



Structure and morphological properties of clinoptilolite modified by manganese dioxide[☆]

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Abstract

The chemical composition and morphological properties of clinoptilolite-bearing materials modified by MnO₂ have been studied using modern physical methods. Scanning electron microscopy, X-ray spectral microanalysis and optical reflection microscopy were applied. It was experimentally shown that MnO₂-modified samples with high and low Si/Al ratios differed in such parameters as the layer thickness, the surface concentration, the degree of particle-surface dealumination, and also in morphological peculiarities of the MnO₂-phase. This phase in the samples with high Si/Al ratios exhibited the structure formed by nanorods of 10–20 nm in diameter and 500–700 nm in length. These nanorods are intermeshed in the net which is cross-linked with the surface of clinoptilolite particles. The MnO₂-modification of the samples was established to result in improving their mechanical and chemical strength as compared with the initial forms.

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Introduction

The materials modified by manganese dioxide (MnO₂) are currently widely used in various areas [1–6], including the purification of waters and various technological solutions [1, 2, 6, 7–14]. In this regard, creating MnO₂-modified materials based on

clinoptilolite (CL), a natural zeolite, is a promising direction [15–18], since it allows to obtain new materials with sufficiently high performance characteristics (sorption capacity, catalytic activity, chemical resistance and mechanical strength).

It is important for sorption-enhanced catalytic processes occurring in an aqueous medium that the MnO₂ phase be in a hydrated state. This requirement imposes certain restrictions on the conditions in which this phase can be synthesized, particularly on the CL surface that is sensitive to acidic and alkaline media.

The most common technology is aimed at stabilizing a divalent manganese ion in the CL matrix with the ion's subsequent oxidation [16–18].

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Using the MnO_4^- ion as an oxidant allows to produce a hydrated MnO_2 phase with the maximum yield and maximum active oxygen content; however, the behavior of this reaction under heterogeneous synthesis on the CL surface is currently poorly understood.

There is a large number of CL-containing rocks of good quality [19, 20], differing in chemical composition, porous structure, and other properties, to be found in Russia; to a significant extent, these differences affect the structure and composition of the resulting MnO_2 phase.

The goal of this study is in expanding the understanding of structural and morphological properties of the MnO_2 phase and the mechanism of its formation on the surfaces of clinoptilolite rocks of different properties.

Experimental procedure

We have examined five samples of CL-containing rocks with a high content of the zeolite phase, obtained from different deposits: Badinskoe, Holinskoe, Shivyrtuyskoe (Trans-Baikal region, Russia), Chuguevskoe (Primorsky Krai, Russia) and Sokirnitskoe (Western Ukraine). The last of these samples was taken for comparison, since, until recently, it was fairly widespread in the Russian market.

The content of the zeolite phase in the samples was determined by the standard thermochemical method [19, 20]. The volume limits of the sorption space W_s^w (in water) and the W_s^b (in benzene) were determined by the desiccant method [21]. The volume of the micropores inaccessible to benzene molecules (with pore entrance sizes less than 5.85 \AA) was defined as

$$V_\mu = W_s^w - W_s^b.$$

The values of the static sorption capacity $A^{\text{Mn}^{2+}}$, A^{SLS} and A^{MB} , respectively, for the Mn^{2+} ion, for sodium lauryl sulfate and for methylene blue were found by the static method from solutions with a concentration of 100 mg/l , with the solid/liquid ratio of 1:100, and under occasional stirring. The sorption time was 24 h, the temperature was $20 \pm 1^\circ \text{C}$.

The mechanical strength of the samples was evaluated as the mechanical degradability MD (wt.%), which was determined by the formula

$$\text{MD} = 100\% - \text{MS}(\text{at}),$$

where MS(at) is the mechanical abrasion resistance, determined in accordance with GOST 16188-70 [22].

The chemical strength of the samples was evaluated as the chemical degradability CD (wt.%), which was

described by the formula:

$$\text{CD} = 100\% - \text{RR},$$

where RR is the chemical resistance, determined, after the samples were treated with a sodium chloride solution according to GOST R 51641-2000 [23] and subsequently dried, by the sieving method in accordance with GOST 16188-70.

The MnO_2 content (in the particle volume) was determined by the oxalate method [24].

The synthesis of the MnO_2 phase on the surface of the CL rock samples was performed in three stages:

- sorption introduction of the Mn^{2+} ion into the CL exchange complex (i.e., obtaining Mn^{2+} -CL);
- treating the Mn^{2+} -CL with the KMnO_4 solution (obtaining MnO_2 -CL);
- washing the obtained MnO_2 -CL to remove the residues of the KMnO_4 solution, and then drying the product at $80 \pm 2^\circ \text{C}$ for 8 h.

The first two stages were carried out at a temperature of $20 \pm 1^\circ \text{C}$ and with a solid/liquid ratio of 1:10.

The thickness of the MnO_2 phase layer in CL rock particles was determined by linear measurements in the photographed thin sections of these particles, obtained by reflected-light optical microscopy. For this purpose, the MnO_2 -CL particles were fixed in an epoxy compound; the resulting block was then cut with a diamond micro tool array, ground and polished. The obtained thin sections with the particles were analyzed in reflected visible light using a Biolam-I microscope equipped with a Myscope 130 M digital camera (by Webbers). The camera was calibrated by an OMO-1 reflected-light stage micrometer.

The morphology of the obtained CL-modified MnO_2 samples, as well as the chemical composition of the surface layer of these materials were evaluated by scanning electron microscopy (SEM) using a Supra 55VP device (by Carl Zeiss AG) with an X-MAX X-ray microanalysis detector (Oxford Instruments). The size of the X-ray excitation band in the studied materials was $1.5 \mu\text{m} \times 1.5 \mu\text{m}$.

Experimental results

The compositions of CL rock samples used in the study before and after modification with MnO_2 are listed in Tables 1 and 2.

For the purpose of our discussion, the unmodified samples can be divided into two groups by their aluminosilicate contents (see Table 2): the high-silica (the

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