Journal of Engineering Physics and Thermophysics, Vol. 70, No. 4, 1997

SYNTHESIS OF OXIDE CATALYSTS BY THERMOLYSIS OF SOLUTIONS IN A PLASMA FLOW

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UDC 66.01:661.097.3+533.9

Thermodynamic and kinetic regularities of the process of obtaining oxide catalysts by thermolysis of solutions in a plasma flow are investigated. A plasmochemical method of catalyst synthesis is developed and experimentally studied. Working parameters of the process are found and the catalyst synthesis conditions are related to its properties. A flow diagram of catalyst synthesis is suggested and tested in experiments.

Introduction. By decreasing the activation energy of a chemical reaction and improving its selectivity, catalysts favor energy and raw-material conservation in technological processes. Therefore, about 90% of products in chemical and petroleum industries are produced with the aid of catalysts. However, despite the great practical importance of catalysts, the existing technologies of their production possess a number of drawbacks, among which are a low rate, a multistage and cyclic character of the technological process, and a great amount of waste water. Moreover, the catalysts used are often chemically inhomogeneous, which exerts an adverse influence on their quality [1].

In connection with this it is urgent to develop new methods to upgrade the technology and improve its ecological purity and the quality of the catalysts obtained. One method is the use of concentrated energy sources, in particular, of plasma [1]. Thus, processing of dispersed substances in plasma jets allows enhancement, as shown by a number of authors [1-6], of heat and mass transfer processes and chemical transformations by several orders of magnitude.

The essence of the method described lies in the fact that an aqueous solution of salts constituting metals in a ratio identical to the composition of the catalyst to be obtained is dispersed by a nozzle and is fed in aerosol form to a reactor, where it is mixed with jets of the air plasma generated by electric-arc plasma generators. In the reactor the processes of solution dehydration, thermal decomposition of salts, and formation of a crystalline structure of the catalyst proceed as a single stage. After quenching the catalyst powder is filtered from the gaseous phase.

The goal of the present work is to elaborate physicochemical principles of the technology of obtaining mixed-type oxide catalysts by thermolysis of aqueous solutions of metal salts in a plasma flow; to relate catalyst synthesis conditions to catalyst properties; to evaluate the efficiency of applying the plasmochemical technology of catalysts. For this, it is necessary to solve the following problems:

a) On the basis of thermodynamic analysis of high-temperature heterophase multicomponent systems, to calculate the main technological parameters, namely, temperature, pressure, ratio of components, to determine the kind of initial raw material and specific power consumption.

b) To determine kinetic regularities of the physical and chemical processes in synthesis of oxide catalysts from solutions of metal salts in an air plasma flow.

c) To develop a plasmochemical method of synthesis of oxide catalysts, to determine experimentally technological parameters, to synthesize oxide catalysts, and to investigate their properties depending on the synthesis conditions.

Small-Scale Scientific-Industrial Enterprise "Plasma," Kiev, Ukraine; Institute of General and Inorganic Chemistry, National Academy of Ukraine, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 70, No. 4, pp. 601-608, July-August, 1997. Original article submitted March 25, 1997.

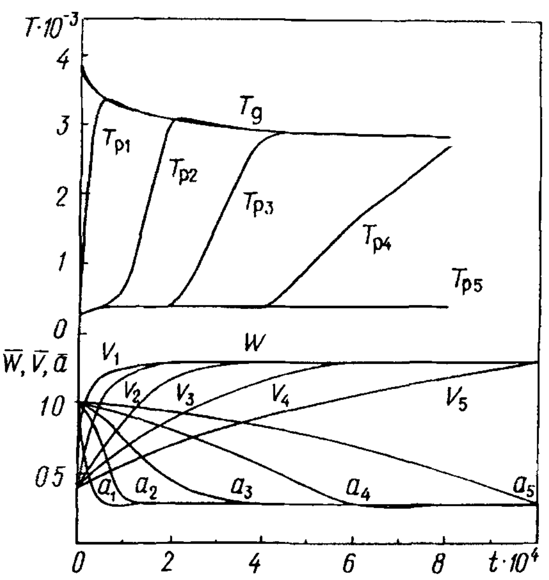

Fig. 1. Time variation of the dimensionless values of the diameter ($\bar{a}$) and velocity ($\bar{V}$) of droplets, gas velocity ($\bar{W}$) as well as gas (T_g) and condensed particles (T_p) temperatures calculated for the following initial diameters of droplets: 1) 7.5, 2) 20, 3) 30, 4) 45, 5) 60 μm.

d) To elaborate the technology of synthesis of mixed-type oxide catalysts by thermolysis of aqueous solutions of metal salts in a plasma flow and to test it on pilot installations.

