



HYBRID ORGANIC-INORGANIC STRUCTURES FOR SOLVING OF ECOLOGICAL PROBLEMS

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Abstract

Hybrid organic-inorganic materials belong to a category of fast growing part of materials science. It is the area where ceramics and organics meet at the same chemical dimension to yield new composite materials with opportunities for the development of new functional materials.

The possible applications is using such hybrid structures are new selective gas sensors; selective adsorbent; catalysts; solar cells etc.

The using of hybrid structures for different application can be developed by implementation of electric conductivity of inorganic layers and pore's size and shape control by choice of organic cation. The hybrid structures can be divided for three groups: intercalated iron containing and manganese micas; layered oxides of transition metals NaXO_2 ($X = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$ and Fe); layered double hydroxides or its derivatives layered double oxides.

Here we describe the obtaining of new organic-inorganic hybrid structure based on intercalation of NaMnO_2 by benzylamine and Cu^{2+} extraction experiments.

Keywords:

Hydride structures, Layered structures, Adsorbents, Heavy metals

1 INTRODUCTION

The organic-inorganic hybrid structures are a fast growing group of new materials which presents wide area of functional materials. Creation of new hybrid organic-inorganic materials has become one of the major areas of modern materials science. The basic idea in creating such hybrid materials is to combine advantages of both organic and inorganic components. Properties of these materials can be controlled by using different synthesis routes and by adjusting the preparation parameters. The inorganic component typically improves the mechanical, thermal and structural stability of these substances at the same time as the organic component allows you to vary the functional properties. The interest to these materials stimulated by possible application as materials with interesting magnetic, optical, electrochemical and mechanical properties as well as advanced materials for sensors, catalysts, energy storages, CO_2 capture and molecular sieves, as well as highly selective sorbents high capacity and new generation [1 - 4].

Analysis of crystal structure for known layered materials shows many prospective systems that can be used as an inorganic matrix. These include a number of oxides – KPrO_2 , CuPrO_2 , NaCoO_2 , CuFeO_2 , NaNiO_2 , NaMnO_2 ; sulfides - KCeS_2 , KCeS_2 , NaGdS_2 , CaDyS_2 , RbTbS_2 and selenides - NaVSe_2 etc. However, only very few of them can find an application due to chemical and physical properties as well as production expenses and accessibility.

Manganates are very attractive as starting materials in our research, due to their ion-exchange, molecular adsorption, catalytic, electrochemical, and magnetic properties. Depending on the method of synthesis can be formed a compounds with tunnel or layered structure [5]. One of such examples is NaMnO_2 with a two-dimensional layered structure, comprises of edge shared MnO_6 octahedral layers. Layered manganese oxide materials have porous structures and cation exchange and molecular



adsorptive properties. Therefore, they can be used as ion sieves, molecular sieves, and catalysts, similar to zeolites. Porous layered birnessite-type materials have been used as ion exchange materials for the cleaning of aqueous radioactive wastes from nuclear power plants and research centers [6]. Pillared layered manganese oxides have potential applications as catalysts because of their high surface area, good porosities, and high thermal stabilities.

2 EXPERIMENTAL

This study aimed to obtain hybrid organic-inorganic structures based on layered α - NaMnO_2 . We know several approaches to the synthesis of mineral birnessite (NaMnO_2): - oxidation of $\text{Mn}(\text{OH})_2$ [7 - 9]; reduction of permanganate in aqueous solution by organic reducing agents [10 - 13]; solid state synthesis [1, 14]; hydrothermal synthesis and sol-gel synthesis [5].

Layered sodium birnessite synthesized by solid state reaction of equivalent amount of Na_2CO_3 and manganese oxide Mn_2O_3 at 600°C for 8-24 h [15]. Protonic layered manganates (H-MnO_2) were prepared by treating α - NaMnO_2 with 0.01–1 M HNO_3 solutions at room temperature.

The hybrid organic-inorganic structure was prepared by continuous shaking H-MnO_2 in a 2 M benzylamine solution for 8-24 hours at room temperature. Process was repeated for 3 times. The products were washed with distilled water and then dried.

