

Modification of Zn–Al Hydrotalcite as Potential Photocatalyst

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Zn–Al hydrotalcite with Zn/Al = 3 was prepared by coprecipitation. Its crystal, porous and electronic structure has been modified using hydrothermal and mechanochemical treatments. The samples with physicochemical parameters, which varied in wide limits, have been obtained. As a result, compositions, which are zinc oxide dispersed in interlayer space of hydrotalcite, absorb visible light and becomes photocatalytic activity under visible irradiation.

topics: hydrotalcite, structure modification, photocatalysis

1. Introduction

Layered double hydroxides (LDHs), particularly Zn–Al hydrotalcites (HT), are versatile lamellar materials made up of positively charged brucite-like layers $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}$ with M^{3+} substitution for M^{2+} , and an interlayer region containing charge compensating anions (for example, carbonate) and solvation molecules [1]. These molecules cause LDH to be used, among others, for the solution of environmental problems. The high adsorption ability of LDHs with respect to dyes has been reported in the literature [2, 3]. Examples of their use as photocatalysts are also known [3–5]. There are two variants of the use of LDHs in photocatalytic processes: as pristine LDHs or as mixed oxide compositions after calcination of LDHs. It should be noted that the first variant is rarely studied. In fact, as a rule, the photocatalytic properties of LDHs are investigated under UV irradiation. This is due to the fact that the pristine precipitated LDHs have a sufficiently broad band gap, namely higher than 3.25 eV [6], and this makes the use of visible radiation ineffective. Also, materials must have an optimal porous and crystalline structure in order to be effective photocatalysts. The hydrothermal and mechanochemical treatments (HTT and MChT, respectively) are promising techniques for regulating these physicochemical parameters, which has been repeatedly confirmed by example of oxides and hydroxides [7] as well as LDHs [1, 5]. However, the effect these treatments have directly on the photocatalytic properties of LDHs remains poorly understood. Therefore, the aim of this work

is to study the influence of HTT and MChT on the physical–chemical properties of the precipitated Zn/Al LDH and, consequently, its photocatalytic activity under visible light.

2. Experiment

Carbonate form of Zn–Al LDH with Zn/Al ratio 3 and composition $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ was prepared using the coprecipitation method as follows [1]. This Zn/Al ratio was chosen because the hydrotalcite of this composition has a minimum value of the band gap [3]. In this study, HTT and MChT are used not as direct syntheses, but as post-synthetic modifications of the ready-made hydrotalcite. HTT was carried out in the form of wet gel and dried xerogel (Table I) using steel autoclaves with the volume of 45 ml at 150–250°C and the autogeneous pressure for 3 h. MChT in air and water was performed under the rotation speed of 300 rpm for 0.5 h using a planetary ball mill Pulverisette-7, premium line (Fritsch GmbH) with a vessel of silicon nitride. As working bodies, 25 balls from Si_3N_4 with a 10 mm diameter were used (total ball mass — 40 g).

The obtained samples were studied by means of X-ray powder diffraction (XRD) using Philips PW 1830 diffractometer with $\text{Cu } K_\alpha$ radiation. The porous structure of initial and modified samples was studied using the adsorption–structural methods. Nitrogen isotherms of adsorption–desorption were obtained using an automatic gas adsorption analyzer ASAP 2405N (“Micromeritics Instrument Corp”) after outgassing the samples at 150°C

TABLE I

Some physicochemical and photocatalytic characteristics of initial and modified samples.

