



THE DEVELOPMENT OF HYBRID ORGANIC-INORGANIC MATERIALS FOR ENVIRONMENTAL TECHNOLOGIES

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Abstract:

The present research dedicated to the development of synthesis methods and properties investigation of new hybrid organic-inorganic materials which are highly prospective materials for environmental technologies. The possible applications of such hybrid structures are very wide: selective gas sensors; selective adsorbent; catalysts; solar cells etc.

The area of our interests are products of intercalation (pillaring) of 2D layered oxides and oxyfluorides of transition metals by large organic molecules (protonated amines).

Pillaring of layered oxides of manganese NaMnO_2 (birrnesite) is well investigated due to relatively easy synthesis and possibility to work in water solutions. However, instability of Mn^{3+} ions in water solutions leads to uncontrolled red-ox-reactions and the interpretation of properties is complicated and controversial.

Much more interesting will be other layered oxide systems NaXO_2 , where $X = \text{Mn, Co, Ni, Cu and Fe}$. The layered structure and possibility of intercalation together with electric conductivity makes them prospective for production of microporous materials with controlled pore size and shape. However, despite the fact that NaCoO_2 is well known material (superconductor), almost no information about attempts of intercalation/pillaring of Co/Fe-layered oxides.

Here we present the first results of successful preparation of hybrid organic-inorganic materials by the pillaring of Co and Fe layered oxides (NaXO_2) by organic cations in non-aqueous solutions.

Keywords: layered oxides, transition metals, hybrid organic-inorganic structures

INTRODUCTION

Development of new functional materials should be based on creating systems with controlled properties. The easiest way to control the properties of materials is to control the content of functional groups in material. The most promising expected to be a new generation materials known as organic-inorganic hybrid structures, which are also known as functional hybrid materials.

Hybrid materials are multifunctional because of combining of the properties of organic and inorganic matter. It provides us an opportunity to create new materials when we combine the properties at the molecular level. Properties of these materials can be controlled by using different synthesis routes and by adjusting the preparation parameters. An unlimited number of organic-inorganic materials can be prepared because of the large number of inorganic substrates and organic functional groups. That is why they can be used in wide areas of technique, science etc.

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].

There are different types of hybrid materials, we focused on inorganic-organic layered materials, especially on intercalation of 2D layered oxides by large organic molecules. It means intercalation of organic cations to inorganic matrix, for example, dyes, polymeric cations, amines, diamines.

Here we present the first results of successful preparation of hybrid organic-inorganic materials through pillaring of Co and Fe layered oxides (NaXO_2) by organic cations in non-aqueous solutions.

MATERIALS AND METHOD

Chemicals used were of reagent grade quality and were obtained from commercial sources without further purification.

This study aimed to obtain hybrid organic-inorganic structures based on layered α - NaFeO_2 , NaCoO_2 . Layered modification of NaFeO_2 was obtained as a result of solid phase reaction between Fe_2O_3 and Na_2O_2 at 600 °C for 48-72 hours [5]. Layered modification of NaCoO_2 was obtained in a similar way.

The second step was the intercalation of benzylamine into the layered NaFeO_2 and NaCoO_2 oxides. It is known, that NaMnO_2 (7), NaFeO_2 and NaCoO_2 oxides with three-valent transition metals react with water. So, we were concentrated on the search of water-free solvent. After examining of several solvents, acetonitrile was selected as a solvent for benzylamine intercalation.

A small amount of sample is intensively stirred with solution of benzylamine in acetonitrile for 8-24 hours. This process was repeated 3 times, each time fresh portion of solvent was added to sample. After this procedure the sample was washed and dried at room temperature. The same method was used to intercalate the benzylamine into NaCoO_2 .

Samples were examined by X-ray diffraction analysis using DRON-2 diffractometer with $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Obtaining organic-inorganic materials based on NaFeO_2 and NaCoO_2 passes through several phases: synthesis and identification of layered NaFeO_2 and NaCoO_2 ; preparation of intercalated hybrid material, which contains inorganic layered part and organic cations between the layers.