Theoretical. A thermodynamic analysis of high-temperature heterophase systems, including the initial substances, plasma and reaction products, was made to determine limiting temperatures of the process, pressures and specific power consumptions. For this, we employed the method of maximum entropy [7]. As the initial raw material, we used nitrates, carbonates, sulphates, and chlorides of the corresponding metals. Oxygen, nitrogen, steam or air served as a plasma-forming gas. Mass ratios of the solution and the plasma-forming gas were chosen in the limits from 1 to 10. The mass concentration of the raw material in terms of the sum of metal oxides was varied from 5 to 29%. Calculations were performed in the temperature range of 300–5000 K at pressures from 10^4 to 10^7 Pa.

As a result of the thermodynamic analysis of systems, we determined the following synthesis conditions for oxide catalysts [8]: the pressure – 10^5 Pa, the temperature – 800–1600 K, the mass ratio of the solution and the plasma-forming gas – 3–5, the solution concentration in terms of the sum of metal oxides – 20–28%. As a plasma-forming gas, it is expedient to use air, and as initial substances, a solution of metal nitrates. In these conditions specific power consumptions are from 3 to 9 MJ/kg of the catalyst. On adding hydrogen, ammonia or methane to the plasma-forming gas, partially reduced catalysts can be obtained in which one of the components is a metal and the remaining are oxides.

The kinetics of the physical and chemical processes exerts a decisive influence on the properties of the catalysts obtained. We determined successively the rates of the underlying processes, namely, of heat and mass transfer between solution droplets and the plasma flow, thermal decomposition of metal salts, cooling (quenching) of the reaction products.

To determine the rate of heat transfer between solution drops and the plasma flow, we used the mathematical model described in [9]. However, unlike this model, which is based on the assumption that the flow is homogeneous, we allowed for a nonuniform drop size distribution over the initial section. For this, the experimentally determined law of droplet diameter distribution was approximated by a power law, i.e., it was assumed that there were five groups of droplets, each of which had the same droplet diameters, velocities and temperatures. In each two-phase flow cross-section its state was characterized by the following parameters: velocity, temperature, pressure and density of the gas as well as by the diameters of droplets, their velocities and temperatures, mass portion of droplets of each group. By solving the system of the equations of motion, heating

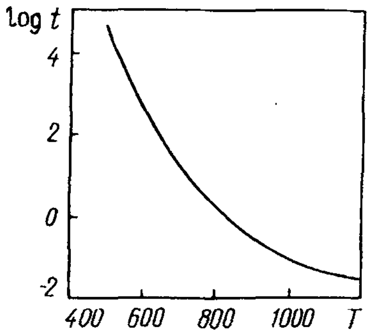

Fig. 2. Time of complete (99.5%) transformation of metal salts into a catalyst versus temperature.

and evaporation of droplets, in each section of the heterophase flow, we determined the droplet diameter and the velocity and temperature of the gas and droplets as well as of catalyst particles formed from them [8, 10].

Calculation results for an initial plasma temperature of 4000 K are given in Fig. 1. It is seen that the total rate of heat and mass transfer processes strongly depends on the initial droplet diameter. Thus, the heating rate of particles with a diameter of 7.5 μm is equal to $\sim 5 \cdot 10^6$ K/sec, while for particles sized to 45 μm it is smaller by an order of magnitude.

The kinetics of the reaction of thermal decomposition of salts was investigated by the predicted – experimental method [1]. Investigations have shown that at a temperature of 800–1600 K, which are typical for the described process, the complete transformation of a salt solution into metal oxides takes 10^{-3}–10^{-2} sec (Fig. 2).

A high rate of temperature variation is achieved also during quenching of reaction products which is necessary to prevent undesirable structural transformations of the catalyst. We investigated several methods of quenching: in a surface heat exchanger [12], by liquid injection [13], by gas blast into a liquid [14]. A comparison of the quenching methods has revealed that the highest cooling rate is achieved by liquid injection into reaction products. The cooling rate mainly depends on the liquid-to-gas mass ratio and the droplet diameter [5]. Thus, with this ratio being equal to nine, the mean cooling rate is $7 \cdot 10^4$ K/sec at temperatures from 2000 to 1800 K and $1 \cdot 10^4$ K/sec in the range 1200–400 K.

