LAYERED DOUBLE HYDROXIDES AS THE UNIQUE OBJECT FOR WIDE APPLICATION IN THE CHEMICAL TECHNOLOGIES

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In the modern chemical technologies, medicine and analysis the most perspective substances are universal, easy changing for different requirements. These substances must be single “bricks” for construction of materials, similar “LEGO” constructor. One of the most famous substances of this type are MXene [1]. Layered Double Hydroxides (LDHs) are less known, but also have unique properties and could be for synthesis of different substances for wide range of applications.

What are LHD? For answer to this question metal hydroxide must be analyzed.

Well known, that divalent metal hydroxide usually exist in the two forms:

a) β-form with formula $Me(OH)_2$. This form has hexagonal crystal structure with under-layer distance 4.6 Å, named single layer lattice. This form has high stability, but lower chemical and electrochemical activity;

a) α-form with formula $3Me(OH)_2*3H_2O$. This form also has hexagonal crystal structure, but under-layer distance is 7.6 Å. This lattice is named double layer, because it consists of regular layer (included Me, O, H) and irregular layer with crystalline water. This form has higher chemical and electrochemical activity, but lower stability.

Formally, LDH can be obtained by change in the metal hydroxide lattice (Me-host hydroxide) some Me-host cation to Me-guest cation, for example Zn^{2+} to Al^{3+}. As a result, extra charge (+3) - (+2) = +1 is obtained in the lattice. But This extra charge can be compensated by intercalation of different anions into the under-layer distance. Therefore general formula of LDH is $Me1^{n+}{}_xMe2^{m+}{}_{1-x,}(OH)_2A^{k-}{}_{(m-n)/k}*0,66H_2O$, where are:

a) Me1 (metal-host) are Me^{2+} (Zn, Ca, Mg, Ni, Co etc)

b) Me2 (metal guest) are Me^{3+} (Al, Co, Fe etc) or Me^{4+} (Ti, V, Zr etc)

c) A – intercalated anion:

1) Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-} etc. – usually counter anion from metal salts;

2) inorganic anions WO_4^{2-}, MoO_4^{2-}, CrO_4^{2-}, $[Fe(CN)_6]^{3-}$ etc. – functional anions;

3) organic anions (drugs, dyes, vitamins etc.) – functional anions.

Therefor it was concluded that LDHs are not mixture of hydroxides, LDHs are mono-phase system with crystal lattice of Me-host hydroxide. Really, LDHs are molecular (more correct – ionic) constructor, which consists of 3 changed parts – Me-host cation, ME-guest cation and intercalated anions. Also, LDH has ion-exchange properties. Using the different combination of these three components in the LDH, wide range of different functional substances can be synthesized.

Field of application of LDHs:

1) Chemical Power Sources

a) Accumulators (Secondary cells). Pure nickel hydroxide has theoretical specific capacity 289 mA*h/g, practical specific capacity is 200 mA*h/g, K_{effic}=69-70%. But Ni-Al LDH has practical specific capacity up to 390 mA*h/g, K_{effic} up to 135% (per 1 e) [2, 3].

b) Hybrid supercapacitors. Specific capacity Ni-Al LDH is about 1500-2000 F/g [4].

2) Elecrtochromic device (Smart Window) – devices, which can change transmittance of window under current. Using LDHs can increase the efficiency and color in the colorizing mode [5, 6, 7].

3) Electrocatalytic oxidation of organic and inorganic substances. Application of LDHs with electrochemically active Me-host (Ni, Co) for electrocatalytic oxidation of organic substances based on mediator mechanism of catalytic behavior. Ni-Ti and Ni-Ti-molibdate LDHs ware synthesized special for deep electrocatalytic oxidation of formaldehyde [8, 9].

4) Synthesis of inorganic materials with hydroxide or oxide nature (catalyst etc.). The most effective catalysts for Multi-walled Carbon Nannotubes were synthesized from LDHs precurcors.

5) Obtaining of the pigments. LDHs can be used as the colorizing pigments and special pigments. For colorizing pigments can be formed by using of colored cations of ME-host or Me-guest, or colorizing intercalated anions.

a) Cosmetics pigments. As a nail polish pigments it were synthesized LDHs, intercalated by anion of food dye – Indigocarmin [4], Orange Yellow S [10], Tartrazine [11].

b) Paints pigments. In the paints can be used two type of LDHS-based pigments – colorizing pigments and special pigments, for example anticorrosive Zn-Al-$P_3O_{10}^{5-}$ [12], which give the paints the active protective properties [13].

c) Polymers

6) Pharmaceuticals: «encapsulation» of anionic drags and using own medicinal properties [14].

7) Food additives obtaining. LDHs can be used for obtaining of food additive via intercalation in the LDHs or formation of composite with LDH [15, 16].

8) Sensors

a) Fluorescent sensors. It is possible to synthesize the solid LDHs, intercalated anionic fluorescent-active substances.

b) Ion-Selective Electrode. Based on ion-exchange properties, it is possible to synthesize electrode-active LDHs, intercalated anion, which must detected (for example CrO_4^{2-}, Diclofenak-anion, Ascorbic-anion etc.)

9) Water purification from anionic pollutants. LDHs can be used for purification from different anionic pollutants, especially organic surfactants, dyes [17] etc.

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