A powder X-ray diffractometer (DRON-2 - with $\text{CuK}\alpha$ radiation) was used for the structure investigation. Average oxidation state of Mn was calculated by applying the standard iodometry method with experimental error of 2 %.

The ion exchange experiments on hybrid material was carried out using the batch method. Batch adsorption experiments were conducted using 0.5 g of adsorbent and 50 ml of solutions containing Cu^{2+} ions of desired concentrations at constant temperature. The mixture was shaken for 1 hour and solutions containing metal ions were filtered. The concentrations of metal ions were determined by Atomic Adsorption Spectrometer (ContrAA 700). The flame type was air- acetylene and adsorption wavelength 324nm. The amount of adsorbed metal was calculated using the equation: $a = ((C_i - C_k) / m \times 1000) \times V$. The adsorption degree was calculated using the following equation: $\alpha = ((C_i - C_k) / C_i) \times 100\%$, where C_i – initial concentration of Cu^{2+} ions, mg/ml; C_k – final concentration of Cu^{2+} ions, mg/ml; m – amount of adsorbent, g; V – volume of solution, ml.

3 RESULTS AND DISCUSSION

An unlimited number of organic- inorganic materials can be prepared because of the large number of inorganic substrates and organic functional groups. Chemical and physical properties of the material can be modified by rational choice of organic reagent. It makes possible creating materials with controlled properties and a large number of application areas:

1. Selective sorbents. Hybrid materials with layered structure have high efficiency for sorbing metal ions from water solutions. Also this materials has good stability and recyclability under different conditions.
2. Membranes. Organic- Inorganic solids have pores in their structure. The size of these pores can be controlled by exchange of organic reagent. These membranes can be used for development ion-selective electrodes, sensors.
3. Catalysts. Because of their high surface area, porosity, thermal stability hybrid materials are good catalysts. For example layered manganese oxides pillared by different ions have high catalytic activity.



4. Degradation of organic compounds. There are a lot of studies which describes the role of hybrid materials in abiotic degradation of atrazine, phenolic compounds, etc.
5. Battery materials. Organic- Inorganic materials have high surface area, and metal oxide content what makes them useful as battery materials.
6. Optical materials. Hybrid materials can be used as colored glasses, photoprotection, laser etc.
7. CO₂ capture materials. Hybrid materials have high adsorption capacity, selectivity, chemical stability that is why they can be used as efficient CO₂ capture materials.

3.1 Benzylamine intercalated NaMnO₂.

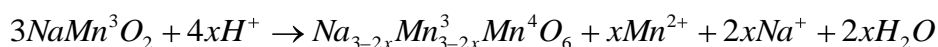
Obtaining organic-inorganic materials based on NaMnO₂ passes through several phases: synthesis and identification of layered NaMnO₂; preparation and study of protonated forms of layered manganates (H-MnO₂); preparation of intercalated hybrid material, which contains inorganic layered part and organic cations between the layers.

Fine black powder was obtained after the inorganic component synthesis. By chemical composition analysis was determined the total content of manganese in the sample - 50.35 + -0.7 %. Theoretical content of manganese was also calculated, it is 49.97 %. Since the theoretical and practical content of Manganese is almost the same, we can claim that the average valence of manganese in the compound was 3 and the gross formula of the product is close to the expected NaMnO₂.

The X-ray diffraction (XRD) method was used for identification of obtained samples. They were identified as single-phase and contain layered NaMnO₂, which crystallizes in monoclinic structure (C2/m), with lattice parameters are $a = 0.563$ nm, $b = 0.286$ nm, $c = 0.577$ nm and $\beta = 112.9$ what is in agreement with literature data [ICSD-16270].

Characteristic for layered compounds is texturing in crystallographic direction c , which is shown in strong intensity of reflections with indices $00l$ (Fig. 1a). In this case, the XRD pattern of synthetic birnessite has a clearly visible increase of the intensity of reflexes $00l$ at approximately 12 degrees. The intensity of the other reflexes are disproportionate small.