The crystal structure of NaXO_2 layered oxides (Fig. 1) consist of two dimensional negatively charged octahedral layers XO_6 divided by the layer alkaline cation. The peculiarities of the structure open possibilities for substitution of alkaline cations with large organic cations. However, the coexistence of inorganic and organic components is object of investigation as well as the coexistence of inorganic component with solvents.

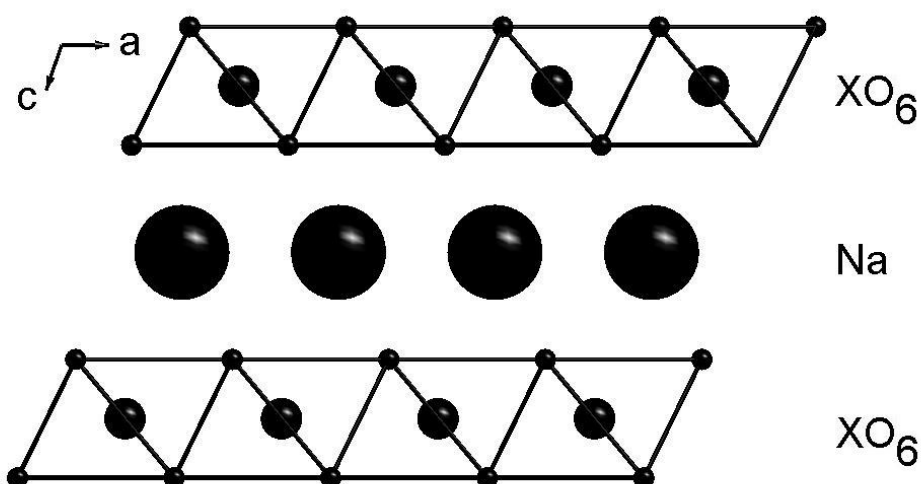


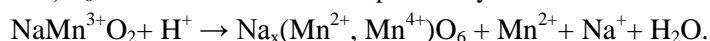
Figure 1. Crystal structure of NaXO_2 layered oxides ($X - \text{Mn}^{3+}, \text{Co}^{3+}, \text{Fe}^{3+}, \text{Ni}^{3+}$).

Unit cell parameters of known layered NaXO₂ oxides summarized in Table 1. The distance between two octahedral layers can be calculated from unit cell parameters and expressed as $b^* = b \cdot \sin \beta$. Interlayer distances observed to be in the range 5.24 – 5.59 Å (Table 1). This value is equal to the position of 001 reflex on X-ray diffraction pattern (d_{001} , Å).

Table 1. Crystallographic parameters of NaXO₂ layered oxides.

Source	ICSD-16270 [6]	ICSD 97199 [7]	ICSD-155502 [8]	ICSD-75589 [9]	ICSD-26609 [10]
Composition	NaMnO ₂	(Na _{0.29} (H ₂ O) _{0.75})MnO ₂	Na _{0.75} CoO ₂	Na _{0.5} FeO ₂	NaNiO ₂
Syngony / Space group	Monoclinic / C2/m (Nr. 12)	Triclinic / P-1 (Nr. 2)	Monoclinic / C2/m (Nr. 12)	Monoclinic / C2/m (Nr. 12)	Monoclinic / C2/m (Nr. 12)
Cell parameters	$a = 5.63(1) \text{ Å}$ $b = 2.860(4) \text{ Å}$ $c = 5.77(1) \text{ Å}$ $\beta = 112.90^\circ$	$a = 5.1746(2) \text{ Å}$ $b = 2.8474(1) \text{ Å}$ $c = 7.3319(4) \text{ Å}$ $\alpha = 89.44(0)^\circ$ $\beta = 103.18(0)^\circ$ $\gamma = 89.95(1)^\circ$	$a = 4.9020(5) \text{ Å}$ $b = 2.8723(3) \text{ Å}$ $c = 5.7789(7) \text{ Å}$ $\beta = 111.76(1)^\circ$	$a = 5.2603(6) \text{ Å}$ $b = 2.8965(2) \text{ Å}$ $c = 5.9062(6) \text{ Å}$ $\beta = 108.92(1)^\circ$	$a = 5.3300 \text{ Å}$ $b = 2.8600 \text{ Å}$ $c = 5.5900 \text{ Å}$ $\beta = 110.50^\circ$
$V, \text{ Å}^3$	85.58(24)	105.18(10)	75.57(21)	85.13(20)	79.82
Z	2	1	2	2	2
$d_{001}, \text{ Å} =$ $b^* = b \cdot \sin \beta$	5.32	7.14	5.37	5.59	5.24

