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Cement-Containing Catalysts of Ozone Decomposition Based on Iron Oxides

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Abstract—Cement-containing catalysts of ozone decomposition were synthesized on the basis of iron oxides obtained by ozonation of iron-containing aqueous solutions. X-ray diffraction analysis and Mössbauer spectroscopy showed that α-Fe_2O_3 occurs in the catalyst as highly dispersed nanoparticles. The catalysts obtained are efficient in the reaction of ozone decomposition and are as active as the best representatives of cement-containing catalysts of the GTT type.

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Ozone is widely used in chemical technologies; however, due to its toxicity, the problem of decreasing the concentration of residual ozone to maximum permissible concentrations (MPC) is very important. The best way to destroy residual ozone is its catalytic decomposition. Decomposition catalysts of the GTT type based on cement talum and transition metal oxides (Mn, Cu, Ni) are highly efficient mechanically robust catalysts [1] operating in both dry and wet gas flows, which makes it possible to use them in modern processes involving ozone. However, GTT catalysts have some drawbacks since they contain nickel oxides, which belong to hazard class I, as well as manganese and copper oxides, which belong to hazard class II. Therefore, design of new environmentally safe and inexpensive catalysts, for example, on the basis of iron oxides (hazard class III) remains among the important problems of state-of-the-art ozone technologies.

EXPERIMENTAL

Iron(III) oxide used for preparation of catalysts was obtained by ozonation of an aqueous solution of iron(II) sulfate, as well as water from the artesian well of the Lianozovskii milk plant, in which the iron content is 0.57–1.19 mg/L and considerably exceeds the MPC level (0.30 mg/L). Ozonation of artesian water led to the formation of a precipitate, which consists mainly of iron hydroxides; it accumulates in large amounts as a by-product. The precipitate was filtered off and dried, studied by X-ray powder diffraction and Mössbauer spectroscopy, and then used as the major component for preparation of iron-containing catalysts. As the other components, high-alumina cement (talum) and clay were used.

Two series of catalyst were synthesized: In the first series, clays of different compositions were used as a binder; in the second series, talum and clay were used as a binder. Cement-containing catalysts were prepared by hydrothermal synthesis [2] involving the following processes: mixing of initial components in specified ratios in the presence of water; extrusion of the resulting mass and keeping the resulting extrudates in humid air and then in hot water at 80–90°C at the stage of hydrothermal treatment; drying; and calcination at 450°C. Catalysts free of high-alumina cement were synthesized analogously, excluding the stage of hydrothermal treatment. The kinetics of ozone decomposition was studied in a flow-type catalytic setup. Ozone, obtained in a barrier discharge, was passed through a U-shaped glass reactor with an inner diameter of 1.5 cm where a catalyst (2 g) was placed. The outside geometric surface area of this sample was 30–40 cm^2. The ozone concentration was no more than 20 mg/L and was determined on a Medozon-254/5 spectrometer.

As a measure of the activity of the catalysts, the value of γ was used, which shows the fraction of active, i.e., leading to ozone decomposition, collisions between the molecules and the surface. The γ value was calculated by the equation [3]

$$\gamma = \frac{4\omega \ln [O_3]_0/[O_3]}{us},$$

where $[O_3]_0$ and $[O_3]$ are, respectively, the ozone concentrations at the inlet and outlet of the catalytic reactor filled with catalyst grains, ω is the gas flow rate (cm^3/s), u is the thermal velocity of molecules (cm/s), and s is the outside geometric surface of the catalyst grains (cm^2).

The texture characteristics of a catalyst were determined by the low-temperature nitrogen desorption method on a Quantachrome Autosorb-1 instrument. X-ray powder diffraction patterns were obtained on a

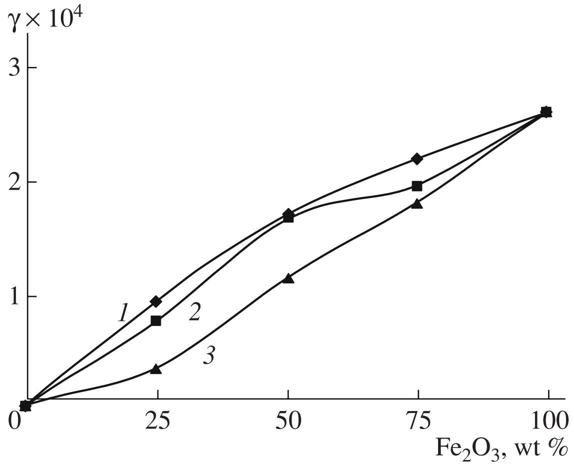
DRON-3M diffractometer with filtered CoK_α radiation. Mössbauer spectra were measured on an MS-1104Em spectrometer.

