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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Fabrication of Catalysts for Synthesis of Carbon Nanotubes by "Wet Burning" Method in Continuous Apparatus

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Abstract—Several reactor designs for continuous production of finely dispersed metal oxides by "wet burning" were developed and tested. Basic dimensions of the reactors were determined on the basis of calculations of the specific heat release and gas evolution, and laboratory prototypes of the reactors were fabricated and tested.

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Catalytic pyrolysis of hydrocarbons is becoming one of the principal methods for industrial production of carbon nanotubes (CNT) and nanofibers [1]. The method employs metals-catalysts with nanosize particles on metal oxide supports. The method of "wet burning," whose fundamentals are described in [2, 3], has found comparatively wide application for fabrication of catalysts of this kind. It was first used to synthesize catalysts in [4].

The method consists in that a homogeneous aqueous or organic solution containing nitrates of a metal-catalyst (Fe, Co, Ni) and of a metal whose oxide serves as the catalyst support (CaO, MgO, Al_2O_3) and a reducing agent (urea, citric acid, glycine) is prepared. The solution is placed in an open cup in a furnace heated to 500–550°C, which results in that the solvent rapidly evaporates, the solution is concentrated, and a strongly exothermic reaction is initiated between the metal nitrates and the reducing agents. The reaction accompanied by strong gas evolution yields finely dispersed oxides with a large specific surface area and homogeneous distribution of the mixture components. In this way, mixed oxides, their solid solutions, and salts (metallates) and composites can be obtained.

The most widely used catalyst support is MgO [5]. The oxides CoO, NiO, and, possibly, FeO form with MgO solid solutions and their reduction makes it possible to release Co, Ni, and Fe in the form of nanosize particles distributed in the MgO matrix.

In chemical essence, the starting mixture in the wet-burning method is similar, before the initiation of the reaction, to blasting powder, which conventionally contains an oxidizing agent (potassium nitrate) and reducing agents (sulfur), and the thermal mode of the process is analogous to that of self-propagating high-temperature synthesis. The specific features of the "wet burning" synthesis are the strong gas evolution and heat release and the high rate (the reaction is complete in minutes). This hinders performing the process in the continuous mode, and, therefore, the process has been described only in a batch variant with small portions of the solution.

A method for continuous production of catalysts for CNT synthesis has been used only in a single study [6], in which the reaction was initiated by dispersion of the starting solution in a burner flame. An aqueous solution of ethanol served as a solvent for making lower the solution viscosity. The resulting finely dispersed oxides (Fe,Mo/MgO catalyst with an atomic ratio of 1.00 : 0.05 : 13.00 between the metals) were collected with an electrostatic filter. Despite having apparent advantages over the batch variant, this process has shortcomings associated with the difficult isolation of finely dispersed particles from strongly diluted gas flows.

An analysis of the reactions used to obtain finely dispersed metal oxides and, in particular, catalysts for CNT synthesis made it possible to suggest another method for performing these reactions in the continuous mode [7] and to develop several apparatus designs.

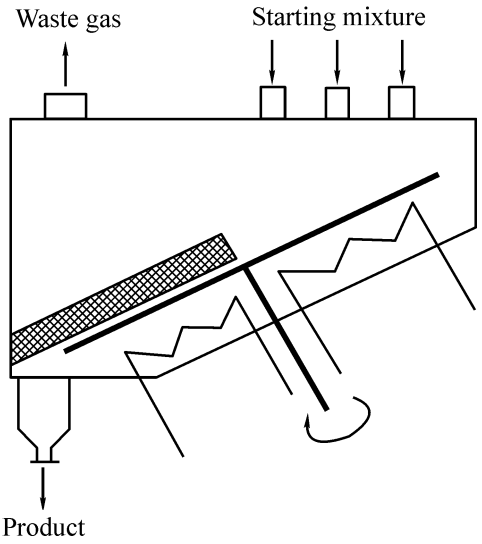

Fig. 1. Schematic of the reactor with a rotating disk.

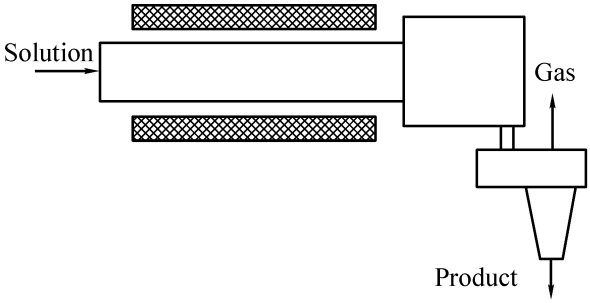

Fig. 2. Schematic of the reactor with a rotating retort.

