and a significant amount of Zn/Al oxides solid remained. There was no intercalation of TC into the interlayer space of restored LDHs.
3. Calcined ZnAl LDHs posses the higher adsorption capacity to TC in comparison with as prepared LDHs. The influence of zink oxide crystallinity in calcined ZnAl LDHs on adsorption capacity to TC is not significant. The adsorption of TC on calcined and uncalcined ZnAl LDHs occurs on the centers of one particular type. It is suggested that surface complexation of the A-ring ligand of TC with Al-OH centers takes place.
4. TC adsorption on active centers prevents carbon dioxide molecules access to the interlayer space that reduces the degree of layered structure renconstruction in calcined ZnAl LDHs with defect zink oxide structure.

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Г. М. Старух[1], О. І. Оранська[1], С. І. Левицька[2]
[1] Інститут хімії поверхні ім. О. О. Чуйка НАН України, вул. Генерала Наумова, 17, Київ, 03164 Україна
[2] Інститут сорбції та проблем ендоекології НАН України, вул. Генерала Наумова, 13, Київ, 03164 Україна

РЕКОНСТРУКЦІЯ ПРОКАЛЕНИХ Zn –Al ШАРУВАТИХ ПОДВІЙНИХ ГІДРОКСИДІВ ПІД ЧАС АДСОРБЦІЇ ТЕТРАЦИКЛІНУ

Zn-Al змішані оксиди, які містили ZnO різного ступеня кристалічності, були отримані при прокалюванні Zn-Al шаруватих подвійних гідроксидів (ШПГ). Реконструкція прокалених Zn-Al ШПГ проводилась при перемішуванні їх водних суспензій. Було показано, що здатність Zn-Al ШПГ відновлювати шарувату структуру шляхом гідратації змішаних оксидів, залежить від ступеня кристалічності ZnO. Часткова реконструкція Zn-Al шаруватої структури відбувається в розчинах тетрацикліну незалежно від ступеня кристалічності ZnO в прокалених ШПГ. Прокалені ШПГ проявляють високу адсорбційну здатність до тетрацикліну.

Ключові слова: Zn-Al шаруваті подвійні гідроксиди, реконструкція шаруватої структури, тетрациклін, адсорбція.

Г. Н. Старух[1], Е. И. Оранская[1], С. И. Левицкая[2]
[1] Институт химии поверхности им. А. А. Чуйко НАН Украины,
ул. Генерала Наумова, 17, Киев, 03164 Украина
[2] Институт сорбции и проблем эндоэкологии НАН Украины,
ул. Генерала Наумова, 13, Киев, 03164 Украина

РЕКОНСТРУКЦИЯ ПРОКАЛЕННЫХ Zn–Al СЛОИСТЫХ ДВОЙНЫХ ГИДРОКСИДОВ ВО ВРЕМЯ АДСОРБЦИИ ТЕТРАЦИКЛИНА

Zn-Al смешанные оксиды, содержащие ZnO разной степени кристалличности, были получены при прокаливании Zn-Al слоистых двойных гидроксидов (СДГ). Реконструкция смешанных оксидов проводилась при перемешивании их водных суспензий. Было показано, что способность Zn-Al СДГ восстанавливать слоистую структуру путем гидратации смешанных оксидов, зависит от степени кристалличности ZnO в прокаленных СДГ. Частичная реконструкция Zn-Al слоистой структуры происходит в растворах тетрациклина независимо от степени кристалличности ZnO в прокаленных СДГ. Прокаленные Zn-Al СДГ проявляют высокую адсорбционную способность к тетрациклину.

Ключевые слова: Zn-Al слоистые двойные гидроксиды, реконструкция слоистой структуры, тетрациклин, адсорбция.

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