

Synthesis of Layered Hydroxides Stable in Redox Media

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Abstract—The introduction of hydrogen peroxide into the synthesis of iron-containing hydrotalcite-like layered hydroxides enhances the resistance of these materials to the postsynthesis action of H₂O₂. Hydrogen peroxide raises the relative magnesium content of the resulting hydroxides without causing any significant changes in their structure, morphology, or texture.

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Natural and synthetic layered hydroxides consist of positively charged brucite-like layers and anions located in the interlayer space [1, 2]. For catalytic processes, it is essential that the layered hydroxides have a large specific surface area and high basicity. The layered hydroxides are describable in terms of the idealized formula $M_{1-x}^{2+}M_x^{3+}(\text{OH})_2(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are metal cations and A^{n-} can be almost any anion. They readily undergo targeted modification since the cationic composition of the hydroxide layers and the anions in the interlayer space can be varied in wide ranges. Furthermore, the layered hydroxide structure allows molecules of various sizes to be inserted in the interlayer space. For example, hydrogen peroxide was intercalated into layered lithium aluminum hydroxide [3]. In this case, the layered hydroxide becomes an oxidizer storage medium, retaining its initial structure.

It is not obvious that other hydroxides will retain their layered structure in the presence of H₂O₂. It is, therefore, interesting to estimate the degree of involvement of the cations of the layered hydroxide lattice in redox processes. The objects of this study were hydrotalcite-like hydroxides in which part of the aluminum cations were replaced with iron(III).

EXPERIMENTAL

The iron-containing layered hydroxides were precipitated from salt (nitrate or chloride) solutions by adding a mixture of sodium carbonate and sodium hydroxide. Next, they were aged by temperature-controlled heat treatment and dried. Details of the synthesis were reported in an earlier paper [4]. Some hydroxides were precipitated in the presence of hydrogen peroxide.

For anion exchange, a sodium carbonate solution was poured over a dry sample and the reaction mixture was left standing for 12 h. Thereafter, the liquid was decanted. This procedure was repeated three times. The resulting solid was washed until free of chloride ions.

Dry layered hydroxide samples were treated with a 30% hydrogen peroxide solution for 12 h and were then washed with distilled water and dried at 105°C.

X-ray diffraction patterns were obtained on a DRON-3 diffractometer using CuK_α radiation. Texture parameters were determined by low-temperature nitrogen adsorption. Morphology was studied by scanning electron microscopy (SEM) using a Quanta 200 3D microscope. Metals in the layered hydroxides were quantified by atomic absorption spectrometry. Thermogravimetric and differential thermal analyses were carried out on an SDT Q600 thermal analyzer in air at a heating rate of 10 K/min.

The catalytic condensation of benzaldehyde and malononitrile (Knoevenagel reaction) was performed in a static system in a nitrogen atmosphere at 98°C. the solvent was 1,4-dioxane. The products were analyzed by GLC using a 30-m-long HP-5 capillary column with (5% phenyl)-methylpolysiloxane as the chromatographic phase.

RESULTS AND DISCUSSION

Experiments were carried out on well-crystallized iron-containing layered hydroxides. The action of aqueous hydrogen peroxide breaks the layered structure of the non-ion-exchanged hydroxides, and the destruction rate increases with an increasing iron content of the sample. As was expected, the iron cations interact with hydrogen peroxide. The resistance of the hydroxides to H₂O₂ can be somewhat enhanced by exchanging the chloride ion for carbonate. This is possibly due to the fact that hydrogen peroxide reacts both

Chemical composition and unit cell parameters of the layered hydroxides in carbonate form

Sample*	Introduction of H ₂ O ₂ into the synthesis	Mg/ Σ M ³⁺	Chemical formula	<i>c</i> , Å	<i>a</i> , Å	<i>V</i> , Å ³
Mg/AlFe10	No	2.14	Mg _{0.682} Al _{0.285} Fe _{0.033} (OH) ₂ (CO ₃) _{0.159} · 0.94H ₂ O	23.60	3.07	192.6
Mg/AlFe11	Yes	5.33	Mg _{0.842} Al _{0.141} Fe _{0.017} (OH) ₂ (CO ₃) _{0.079} · 0.88H ₂ O	23.70	3.07	193.4
Mg/AlFe23	No	2.70	Mg _{0.730} Al _{0.208} Fe _{0.062} (OH) ₂ (CO ₃) _{0.135} · 0.94H ₂ O	23.70	3.07	193.4
Mg/AlFe20	Yes	4.96	Mg _{0.832} Al _{0.135} Fe _{0.033} (OH) ₂ (CO ₃) _{0.084} · 0.91H ₂ O	23.70	3.07	193.4

* The number after the symbol of iron is the atomic fraction of the Fe³⁺ cations among all trivalent cations.

with iron cations and with chloride ions in the inter-layer space.