With a constant plasma-to-solution mass ratio, the plasma temperature and the diameter of solution droplets exert the most pronounced influence on the duration of the proceeding processes. An increase in the plasma temperature and a decrease in the droplet diameter reduce the time of the complete solution transformation into a catalyst, while a decrease in the temperature and an increase in the diameter result in increasing the time of this process. Depending on the initial values of parameters, the time of the process can change more than by an order of magnitude.

Calculations made using our elaborated mathematical models show that the time characteristic for the conditions discussed of the processes of heating and dehydration of solution droplets is $1 \cdot 10^{-3}$–$2 \cdot 10^{-2}$ sec, of thermal decomposition of salts – $2 \cdot 10^{-2}$–$3 \cdot 10^{-3}$ sec, of quenching of reaction products – $3 \cdot 10^{-3}$–$4 \cdot 10^{-2}$ sec, of the total process for the initial parameter values adopted in calculations – $6 \cdot 10^{-3}$–$9 \cdot 10^{-2}$ sec, i.e., the times of physical and chemical processes are comparable and, as a rule, are no more than hundredth or thousandth fractions of a second, while the total process covers $1 \cdot 10^{-1}$ sec.

Thus, the calculations showed that the method discussed shows promise, as compared to the traditional one [1], for multiple (by several orders) enhancement of the technological process of catalyst synthesis.

Experimental. Bearing in mind the complexity of the processes investigated, we made some simplifying assumptions in developing their mathematical models [8]. Among those, the assumptions of instantaneous mixing of solution droplets with the plasma flow as well as of cross-sectional isothermicity of heterophase flow are the strongest ones. In actual practice mixing is not instantaneous, there is a radial temperature gradient in the flow, which must increase the time of residence in the reactor. To refine space-time characteristics of the processes, to determine technological parameters of catalyst synthesis as well as to study the influence of the synthesis conditions

TABLE 1. Influence of the Technological Parameters on the Temperature and Residence Time of a Substance in the Reactor and on Activity of the Catalyst of Low-Temperature Transformation of Carbon Monooxide

Nos.	Experimental conditions					Experimental results				
	N	L	G_s	G_g	C	T		$t\cdot 10^3$		K
						calc.	exper.	calc.	exper.	
1	49.20	650	2.0	0.75	10.5	1177	1158	31	309	5.25
2	49.45	850	2.5	0.75	6.5	1102	1065	32	823	6.75
3	31.60	450	2.5	0.75	14.5	1002	998	46	236	1.88
4	24.55	850	3.0	0.75	2.5	661	648	66	407	2.35
5	33.20	850	1.5	1.00	14.5	1016	963	43	573	1.37
6	41.20	1050	1.5	1.00	6.5	1084	998	34	805	2.83
7	40.90	850	2.0	1.00	2.5	1056	968	39	255	3.65
8	40.70	650	2.5	1.00	10.5	1094	1058	36	777	3.25
9	49.50	450	1.5	1.25	2.5	1390	1282	39	407	1.25
10	24.50	450	2.0	1.25	10.5	924	813	65	324	6.10
11	33.35	1050	2.0	1.25	14.5	962	828	43	464	6.13
12	24.98	1050	3.0	1.25	6.5	717	648	67	765	1.90
13	32.90	650	1.5	1.50	2.5	1009	938	48	407	4.80
14	24.50	650	2.5	1.50	10.5	834	768	67	909	2.20
15	41.00	450	3.0	1.50	6.5	1029	893	88	609	4.20
16	49.70	1050	3.0	1.50	14.5	1101	998	33	614	4.00

on catalyst properties, we carried out a cycle of experimental studies on a specially designed plasmochemical pilot installation [16].

The main units of the installation were: a tank with a solution of salts, a plasmochemical reactor with three electric-arc plasma generators and a pneumocentrifugal nozzle installed on its cover [16]. The plasmochemical reactor represented a cylinder with an inner diameter of 100 mm and a length from 450 to 1050 mm regulated by a set of sheet steel drums. In a bag-type filter use was made of filtering glass fabric or metal-ceramic elements. Air served as the plasma-forming and cooling gas. The initial substances were aqueous solutions of nitrates of the corresponding metals.

On the installation we studied successively the thermal and gasdynamic structures of plasma and aerosol jets as well as of the entire flow in the reactor [17, 18]. It is established that a plasma jet has a shorter, as compared to theory, length of the initial section and is strongly turbulized. The dimensionless values of the velocity head, specific heat flux and temperature fade rather quickly along the jet axis, and each of them is described by a common curve [17].