The difference between XRD patterns of as synthesized NaMnO₂ and NaMnO₂ washed by water is due to disproportion reactions occurring in aqueous solution [16]:



However, it does not prevent the identification of synthesized product NaMnO₂ [ICSD-16270] and the product of interaction with water as birnessite Na(H₂O)_nMnO₂ [ICSD 97199]. Both have a layered structure, they differs in different fullness of interlayer space. In NaMnO₂ structure, the space between the layers [MnO₆] completely filled with sodium cations, and in birnessite - partially. So this shows that sodium ions can be easily filled by other ions or molecules, which help us in intercalation of organic cations. A necessary phase in creation of hybrid compounds is protonation of the layered material, which is in substitution of metal cations on the protons. It was expected that the replacement of alkali metal cations on the more mobile protons will facilitate the intercalation of organic cations [16].

Protonated forms of H-MnO₂ were prepared by treating NaMnO₂ with HNO₃ solution at room temperature. To find the optimal conditions for protonation, we prepared a series of solutions with different pH from neutral to acidic close to 1, 3, 5, 7. Protonation products were investigated by X-ray diffraction method and found that the crystal structure has not changed. Products contain monoclinic phase, similar to the original NaMnO₂, and lattice parameters slightly changed as it described in [17]. This changes indicates an increase of thickness of the interlayer space in H-MnO₂. If the initial



distance between layers in monoclinic H-MnO_2 was 0.7032 nm, in protonated samples at pH = 3, 5 and 7, it increased to 0.7156 nm, and with a solution of pH = 1, increased to 0.7309 nm.

Comparison of ionic radii of sodium and hydrogen, gives reason to believe that the distance between the layers should be reduced, but the opposite process occurs. This is due to the fact that the interlayer space contains water molecules besides protons. They determine the distance between MnO_6 layers. After protonation a series of experiments were carried out to obtain intercalated samples.

Intercalation by 2M aqueous benzylamine solution was made in two ways: intercalation for 3 days without stirring (Sample 1) and intercalation for 7 days with stirring (Sample 2). XRD patterns of both NaMnO_2 samples are shown on Fig. 1b-c.

