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BRIEF COMMUNICATIONS

Preparation and Properties of Modified Hopcalite

A. S. Kireev, V. M. Mukhin, S. G. Kireev, V. N. Klushin, and S. N. Tkachenko

Mendeleev Russian Chemical Engineering University, Moscow, Russia
Neorganika Ecological Research and Production Company Public Corporation, Electrostal', Moscow region, Russia
Lomonosov State University, Moscow, Russia

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Abstract—A procedure was developed for the modification of the manganese-oxide catalyst hopcalite GFG allowing the new quality, water resistance of granules, to be reached. This procedure can be used for the reactivation of the exhausted catalytic contact.

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Industrial Russian manganese-oxide molded catalyst hopcalite GFG based on manganese dioxide and copper oxide [1] is widely applied to the oxidation of carbon oxide and in some cases also to the decomposition of residual ozone. To improve qualitative and operating characteristics of the catalytic contact, both the technique directed on perfecting the technology of its preparation [2] and the methods involving the catalyst composition modification are used. For example, the modification of a binder results in increased strength of granules [3], and the introduction of a NaA-type zeolite into GFG allows increasing the protective power of the catalyst with respect to carbon oxide by 25–30% [4].

In regard to the use of hopcalite as an ozone destructor, in particular, in technologies of water purification and ozone-involving water treatment, its application in this field is restricted. This catalyst does not possess water-resistance – on contact with condensed moisture GFG granules are destructed. By this reason its operation is possible only in dry air-gas flows or it requires maintaining a reactor working temperature of no less than 110–120°C [5].

Hopcalite GFG cannot be water-resistant as it is produced with the use of bentonite clay as a binder, whereas one of the best Russian ozone destructors GTT contains [6] the aluminum-calcium cement talum. However the catalytic mass in the form of a pasta with a humidity of 30–33% consisting of manganese dioxide and other hopcalite components in a mixture with talum has such rheological properties, which exclude molding of small granules (~1 mm in diameter) by the extrusion method.

The aim of this work was the search for ways of making a water-resistant catalyst based on hopcalite components, manganese dioxide and copper oxide, and the study of its physicochemical properties.

EXPERIMENTAL

We used calcium oxide in an amount of 15–20 wt % as a binder for the preparation of the molded catalyst. Granules of the resulting catalyst had water-resistance and strength comparable with those of GTT, whereas their activity in ozone decomposing was 0.94–0.97 compared to GFG. The most probable reason of such activity reduction can be a change in the nature of active catalytic centers resulted from their interaction with the active material CaO, which is a solid base.

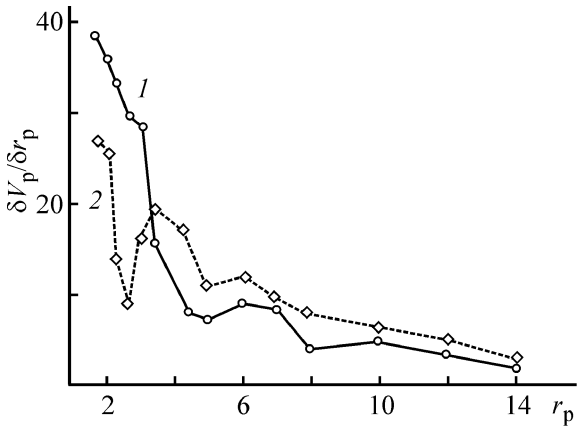
The compositions containing CaO are characterized by long solidification periods, and the prolonged time of holding up an intermediate product required to reach the necessary strength can increase production costs. To reduce the time necessary for reaching the required strength of granules, we applied a standard technique: the addition of the chemical accelerating agent NaCl in an amount of 1.0–1.5 wt %. It resulted in the activity reduction up to 0.88–0.93, which most probably is caused by a reaction of active centers with sodium chloride. Thus, despite of losses of 7–12% of the initial activity in ozone decomposition, hopcalite GFG has gained

Thermal treatment effect on the activity of catalysts

Reaction	Sample	Activity of a catalyst after calcination at temperature, °C				
		200	300	400	500	600
Ozone decomposition	GFG	0.93	1.00	1.00	0.54	0.39
	GFG-ex	0.82	1.00	1.00	0.87	0.30
Oxidation of carbon oxide	GFG	1.00	0.97	0.72	0.41	0.22
	GFG-ex	0.97	1.00	0.97	0.83	0.46

water-resistance – the quality, which was not earlier characteristic of it. It predetermines a possibility for the extension of the area of this catalyst application.