The most investigated layered oxide and its intercalation is NaMnO₂. There is also report about structure changes due to intercalation of water molecules - (Na_{0.29}(H₂O)_{0.75})MnO₂. Incorporation of water molecules leads to extension of interlayer distance from 5.32 Å in NaMnO₂ to 7.14 Å in hydrated (Na_{0.29}(H₂O)_{0.75})MnO₂. However, incorporation of water molecules into the crystal structure of NaMnO₂ is more camlicate as expected. Fast hydrolizis was observed at the contact of NaMnO₂ and water with formation of birnessite Na_x(Mn²⁺, Mn⁴⁺)O₆. The interaction can be expressed by scheme:



Birnessite can be easily intercalated by organic cations [11]. The successful intercalation of benzylamine into the crystal structure of birnessite was reported earlier [12]. However, main disadvantage of this type of hybrid materials is unpredictable oxidation state of manganese cations.

NaFeO₂ layered oxide has a two polymorphic modifications - alpha (layered 2D) and beta (not layered, 3D). Fine dark red powder of layered alpha NaFeO₂ oxide was synthesized by solid state reaction Fe₂O₃ iron oxide with Na₂O₂. Layered NaCoO₂ and NaMnO₂ oxides were synthesized in similar way by using of MnO₂, Co₃O₄ and Na₂CO₃.

The X-ray diffraction method was used for identification of obtained samples. They were identified as single-phase and contain layered NaFeO₂, which crystallizes in monoclinic structure (Table 1).

Fine black powder was obtained after inorganic NaCoO₂ synthesis. The X-ray diffraction (XRD) method was used for identification of obtained samples. They were identified as single-phase and contain layered NaCoO₂.

The attempt of benzilamine intercalation into the crystal structure of NaCoO₂ and NaFeO₂ in water solution was unsuccessful because of hydrolyzis. That is why we have used benzylamine-acetonitrile solution.

As a result of intercalation of NaFeO₂ we obtained dark red powder, by XRD analysis discovered that the product is single phased. Comparing the diffraction patterns of alpha-NaFeO₂ and intercalated NaFeO₂ with benzylamine we can observe full intercalation of benzylamine to interlayer space [1]. The comparison of X-ray patterns shows the shift of 001 reflex in direction of low 2 theta angels (Fig.

2) what associated with the increasing of interlayer distance from 5.59 Å in NaFeO_2 to 17.38 Å in $(\text{C}_5\text{H}_6\text{-CH}_2\text{-NH}_2)_x\text{FeO}_2$.