To obtain an aerosol, we designed a combined pneumocentrifugal nozzle which provided a well filled aerosol plume with a characteristic droplet diameter of 10–60 μm, as evidenced by the dynamic head distribution with respect to its radius and longitudinal axis [19].

The distribution of the specific heat flux in the mixing zone of the plasmochemical reactor is essentially nonuniform with respect both to its length and radius, which is attributed to inhomogeneity of mixing jets as well as to heat losses through the reactor wall. The uniformity of the specific heat flux distribution in the reactor cross-section depends mostly on an angle of convergence of the plasma jets with the aerosol jet. Investigations have shown that the cocurrent input of plasma jets at an angle of 63° to the longitudinal reactor axis is the most efficient one [18].

To verify the results of kinetic studies obtained by mathematical models as well as to relate synthesis conditions to catalyst properties, we carried out experiments in which the parameters were varied as follows: the

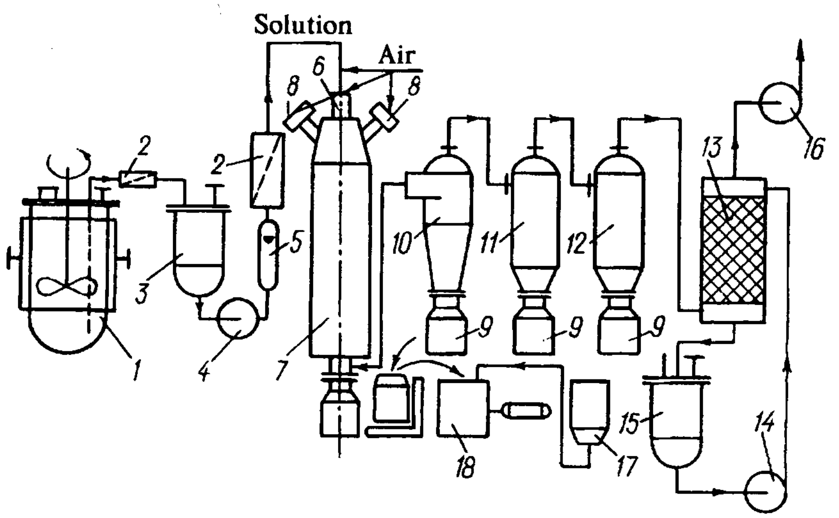

Fig. 3. Schematic of plasmochemical pilot installation intended for synthesis of oxide catalysts: 1) reactor for solution preparation, 2) filter, 3) batcher, 4) metering pump, 5) flowmeter, 6) nozzle, 7) plasmochemical reactor, 8) plasma generator, 9) bunker, 10) cyclone, 11) primary filter, 13) adsorber, 14) centrifugal pump, 15) tank, 16) vacuum pump, 17) decanter, 18) mixer.

electric power of the plasma generators from 20.5 to 49.7 kW; the reactor length from 0.45 to 1.05 m; the solution flow rate from 1.5 to 3 g/sec. On the installation, we obtained one-, two-, three- and four-component oxide catalysts. As an exameple, Table 1 provides experimental results for catalysts with the composition $CuO\cdot ZnO\cdot Al_2O_3$.

As evident from the table, the maximum discrepancy between the mean-mass temperatures of reaction products at the reactor outlet calculated by mathematical models and those measured experimentally does not exceed 20%. As for the total time of heating and dehydration of solution droplets, their values differ from the experimentally found time of residence in the reactor almost by an order of magnitude. This discrepancy is explained by the fact that the mathemtaical models did not account for mixing of the aerosol jets with the plasma flow or the nonuniform distribution of the flow temperature and velocity in the reactor cross-section.

An analysis of the experimental data from Table 1 has also shown that the catalyst activity depends mainly on the temperature and residence time in the reactor, which, in turn, are functions of the electric power of the plasma generators and the reactor length; in this case, the catalyst activity versus power and reactor length passes through a minimum. We can expect that with decreasing power and reactor length, the synthesis proceeds in less strict conditions, providing a maximum specific surface and, consequently, the highest catalyst activity. An increase in the reactor power and its length favors an increase of the number of active centers per unit area of the surface. Simultaneously, the specific surface decreases; however, the contribution of the former effect turns out, apparently, to be more considerable in the investigated region. It might be expected that a further advance in either the "positive" or "negative" directions would result in an increase in catalyst activity. However, this does not occur, since with decreasing power and reactor length beyond some values, thermal decomposition of salts does not manage to occur, while with increasing those parameters the specific catalyst surface abruptly decreases due to the high temperature and prolonged duration of the process. As a result, the catalyst activity decreases in both cases.