| Designation | S [m ² /g] | V [cm ³ /g] | d [nm] | E_g [eV] | K_d ($\times 10^5$) [s ⁻¹] / C [%] |
|---------------------------|----------------------------|-----------------------------|-------------|---------------|---|
| initial | 33 | 0.07 | 3.8 | 3.21 | 0.11 / 6 |
| HTT-gel-150 | 50 | 0.70 | 3.3 | 3.04 | 2.61 / 59 |
| HTT-gel-200 | 67 | 0.76 | 30.0 | 2.94 | 3.35 / 71 |
| HTT-gel-250 | 11 | 0.25 | 31.5 | 2.84 | 2.46 / 56 |
| HTT-xero-200 | 40 | 0.25 | 3.8 | 3.13 | 1.83 / 50 |
| MChT-air-300 | 12 | 0.03 | 3.7 | 3.08 | 1.78 / 47 |
| MChT-H ₂ O-300 | 106 | 0.26 | 3.8 | 3.23 | 1.93 / 53 |

for 2 h. The specific surface area S , volume of mesopores V_{me} and mesopore diameter d_{mei} were calculated from these isotherms.

Diffuse reflectance ultraviolet-visible (UV-Vis) spectra of the powders were registered on Lambda 35 UV-Vis spectrometer (Perkin-Elmer Instruments). The transformation of the spectra into the coordinates of the Kubelka-Munk equation was carried out using the software supplied with the spectrometer. The absorption edge λ was determined by a standard graphical method from these spectra. The band gap E_g [eV] was calculated from the Plank equation, i.e.,

$$E_g = \frac{1239.8}{\lambda}. \quad (1)$$

The testing of the photocatalytic activity in the visible region was carried out using degradation of safranin T (ST) in an aqueous medium (10^{-5} mol./l solution, Philips LED Cool daylight, 100 W) as recommended in [8]. Spectrophotometer UV-2450 — Shimadzu was used for the analysis of changes in dyes concentration during photocatalytic degradation (at 520 nm). An optimal dose of catalysts of 1 g/L was used, as it was established in [8]. The calculation of photodegradation rate constants K_d was based on the concentration changes in the dye solution after the establishment of adsorption/desorption equilibrium and is carried out using the kinetic equation of the first order. Kinetic curves as dependence D/D_0 (D_0 and D — optical density of initial dye solution and that after the determined time of irradiation, respectively) from time of irradiation were plotted. The degree of ST degradation (C) was estimated by bleaching the solution, namely by reducing the intensity of the band at 520 nm relative to its intensity for the initial solution (in [%]).

3. Results and discussion

According to XRD data (Fig. 1), the as-precipitated sample has a hydroxide low-crystalline structure with the basal spacing of 0.865 nm (plane 003), while in the literature [1] the spacing equalled 0.895 nm has been found. The diffraction pattern of the initial dried sample relates to the characteristic peaks of double layered hydroxides, namely at $2\theta = 11.84, 23.61, 34.10$, and

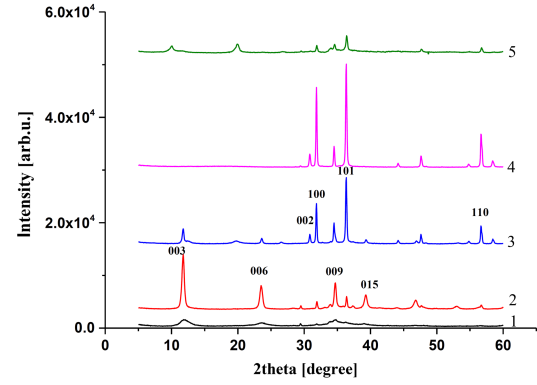


Fig. 1. XRD patterns for initial (1) and modified samples after HTT at 150°C gel (2), 200°C gel (3), 250°C gel (4), 200°C xerogel (5).

39.05° (curve 2). The respective diffraction lines correspond to the planes reflections (003), (006), (009), and (015) for Zn-Al hydroxide (JCPDS 48-1023), which is also confirmed by differential thermal and thermogravimetric analysis (DTA-TG) and FTIR results. Thus, total mass loss over the entire temperature range Δm_{exp} is 29.9%w/w. This value is in good agreement with the calculated value Δm_{calc} (30.7%w/w), which corresponds to the complete decomposition of $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Mechanochemical treatment (MChT) in air partially destroys hydroxide structure without the formation of other phases, while milling in water only modifies it (these diffractograms do not shown). The position of the reflex from (003) plane is shifted from $2\theta = 10.23^\circ$ to $2\theta = 11.27^\circ$ after MChT in air (Fig. 1), which corresponds to a decrease in basal spacing to 0.786 nm.

