Structure of nanostructured layered double hydroxides according to x-ray diffraction analysis data

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Abstract. Nowadays, in many areas of industry, in particular, the petrochemical industry, the problem of multifunctional, efficient and environmentally friendly materials use is of great importance. One such material is double layered hydroxides (LDHs) used in various synthesis reactions, catalytic and adsorption processes. This paper presents studies on the effect of the elemental composition of LDH on their structure. Under experimental conditions, 4 samples of LDHs based on Mg and Al, Mg and Fe, Zn and Al (2 samples with different cation ratios) were synthesized by co-precipitation of a base solution with a mixture of M(II) and M(III) salts solution. The phase composition of the obtained LDHs were analyzed by powder x-ray diffraction method. During the experiment, the characteristics of the Zn-Al LDH samples turned out to be lower than MgFe and MgAl LDHs due to the presence of a phase of zinc oxides in their composition, as well as the structure of the obtained products. Similarly, the size of ZnAl crystallites of LDH at a trivalent cations share of 0.33 compared to 0.4 was larger by about 3.5 times.

1. Introduction

Year by year, requirements to quality, environmental friendliness and payback of the received products in the oil refining and petrochemical industries increase. In this regard, the world's scientific groups are developing new materials that can improve these indicators. Recently, researchers have been particularly interested in double layered hydroxides due to the simplicity of their preparation and the wide possibilities of their application: as catalysts, carriers, precursors of catalyst carriers, adsorbents, etc. Layered double hydroxides, also called hydrotalcite-alike compounds or anionic clays, represent layered materials. Natural double layered hydroxides apart from hydrotalcite group are quintinite, fulgurite, woodwardite, glucocerinite, wermlandite, calcibite and a separate group of minerals (kaolinite, brugnatellite, muskoxide) [1]. However, due to certain restrictions on the composition of the material in catalysis processes, hydrotalcite-alike synthetic compounds are mainly used. Depending on the composition, these materials are capable of catalytic activity in such reactions as partial oxidation and steam reforming of methane for hydrogen production, one-stage liquid-phase heterogeneous synthesis, co-oxidation and dry reforming of methane to synthesis gas, alkylation, isomerization-aromatization of olefins, selective oxidation of phenol to catechin and hydroquinone, benzene to phenol, hydroxylation of benzene, liquid-phase oxidation of aromatic hydrocarbons, etc. [2-8]. Hydrotalcite-alike compounds can be produced artificially by deposition methods [9, 10]. In subsequent anion-exchange processes, by
choosing a certain anion $A_n^-$, which occupies the interlayer space, it will be targeted to improve the catalytic activity and selectivity of the obtained materials due to the change of the basal distance in the structure of LDHs [9, 11].

In the world there is an increasing interest in developing reserves of alternative types of hydrocarbon resources, gas hydrates, shale oil and gas, heavy oils and natural bitumen. The world reserves of heavy oil and natural bitumen, according to the UN, are 260 billion tons [8-16]. Their development is impossible without the creation of innovative technologies of production and refining, capable of converting non-traditional type of hydrocarbon resources into demanded petrochemical feedstock. In recent years, scientists have been particularly interested in the use and synthesis of nanostructured catalysts in the conversion of heavy oil and natural bitumen [17-25].

The paper discusses the identification of LDH structural features depending on the elemental composition.

2. Methotology

Layered double hydroxides based on Mg and Al, Mg and Fe, Zn and Al were obtained by coprecipitation of the base solution with a solution of a $M^{II}$ and $M^{III}$ salts mixture on an installation consisting of a peristaltic pump, agitator and thermostatically controlled water bath for the solution coprecipitation container. The solutions were poured together to distilled water heated to 70 °C. The experiment time was 6 hours in water and pH=10-11. The resulting mother liquor was settled and separated by centrifugation method followed by washing with water. The analysis of the phase composition of the obtained LDHs was carried out by powder x-ray diffraction on an instrument by Bruker Axs with a Bragg-Brentano shooting geometry in the range of angles $2\theta$ from 5º-65º. Screening step was 0.02º, exposure time was 0.5 second per step. The phase composition of the samples was carried out using the DIFFRAC.EVA software module and diffraction data database PDF-2 Release 2013. Calculation of the specific surface was performed by thermal desorption of nitrogen on the installation 2200e by Quantachrom company (USA).

3. Results and discussions

The x-ray diffractogram of the obtained AlMg LDH (Figure 1) shows that the LDH phase is present alone, without any independent Mg or Al phases. The crystallite size is 25.5 nm, the specific surface area is 100 m$^2$/g.

Figure 1. X-ray diffractogram of MgAl LDH.
Figure 2. X-ray diffractogram of MgFe LDH.

Figure 3. X-ray diffractogram of ZnAl \([M^{III}/(M^{II}+M^{III})=0.33]\) LDH.

Figure 4. X-ray diffractogram of ZnAl \([M^{II}/(M^{II}+M^{III})=0.4]\) LDH.
Figure 2 shows the MgFe LDH x-ray diffractogram. According to the PDF-2 diffraction database, the diffraction maxima correspond to MgFe LDH. There are no independent phases of iron or magnesium in the sample. The crystallite size is 25.5 nm. The specific surface area of MgFe layered double hydroxide is 156 m²/g.

On the ZnAl LDH x-ray diffractograms (Figures 3 and 4) in addition to the highly crystalline phase of LDH, there is a phase of zincite (ZnO). The crystallite size is 85 nm. The specific surface area is 40 m²/g. The crystallite size of AlMg LDH is 25.5 nm, its specific surface area is 100 m²/g. The crystallite size of Mg-Fe LDH is 25.5 nm, specific surface area is 156 m²/g. ZnAl LDH (0.33) – crystallite size is 85 nm, specific surface area is 40 m²/g, ZnAl LDH (0.4) – crystallite size is 9 nm, specific surface area is 5 m²/g.

4. Conclusions

Based on experiments the optimal conditions of LDH synthesis, consumption of initial reagents, thermobaric conditions of co-deposition for controlled particle growth were selected. During the experiment, MgFe and MgAl LDHs showed a larger specific surface area than ZnAl LDH did. However, the crystallite size of ZnAl layered double hydroxides with the ratio of the cations of 0.33 was found to be approximately 3.5 times larger. In the case of ZnAl LDH at M[III]/(M[II]+M[III])=0.4, the small size of the crystallites and the specific surface area can be explained by the similarity of this structure with the three-dimensional one.

In the course of the work, Mg-Fe and Mg-Al layered double hydroxides with a larger specific surface area than Zn-Al LDH were obtained. However, the crystallite size of Zn-Al layered double hydroxides with a cation ratio of 0.33 turned out to be about 3.5 times higher than layered double hydroxides based on Mg and Al, Mg and Fe. In the case of Zn-Al LDH (0.4), the small crystallite size and specific surface area can be explained by the similarity of this structure with the three-dimensional structure. Thus, it is possible to obtain layered double hydroxides predetermined composition and structure.

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