The possibility of using such technology for the reactivation of GFG hopcalite exhausted as a catalyst of ozone decomposition in water treatment processes (GFG-ex) seems the most significant. This catalyst is completely deactivated and, unlike the initial hopcalite consisting mainly of water-insoluble manganese and copper oxides, contains water-soluble Mn^{2+} and Cu^{2+} forms and also the anions of inorganic acids SO_4^{2-}, Cl-, and NO^{3-}, which are probably catalytic poisons [7]. In this work we have made an attempt to use certain properties of catalytic poisons for technological purposes, namely their ability to accelerate the solidification of systems with a calcareous binder. The essence of the technology consists in the following: an exhausted catalyst was mixed with aqueous CaO suspension, and granules were molded from the resulting mass by the extrusion method after plastification. Then the granules were predried, crushed, sieved, washed, dried, and calcinated at technological regimens close to those used in the industrial hopcalite production. The activity of thus reactivated catalyst (GFG-sp) was 0.81–0.85 of the GFG activity.



Pores distribution by sizes for GFG (*1*) and GFG-sp (*2*). (V_p) pores volume, mm^3, (r_p) pores radius, mm.

In this case the loss of initial activity is even greater, but, first, here completely exhausted product is used as a raw material containing metal oxides, which can be returned in economic circulation using the above-described procedure. Second, if the traditional technology is used and water-soluble impurities – catalytic poisons are washed out from GFG-ex, the amount of waist water will be as much as 50 m^3, and the amount of impurities 67 kg, whereas, according to the offered technology, these are about 20 m^3 and 3.2 kg per 1 ton of a final product. The amount of waste water is twice reduced and the amount of impurities is decreased by almost two orders of magnitude that will lead to an essential reduction of expenditures for nature protection provisions. Thus, the concept of low-waste technology is realized as far as recycling nonrenewable natural resources and reducing the ecogenetic loads on the environment are concerned.

The addition of CaO to the manganese-oxide catalyst has changed its properties. The specific surface area has decreased from 180 up to 82 m^2g^{-1} and the adsorption capacity with respect to water vapor has decreased: the capacity of a monolayer (by BET) for GFG – up to 2.2 mmol g^{-1} and for GFG-ex – up to 1.3 mmol g^{-1}.

The porous structure also has changed. The distribution of pore volume over radii, as calculated from the data of adsorption measurings, are shown in the figure. Hopcalite GFG has a maximum of distribution at 6 nm, and in the case of GFG-sp one more peak appears at 3.4 nm, its intensity being much greater. It can point to the formation of finer pores on the addition of calcium oxide to the catalyst basis that probably is caused by both smaller particle sizes of the binder and a change in packing of solid particles.

It is also necessary to note that the GFG-sp thermal stability increases when its activity slightly decreases. The table contains the data describing the activity of GFG and GFG-s samples in ozone decomposition and in carbon oxide oxidation after calcination at various temperatures.

An increase in the thermal treatment temperature results in a decrease in the activity of the catalysts in the both reactions, however the modification of the hopcalite basis with CaO undoubtedly slows down this process, which is most noticeable in the case of the CO oxidation.

CONCLUSIONS

1. The method for the modification of the manganese-oxide catalyst - hopcalite GFG was offered. It allows the catalytic contact to obtain a new quality – resistance of granules against the action of condensed moisture.

2. It was found that the addition of calcium oxide to the catalyst basis results in the decrease of the adsorption activity with respect to water vapor – the capacity of a monolayer by BET decreases from 2.2 up to 1.3 mmol g^{-1} whereas the specific surface area is reduced from 180 up to 82 $m^2\ g^{-1}$.

3. The presence of CaO in the catalyst composition results in an appreciable decrease in the rate of the activity decreasing in the reactions of ozone decomposition and carbon oxide oxidation as the heat treatment temperature increases.

4. The use of this method for the reactivation of hopcalite exhausted in ozone decomposition makes it possible to lower twice the amount of waste water and to reduce the amount of impurities to be neutralized by two orders of magnitude.

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