Elevation in HTT temperature, on the contrary, leads to the decomposition of hydroxide. If its structure is improved at the temperature of 150°C, then hydroxide is partially destroyed at 200°C (Fig. 1). It should be noted that XRD patterns after HTT also contain diffraction lines at $2\theta = 31.88, 34.78, 36.31^\circ$ (curve 3), which are related to planes (002), (100), (101) and can be tentatively ascribed to the presence of a crystalline ZnO phase (JCPDS, 5-0664) dispersed over the brucite-like layers. The formation of ZnO phase in Zn-Al hydroxides has earlier been discussed in [5].

The indicated changes in the crystal structure are accompanied by the development of porous structure, obviously, due to the formation of additional mesoporosity. The specific surface area increases by 3 times, reaching 106 m²/g, and the pore volume grows almost 4 times to 0.27 cm³/g (Table I). Samples hydrothermally modified in the form of wet gel have a high value of mesopores of about 0.70–0.75 cm³/g and a specific surface area of 50–67 m²/g (Table I). The isotherms of nitrogen adsorption-desorption are characterized by these transformations (Fig. 2a, b).

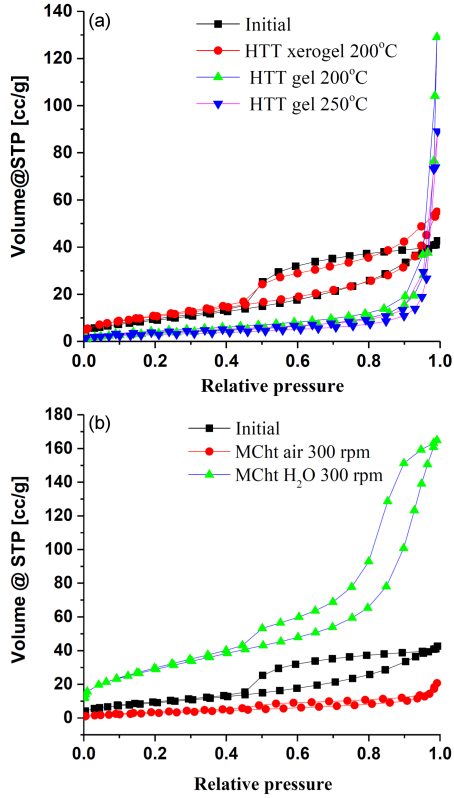


Fig. 2. The nitrogen adsorption-desorption for modified samples after MChT (a) and HTT (b).

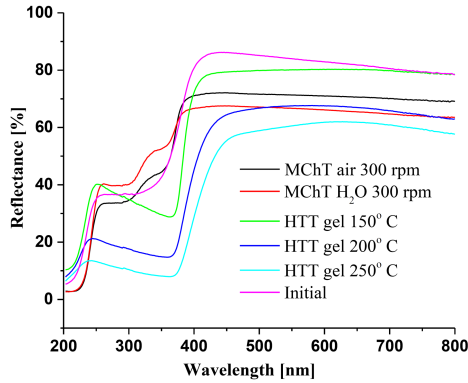


Fig. 3. UV-Vis spectra for initial and modified samples.