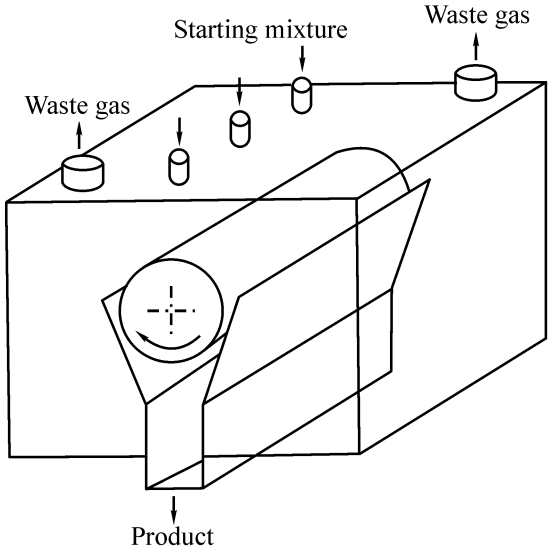

Fig. 3. Schematic of the reactor with paired rotating rollers.

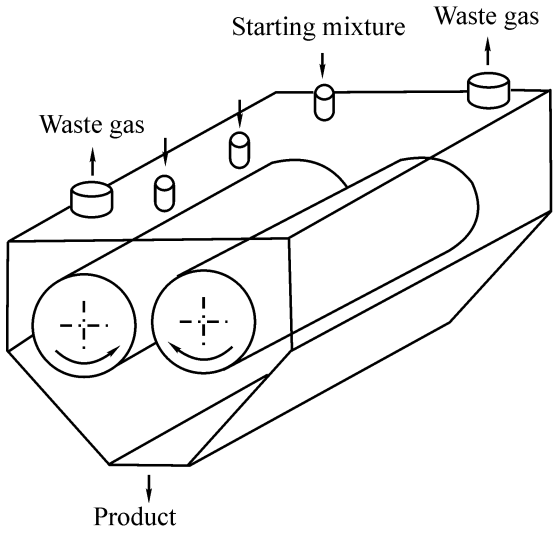

Fig. 4. Schematic of the reactor with a rotating roller.

The aim of this communication is to briefly describe this method and several types of laboratory reactors in which it can be implemented.

EXPERIMENTAL

A single-portion delivery of large solution volumes into the reactor zone heated to a high temperature results in an explosion. Therefore, processes of this kind are regarded as impossible or highly difficult in the chemical industry, especially if it is necessary to provide a high specific throughput (per unit volume or area of an apparatus). However, with batch delivery used and certain limitations observed, it is possible to organize continuous intensive evaporation with initiation of an exothermic reaction accompanied by strong gas evolution.

The method described in the patent [7] consists in a continuous delivery of a preliminarily prepared solution of a nitrate and a reducing agent to a surface heated to the required temperature, with permanent removal of the finished solid product and reaction gases. In preliminary experiments, we first selected temperatures at which the solvent evaporation and ignition of a mixture of nitrates and reducing agents from a small portion of the solution occur during a short time (seconds or tens of seconds). The temperatures, found to be dependent on the composition and mass of a solution portion, varied from 250 to 400°C.

We tested various heater materials and found a material that is not wetted by the starting solution and by the

viscous concentrated solution and shows no adhesion to the soft gel-like half-product.

Further, we studied various designs for continuous removal of the product from the heater. Here, the best solution is to use reactors with a rotating heater.

Finally, we calculated the reaction mixture volumes and removal rates of reaction gases at which the pressure buildup in the reactor can be precluded at a known gas evolution rate (determined by the throughput and the solution composition).

We designed and tested several reactors, each of which can yield tens of grams of the oxide material per hour at a working volume not exceeding 3 dm^3. The heater was placed in a protective case that provided the leak-tightness of the reaction zone. The reactors (shown schematically in Figs. 1–4) were tested with a solution containing $Mg(NO_3)_2$ and a 25% excess of glycine.

In the reactor shown in Fig. 1, the mixture was continuously delivered to a heated rotating disk 150 mm in diameter. After an intensive evaporation, the mixture ignited to give gaseous and solid products. The solid product was removed by a heated blade, with the material collected in a receiver.

The reactor schematically shown in Fig. 2 enabled a continuous delivery of the solution to a horizontal rotating tube (retort) with an inner diameter of 30 mm, heated by an electric furnace. The solid and gaseous substances were transported within the reactor by an air flow. The products were separated in a cyclone.

In operation of the reactors schematically shown in Figs. 3 and 4, the mixture was delivered to the outer heated surface of a rotating roller or two rollers rotating in different directions and placed in a protective case. Solid products were removed from the surface by a heated blade (not shown in the schemes), with the material collected in the receiver.

In addition, we tested reactors with rotating conical heaters and the solution delivered to the outer surface of a truncated cone (with an upwards directed vertex) or to the inner surface of a truncated cone (with a downwards directed vertex).

We examined in most detail the working modes of the tubular reactor (Fig. 2). At an air supply rate of about 14 dm^3 min^{-1}, we studied the effect of the solution delivery rate Q on the throughput of the installation in terms of the solid product, G, at a constant rotation rate N of the retort and also the effect of the rotation rate of the retort on the throughput of the installation at a constant solution delivery rate. We purified the product to remove carbon-containing impurities by its calcination in air at 600°C for 20–30 min. The results obtained are shown in Fig. 5.