Next, the crucial problem is chemical homogeneity of synthesized catalysts (degree of dispersion of the active components). We analyzed the chemical composition of catalyst particles by the methods of Auger electronic and x-ray photoelectronic spectrometry, secondary ion mass-spectrometry, as well as of x-ray microanalysis. As investigations showed, the particles of two- and multicomponent catalysts were distinguished by highly homogeneous component distributions. This is explained by the fact that the chemical composition (in terms of metal oxides) of a forming particle with a diameter of several micrometers must be identical to the composition of the droplet from which it was formed, while the composition of the droplet must be exactly the same as that of the solution. At the same time segregation of the components by the diffusion mechanism has not had time to occur because of the short duration of the entire process (Figs. 1 and 2, Table 1).

The catalysts synthesized by the plasmochemical method differed, as a rule, from those obtained by traditional methods in elevated specific (based on a unit surface area) catalytic activity, which is apparently attributable to the high degree of dispersion of the active components [20].

Based on the results of theoretical and experimental studies, we have developed a technological scheme which differs from the existing schemes in the use of a plasmochemical reactor in which the stages of heating and dehydration of solution droplets, thermal decomposition of the residue and cooling (quenching) of reaction products proceed as a single stage (Fig. 3). This scheme allows synthesis of powders of oxide catalysts with any number of components taken in an arbitrary ratio in a continuous high-rate process (the time of solution transforming into catalyst powder does not exceed one second); the technological process is easy to control, and it advantageously differs from the alternative technologies by a small amount of waste water.

A pilot plasmochemical installation with an output of 80 t/year intended for synthesis of oxide catalysts was designed and tested at an industrial enterprise. Long-term (for more than 1400 hours) tests proved its fitness for work, allowed determination of technological regimes and coefficients of discharge, confirmed the correctness of the calculated and experimental data obtained as well as the technicoeconomic efficiency of the production of catalysts.

CONCLUSIONS

1. As a result of the thermodynamic analysis of high-temperature heterophase multicomponent systems, the following synthesis conditions of oxide catalysts from solutions in a plasma flow were determined: the temperature 800–1600 K, the pressure 10^5 Pa, the mass ratio of the solution and plasma-forming gas – 3–5, the solution concentration based on oxides – 20–28 wt.%, the plasma-forming gas – air.

2. Using the mathematical model describing the processes of motion and heat and mass transfer of solution droplets and catalyst particles formed from them with the plasma flow and accounting for nonuniform droplet size distribution as well as the temperature dependence of thermophysical properties of substances, the total time of heating and dehydration of solution droplets was calculated not to exceed 10^{-3}–10^{-2} sec.

3. For the first time the process of rapid cooling (quenching) of the products of plasmochemical catalyst synthesis was studied systematically. For this, we developed mathematical models of quenching in a surface-type heat exchanger, by liquid or solid particles, by bubbling through a liquid layer. It was shown that the characteristic rate of quenching by the above methods was 10^4–10^7 K/sec, which is sufficient to prevent undesirable structural transformations in catalysts.

4. A method of synthesis of mixed-type oxide catalysts by pyrolysis of salt solutions in a plasma flow was developed and experimentally studied. The range of the working parameters of the process is determined. A number of oxide catalysts were synthesized and their properties studied. It was shown that the catalysts obtained by the developed method outperform, as a rule, alternative industrial catalysts with the identical chemical composition in the specific catalytic activity based on the unit surface and in heat resistance.

5. Based on the theoretical and experimental data, a technological scheme was suggested for synthesis of oxide catalysts by pyrolysis of aqueous solutions of metal salts in a plasma flow which provides a continuous regime and a high rate of the technological process (the time required to convert a solution into catalyst powder is not more than one second); matching, in the same apparatus, of the processes of heating and dehydration of a solution, thermal decomposition of salts, synthesis and cooling of reaction products as well as multiple decreasing (as compared to the technology of chemical coprecipitation) of the amount of waste water.

NOTATION

$\overline{a}$, $\overline{V}$, $\overline{W}$, dimensionless (based on the values in the initial section of the flow) values of droplet diameter, droplet and gas velocities, respectively; T, temperature, K; t, time, sec; N, total electric power of plasma generators, kW; *L*, length of the plasmochemical reactor, mm; G_s, solution flow rate, g/sec; G_g, flow rate of the plasma-forming gas, g/sec; *C*, solution concentration, wt.%; *K*, rate constant of the catalytic reaction, ncm^3 CO/(g·sec). Indices: g, gas; p, particle.

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