RESULTS AND DISCUSSION

According to X-ray diffraction, the main product of ozonation of iron-containing waters is lepidocrocite. Calcination of this product at 450°C yields iron oxide α-Fe_2O_3. Estimates of the coherent scattering length of the sample obtained by ozonation of an aqueous solution of iron(II) sulfate allowed us to determine the particle size, which was no more than 20 nm; i.e., oxide exists as highly dispersed particles.

The presence of the highly dispersed phase in the sample obtained by ozonation of both an aqueous solution of iron(II) sulfate and natural water was confirmed by Mössbauer spectroscopy. The spectra measured at 293 and 77 K showed the presence of the fine hematite and goethite phases with a grain size of no more than 10 nm.

As mentioned above, we synthesized two series of catalysts based on iron(III) oxides and clay (series 1) and based on high-alumina cement and clay (series 2). The figure presents the results of determination of the activity (γ) of iron-containing catalysts with different types of clays. The figure shows that the catalysts containing clay G-1 are the most active in ozone decomposition. The sample containing 75 wt % Fe_2O_3 and 25 wt % G-1 clay is the most efficient ($\gamma = 2.2 \times 10^{-4}$) among the iron-containing catalysts that we prepared. However, all catalysts of series 1 have an important drawback, namely, very low mechanical strength.



Catalytic activity of samples of series 1 as a function of the Fe_2O_3 content: (*1*) G-1, (*2*) G-2, and (*3*) G-3.

The introduction of high-alumina cement into catalysts imparts to them strength and heat resistance, but leads to wear of equipment and complicates extrusion of catalysts [2]. In the second series of catalysts, the main binder clay was exchanged for talum and clay G-1 was used as a plasticizer.

The table shows the compositions of catalysts of series 2, as well as their activity in the ozone decomposition reaction. As is seen, the catalyst containing 65 wt % iron(III) oxide was the most active (2.0×10^{-4}). The catalyst of this composition has the following texture characteristics: the specific surface of the catalyst was 150 m^2/g, the pore volume was 0.27 cm^3/g, and the average pore diameter was 57 Å. These data are close

Activity of iron-containing catalysts of series 2 in the ozone decomposition ozone

No.	Fe_2O_3, wt %	Talum, wt %	Clay G-1, wt %	S, cm^2	$\gamma \times 10^4$	Average value $\gamma \times 10^4$
1	33	60	7	32.2	0.97	1.0
				33.0	1.03	
				32.4	1.04	
2	43	50	7	37.3	1.19	1.2
				35.7	1.21	
				33.5	1.16	
3	60	35	5	39.6	1.69	1.7
				38.6	1.64	
				42.2	1.62	
4	65	30	5	33.8	1.97	2.0
				33.0	2.00	
				33.3	2.02	
5	80	15	5	Extrudates disintegrated		

to the values obtained for GTT catalysts [1]. Catalyst grains containing 80 wt % iron oxide, 15 wt % high-alumina cement, and 5 wt % clay were destroyed in water during hydrothermal treatment. This is consistent with the conclusion that the content of high-alumina cement in a catalyst should be at least 25 wt % [4].

Calcination of the catalyst with the best activity (65 wt % α-Fe_2O_3) at 700°C leads to a decrease in γ to 0.4×10^{-4}. An analogous result was previously obtained for cement-containing catalysts of ozone decomposition containing Mn, Cu, and Ni oxides [5]. This decrease can be explained by agglomeration of catalyst grains at such high temperatures and a possible change in its phase composition.

The catalyst containing 65 wt % iron oxide in dry gas showed an activity (table) close to that of a GTT catalyst ($\gamma = 2.4 \times 10^{-4}$) [1], which is today is one of the best ozone decomposition catalysts. In addition, this iron-containing catalyst does not contain metal oxides from hazard classes I and II.

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