The layered hydroxides precipitated in the presence of hydrogen peroxide, both in chloride and in carbonate-exchanged forms, are the most resistant to postsynthesis treatments. It was interesting to compare the structure and properties of these hydroxides to those of the hydroxides obtained in the absence of hydrogen peroxide.

As is clear from the table, the introduction of hydrogen peroxide into the synthesis changes the chemical composition of the layered hydroxide so that

the crystallizing solid is markedly enriched with magnesium.

The X-ray diffraction patterns of the samples synthesized under various conditions (Fig. 1) are typical of layered hydroxides. The unit cell parameters of chemically similar layered hydroxides obtained in the presence and in the absence of H₂O₂ are nearly equal (table). Electron microscopic examination of the samples did not reveal any significant morphological differences (Fig. 2).

The hydroxide samples are also identical in pore size distribution: for both pairs listed in the table, the

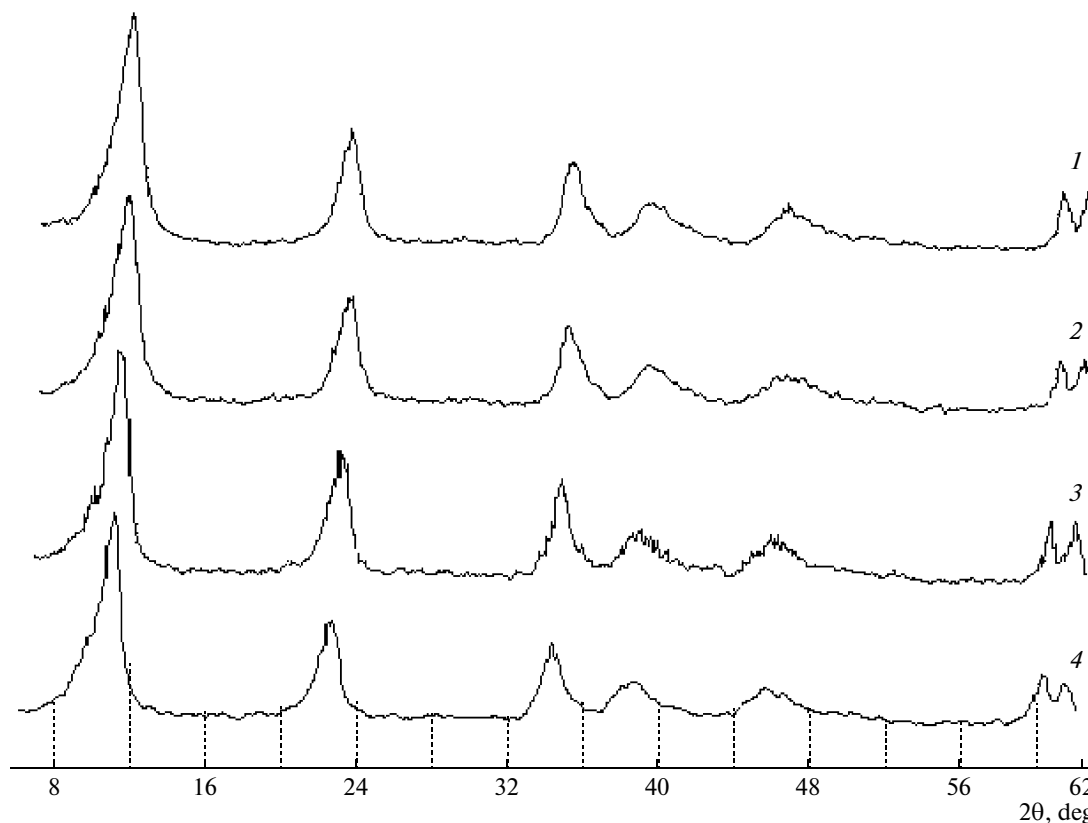


Fig. 1. X-ray diffraction patterns of the layered hydroxides synthesized (1, 2) in the absence and (3, 4) in the presence of hydrogen peroxide: (1) Mg/AlFe10, (2) Mg/AlFe23, (3) Mg/AlFe11, and (4) Mg/AlFe20.