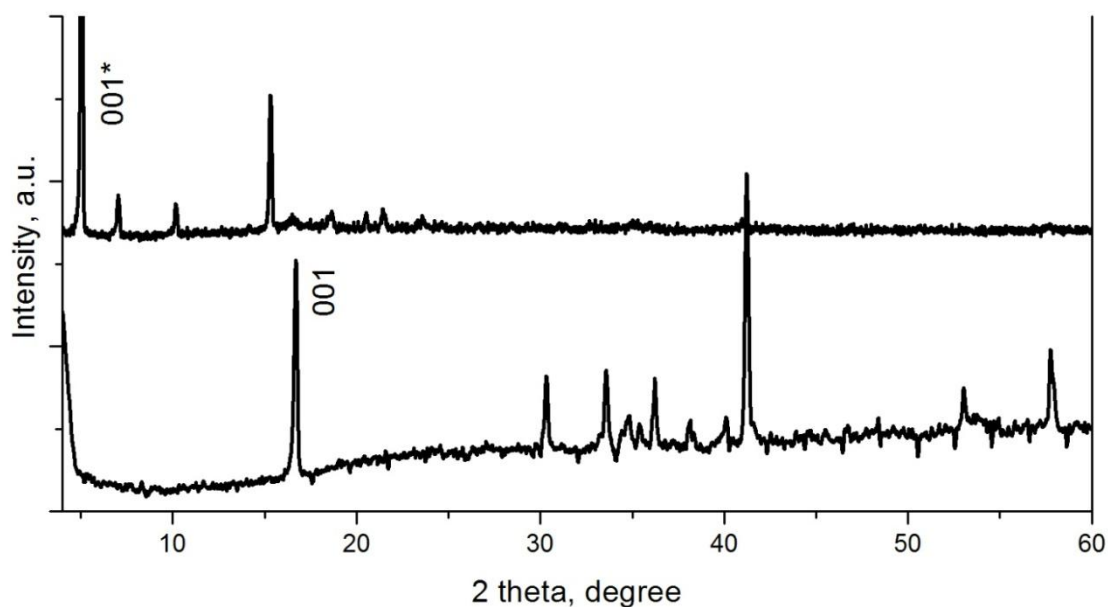


Fig 1. X-ray diffraction patterns of $\alpha\text{-NaFeO}_2$ (bottom) and NaFeO_2 intercalated by benzylamine (top).

After intercalation of NaCoO_2 by benzylamine-acetonitril solution we have obtained the black powder. X-ray diffraction analysis has shown that the product consisted of two phases (Fig. 3).

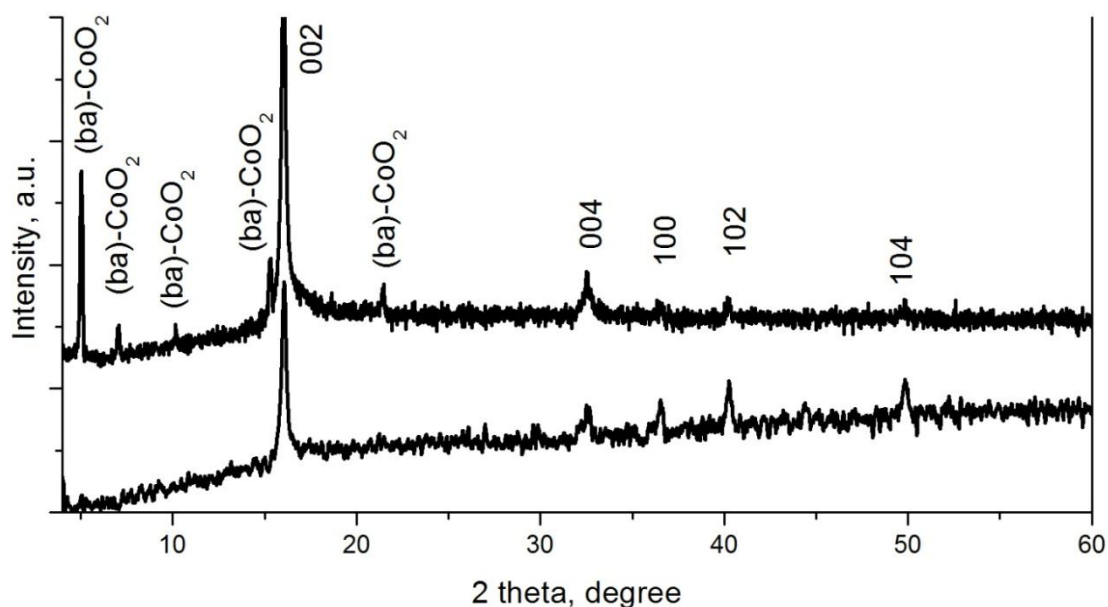


Fig 3. XRD of layered NaCoO_2 (bottom), and benzylamine intercalated NaCoO_2 (top).