The changes in phase composition and crystal structure, which are observed due to MChT and HTT, are accompanied by changing the electronic characteristics determined from UV-Vis spectra (Fig. 3). All modified samples are characterized by the stronger absorption in the visible region compared to the initial sample. Besides, the significant hypsochromic shift of absorption edge occurs for samples subjected to HTT. As a result, a narrowing of the band gap E_g is observed from 3.21 eV for the initial sample to 2.8–2.9 eV for the hydrothermally treated samples (Table I). This effect can be

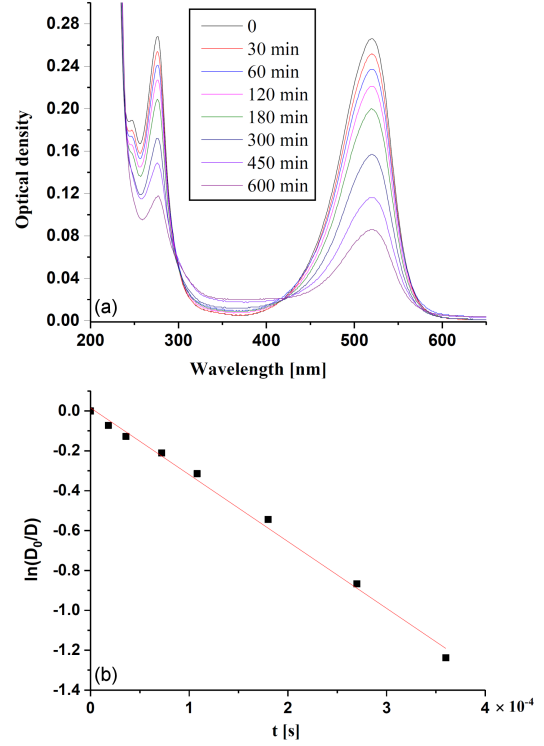


Fig. 4. The spectra of safranin T solution after visible irradiation in the presence of sample HTT-gel-200 as photocatalyst (a) and kinetic curve of safranin T degradation (b).

associated with the formation of the ZnO phase in the hydrotalcite structure during modification and the increase in the crystallite size of ZnO at the elevation of HTT temperature. Similar changes of E_g value were described in other studies [9, 10].

Both mentioned effects (an increase of absorption in the visible region and narrowing the band gap) should enhance the photocatalytic activity of modified samples under visible irradiation. Indeed, the initial sample is practically non-active in the process of photocatalytic degradation of safranin T in an aqueous medium under the given conditions. At the same time, the sample subjected to dry milling at 300 rpm, which has a band gap of 3.08 eV, becomes active. The rate constant of degradation K_d is then $1.78 \times 10^{-5} \text{ s}^{-1}$. The sample, modified by HTT to the form of gel at 200°C, possesses the maximal activity ($K_d = 3.35 \times 10^{-5} \text{ s}^{-1}$) because it simultaneously has $E_g = 2.94 \text{ eV}$ and a high value of specific surface area — 67 m²/g. Examples of temporal changes in optical density of safranin T solution in the presence of sample HTT-gel-250 are presented in Fig. 4a.

As can be seen, the intensity of the band at 520 nm monotonically decreases when the duration of irradiation increases. These changes are well described by the first-order kinetic equation (see Fig. 4b, where D/D_0 — the ratio of the optical density at time t to that for the initial solution).

The results obtained show that changes in physicochemical characteristics (first of all, crystal, porous and electronic structure) occurring at the stage of modification of hydrotalcite decisively affect its photocatalytic performance. The formation of highly dispersed zinc oxide in the hydrotalcite matrix promotes the shift of the absorption edge to the visible region, as a result of which the obtained composition acquires photocatalytic activity under visible light. In addition, an increase in the specific surface area leads to an increase in the adsorption of the dye and, as a consequence, to an increase in the activity of the modified samples.

4. Conclusions

Mechanochemical and hydrothermal treatments allow varying the physicochemical characteristics of Zn–Al hydrotalcite. In particular, the samples, which are oxide-hydroxide compositions, are prepared by HTT of gel at a low temperature. These compositions, i.e, zinc oxide dispersed in interlayer space of hydrotalcite, absorb visible light and possess photocatalytic activity under visible irradiation. Thus, the degree of safranin T degradation reaches 71% for 10 h of illumination. This circumstance opens up the possibility of their practical application for the removal of pollutants from aqueous media.

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