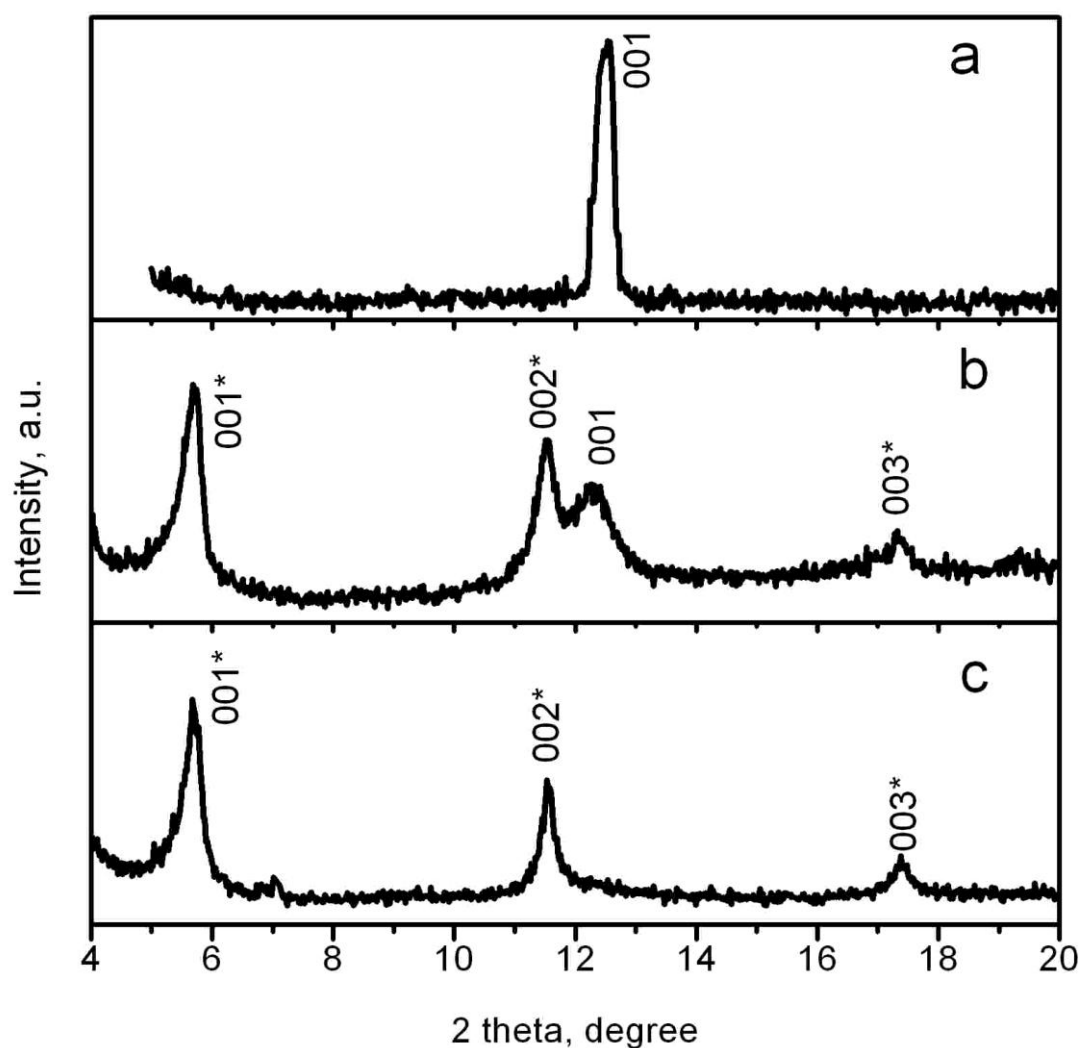


Figure 1: XRD patterns of initial NaMnO_2 (a), partially intercalated NaMnO_2 with benzylamine (b), fully intercalated NaMnO_2 with benzylamine (reflexes marked by star* belongs to product of intercalation)



In the case of short-term cooperation we have received the product partially intercalated by benzylamine. Success of the intercalation confirms appearance of a reflex at $\approx 5.8^\circ$ what corresponds to interlayer distance of 1.542 nm. Comparing the interlayer distance of NaMnO_2 and intercalated sample it can be seen that the crystallographic parameter c increased from 0.72 nm to 1.54 nm, the distance between the layers $[\text{MnO}_6]$ increased by ≈ 0.82 nm. Position of the new reflex indicates entry of benzylamine cations in the interlayer space. But partially preserved original reflexes of precursors, indicate the obtained product contain intercalated and initial phases.

Full intercalation was observed after stirring benzylamine solution and protonated sample within 7 days, as evidenced by the provisions of reflexes at $\approx 5.8^\circ$ and at $\approx 11.5^\circ$ and absence of reflexes characteristic for precursors.

3.2 Adsorption of Cu^{2+} on hybrid material.

The adsorption of Cu^{2+} onto our material as a function of its concentrations was studied at 30°C by varying the metal concentration from 50 to 350 mg/l while keeping all other parameters constant.

The adsorption degree of metal ions was calculated for solutions with different concentration. The average degree of adsorption is 99.96%. With growing of metal ion concentration to 350 mg/l the adsorption degree is decreasing to 99.58%.

4 CONCLUSIONS

Hybrid organic- inorganic structures can be used as selective sorbents, membranes, catalysts, battery materials optical materials etc. Combination of organic and inorganic matter open opportunity to design a new generation of functional materials which can be used for solving of environmental problems.

As example of hybrid material we have described an obtaining of fully intercalated layered benzylamine manganate with layers of $[\text{MnO}_6]$ and organic cations $[\text{C}_6\text{H}_5\text{-CH}_2\text{-NH}_3^+]$ occupying the interlayer space.

Investigation of the copper ions sorption from water have shown that received material can be used for adsorption of heavy metals. Adsorption degree for copper ions from water is over 99%.



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