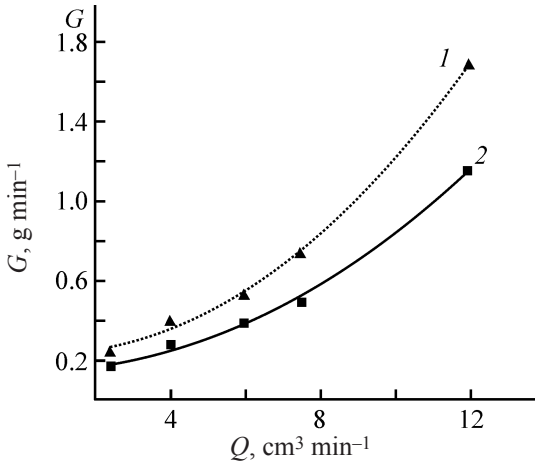

Fig. 5. Reactor throughput G vs. the solution supply rate Q at a constant rotation rate of the retort (N = 45–50 rpm). (*1*) In terms of an uncalcined material and (*2*) in terms of a calcined material.

It can be seen in Fig. 5 that, as the solution flow rate is raised from 2.5 to 12.0 cm^3 min^{-1}, the throughput of the reactor in terms of an uncalcined product increases from 0.2 to 1.6 g min^{-1}. Raising the flow rate to above 12.0 cm^3 min^{-1} resulted in reactor flooding associated with the insufficiently intense heat supply for ignition of the mixture. The nonlinear run of the curves in Fig. 5 is due to the loss of a part of the product with the gas flow.

Characteristics of the materials obtained and the installation throughput

Product composition	ρ_b	P	S_{sp},	d,* nm	G,
	g cm^{-3}		m^2 g^{-1}		g min^{-1}
$Co_{0.01}Mg_{0.99}O$	0.06	3.58 (MgO)	–60	28	–0.6
$Ni_{0.86}Mg_{0.14}O$	0.16	7.45 (NiO)	–21	38	–0.2
$Co_{0.3}Zr_{0.7}O_2$	0.14	5.73 (ZrO_2)	–	–	–0.3
$0.8Al_2O_3$–$0.2ZrO_2$	0.22	3.96 (Al_2O_3)	–	–	–0.3
ZrO_2	0.04	5.73 (ZrO_2)	–6	175	–0.1
Al_2O_3	–0.10	3.96 (Al_2O_3)	–	–	–0.2

* It was assumed that the particles have a cubic shape; the particle size was calculated by the formula $d = 6/(S_{sp}\rho)$; measurements were made with products annealed in air.

The throughput of the reactor increased on raising the rotation rate of the retort, with the dependence being almost linear.

A comparison of curves *1* and *2* in Fig. 5 and results of other experiments made it possible to determine the content of carbon-containing substances in the product. For example, on raising Q from 2.5 to 12.0 cm^3 min^{-1} at N = 45–50 rpm, it decreased from 33.9 to 31.1 wt %, whereas at Q = 7.5 cm^3 min^{-1} and N raised from 31.3 to 83.6 rpm, it increased from 34.6 to 50.0 wt %.

We synthesized oxide materials of various compositions. The characteristics of the materials obtained and the installation throughput achieved for each material at the same process conditions (N = 45–50 rpm, Q = 5 cm^3 min^{-1}) are listed in the table (ρ_b, measured bulk density; ρ, X-ray density; S_{sp}, measured specific surface area; d, calculated average particle size).

Analysis of the data in the table shows that the bulk density of the products differs from the X-ray density by a factor of 20–140 even upon their calcination in air, which points to a high dispersity of the products. At the same time, primary particles are apparently combined into a kind of aggregates.

An electron-microscopic analysis demonstrated that the $Co_{0.01}Mg_{0.99}O$ and Al_2O_3 ZrO_2 powders have an amorphous porous structure and the Al_2O_3 powder is composed of foamed particles with a size of lamellar aggregates of about 10 μm and plate thickness of less than 1 μm.

An X-ray phase analysis demonstrated that $Co_{0.01}Mg_{0.99}O$ is X-ray-amorphous and the product formed in burning of zirconium oxynitrate and glycine is a mixture of zirconium oxides with tetragonal and monoclinic crystal lattices.

A small (about 50 cm long) modified continuous laboratory reactor provides a stable output of 20 g h^{-1} of Co,Mo/MgO catalyst and enables operation of a pilot reactor for synthesis of carbon nanotubes.

Compared with the method described in [6], the technique we developed has certain advantages that are, in particular, associated with the simpler recovery of the solid reaction product, because of the smaller specific volume of reaction gases, and with the higher purity of the solid product (natural gas burning products are not admixed with the reaction gases).

CONCLUSIONS

(1) Several reactor designs for continuous production of finely dispersed metal oxides and, in particular, catalysts for synthesis of carbon nanotubes by the wet-burning method were suggested.

(2) The results of calculation of the specific heat release and gas evolution were used to calculate the basic dimensions of the reactors; their laboratory prototypes were designed and tested.

(3) It was shown that a comparatively small laboratory tubular reactor can yield in a continuous mode 20 g h^{-1} of the catalyst for synthesis of carbon nanotubes.

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