The main phase was starting NaCoO_2 but second phase is a layered with interlayer distance 17.41 Å (Fig. 4). Appearance of new reflex indicates the intercalation of benzylamine molecules in the interlayer space of starting layered material and prove the possibility formation $(\text{C}_5\text{H}_6\text{-CH}_2\text{-NH}_2)_x\text{CoO}_2$ hybrid organic-inorganic material.

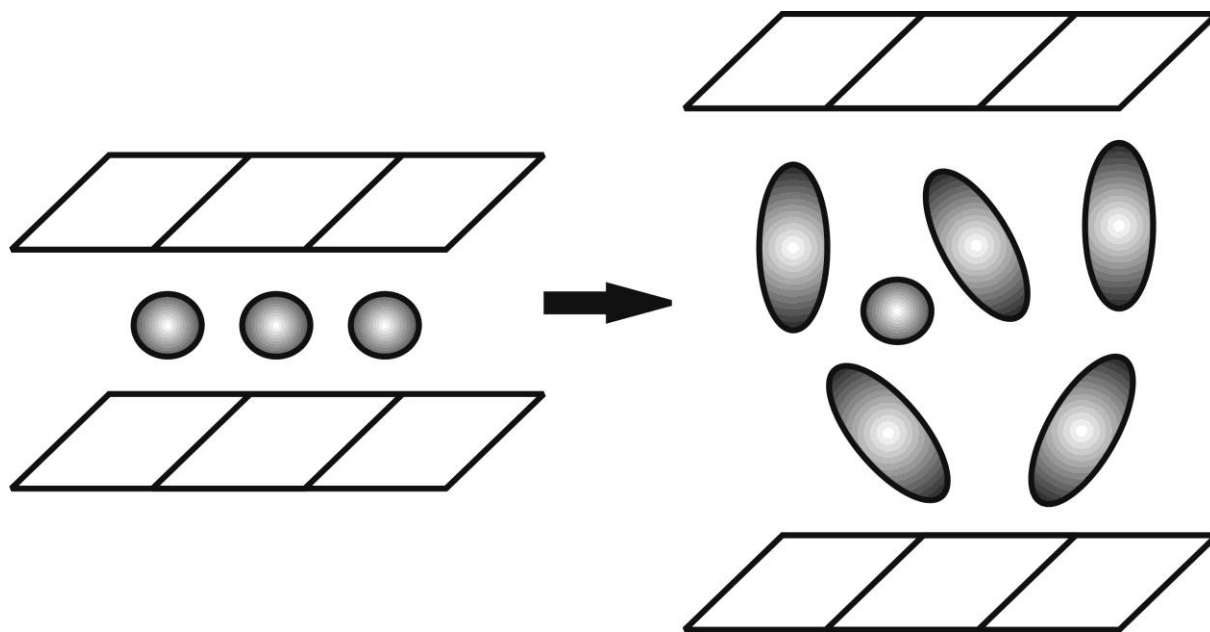


Figure 4. Intercalation of benzylamine molecules into the layered NaXO_2 oxides.

CONCLUSIONS

Hybrid organic- inorganic structures can be used as selective sorbents, membranes, catalysts, battery materials optical materials etc. One of the prospective ways for searching of new functional materials is intercalation of organic molecules into crystal structure of layered oxides of transition metals.

We have observed the possibilities for intercalation of NaCoO_2 and NaFeO_2 layered oxides intercalation of benzylamine molecules with formation of $(\text{C}_6\text{H}_5\text{-CH}_2\text{-NH}_3^+)_x\text{CoO}_2$ and $(\text{C}_6\text{H}_5\text{-CH}_2\text{-NH}_3^+)_x\text{FeO}_2$ hybrid organic-inorganic materials.

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