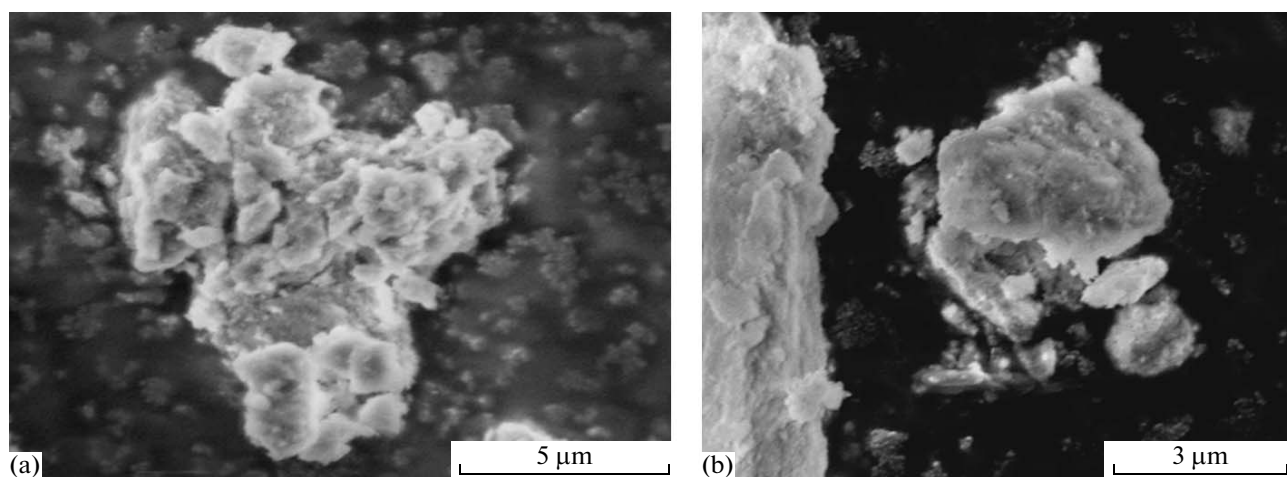


Fig. 2. SEM images of (a) Mg/AlFe20 and (b) Mg/AlFe23.

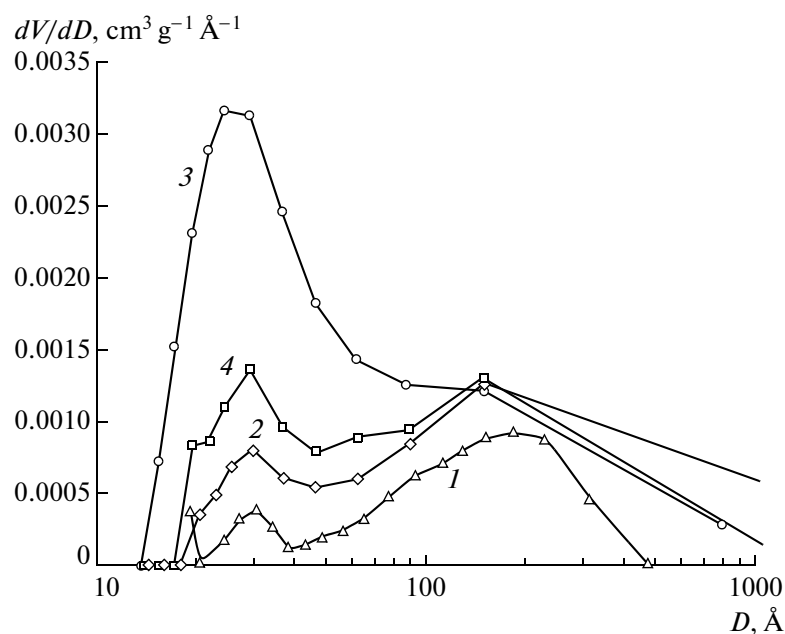


Fig. 3. Pore size distribution in (1) Mg/AlFe10, (2) Mg/AlFe23, (3) Mg/AlFe11, and (4) Mg/AlFe20.

pore size distribution can be considered to be bimodal (Fig. 3). The first maximum is in the pore diameter range of $D = 20\text{--}30\text{ \AA}$, which is roughly equal to the mean distance between adjacent metal hydroxide layers. The second maximum occurs at $D = 150\text{--}200\text{ \AA}$. This value is possibly the distance between particle aggregates, which are clearly seen in the micrographs.

Hydrogen peroxide exerts only a slight effect on the thermal stability of the layered hydroxides: the DSC curves of all samples are practically identical. They show two endotherms at 230 and 400°C accompanied

by weight loss. These endotherms are due to dehydration, anion decomposition, and dehydroxylation.

The catalytic properties of the hydroxides in the Knoevenagel condensation reaction are again similar. In all cases, the only product is benzylidenemalononitrile. Catalytic activity was estimated in terms of the initial benzaldehyde disappearance rate. For the Mg/AlFe10 and Mg/AlFe23 samples, it is 8.87 and 6.94 mmol g⁻¹ min⁻¹, respectively. For the hydroxides synthesized in the presence of hydrogen peroxide, the catalytic activity is higher by a factor of 1.1–1.5. This

is explained by the higher basicity of the samples containing larger amounts of magnesium.

Thus, the introduction of hydrogen peroxide into the synthesis of iron-containing layered hydroxides enhances the stability of their layered structure in redox processes without changing their other physico-chemical properties to any significant extent. The likely cause of the higher stability of the hydroxides synthesized in the presence of hydrogen peroxide is that all possible redox processes in these samples (oxidation of iron, chloride, and other ions) take place already during their synthesis, so the action of H_2O_2 on the final product does not break the hydrotalcite-like structure.

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