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SYNTHESIS AND REGENERATION OF CATALYSTS IN ELECTRIC ARC PLASMA

G. P. Vissokov

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The author considers the state-of-the-art in regeneration and synthesis of highly active catalysts in low-temperature electric-arc plasma. A plasmochemical method is developed and suggested for synthesis and/or regeneration of dead deactivated catalysts used in ammonia production. The author's relevant studies are surveyed.

Introduction. Plasmochemical synthesis (PCS) and/or regeneration of dead deactivated catalysts are a new trend in the theory and practice of heterogeneous catalysis. It is known that the activity of solid-phase catalysts is determined by their chemical and phase compositions, the crystalline structure, and the active specific surface area. A correlation is usually observed between the active and total specific surface areas of the catalysts. On the other hand, in low-temperature plasma (LTP) materials (metals, oxides, nitrides, carbides, etc.) are produced that have a highly developed specific surface area (up to several hundreds m^2/g) and a particle size of several tens of nanometers and usually exhibit a high catalytic activity [1-3]. When PCS of ultrafine powders involves chemical reactions and reaction products are effectively hardened, conditions are created for condensation of ultrafine particles (UFP) with a degenerate crystal structure and with numerous defects in the crystal lattice and these UFP exhibit a high catalytic activity in heterogeneous catalytic processes.

From analysis and generalization of accumulated experimental materials, studies of PCS and activation of catalysts can be divided into two main trends, namely, (1) plasmochemical production and activation of catalysts in the condensed phase and (2) plasma deposition of catalytically active compounds and composites onto carriers [3].

According to Roginskii's supersaturation theory [4], catalysts obtained under energy supersaturation should have a higher activity. The higher the rate of thermal energy supply to the system, the higher its energy supersaturation. For the highest energy supersaturation, the raw material supplied to the system should have a particle radius dispersed as close as possible to $R = \lambda/\alpha$ (λ is the thermal conductivity of particles and α is the coefficient of heat transfer from the heat-transfer agent to the particle).

When catalysts are produced by PCM, their synthesis can be carried out with the following conditions satisfied: high activity, good thermal stability, low sensibility to catalyst poisons, selectivity, mechanical strength, and a short period of formation of the active surface by reduction.

The high catalytic activity of plasma-produced catalysts is determined by their extensive specific surface area (i.e., high degree of fineness), defects of the crystalline structure, the phase composition, favorable distribution of catalytically active components over promoters (and vice versa), etc. With the PCM catalysts are synthesized at high temperatures and condense as high-temperature phases, which determines their higher thermal stability and effective operation. Optimal distribution of ingredients in the composition of plasma-produced catalysts decreases their sensibility to poisons, and the possibility of strict control of their composition ensures their selectivity. The extensive specific surface area of ultrafine plasma catalysts and numerous defects in the crystal lattice lead to their rapid reduction. Compression or deposition onto carriers provides the necessary mechanical strength of the catalysts.

There is a wrong opinion that plasmochemical catalysts are expensive. In view of the main advantages of plasmochemical processes (PCP) [5], namely, single-stage production, high temperatures and rates, miniaturized

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equipment, simple simulation, optimization and control, standard production equipment and organization, etc., it can be stated that the PCM used for production of catalysts proved its undoubted advantages. It should be borne in mind that the percentage of the cost of the catalysts in the total cost of the commercial production is not high (for example, in the production of ammonia it amounts to 2–3%) and, consequently, the cost of the catalysts is not a decisive factor [6].

Experimental. Synthesis and/or regeneration of catalysts are performed on a plasmochemical d.c. electric arc setup with controllable electric power of up to 15 kW and an output of 150 g/h. Its schematic diagram is presented in [1, 2].

Dead deactivated catalysts for reforming of natural gas (vapor conversion of methane), for low-temperature conversion of carbon oxide by steam, and synthesis of ammonia were synthesized and/or regenerated in electric arc LTP for the first time [7, 8]. A universal program is developed that was used for determination of equilibrium parameters of multicomponent heterogeneous Ni-Al-O-Ca-Mg, Cu-Zn-Al-O, and Fe-Al-K-Ca-Si-O systems (in the literature there are no data on these systems in high-temperature plasma) with different variants of initial compositions of the ingredients at 0.1 MPa in the temperature range 1000–3700 K (with a step of 300 K). Concentrations of particular compounds in the gas or condensed phase are plotted versus temperature with an equilibrium composition of the system [9].

Results and Discussion. Conditions of PCS and/or regeneration of some catalysts used in the production of ammonia [1-3, 7-21] are studied. It should be noted that depending on the parameters of the PCS and the type of plasmochemical reactor (PCR) (with "cold" or "hot" walls), catalyst specimens are obtained with different specific surface areas (particle sizes) and phases: for reforming of natural gas, up to 120 m^2/g (the main fraction is 20–60 nm), NiO, Al_2O_3, CaO, MgO, $NiAl_2O_4$ [2, 7-10, 12, 18]; for low-temperature conversion, up to 56 m^2/g (the main fraction is 10–60 nm, in some cases, up to 200 nm), CuO, Cu_2O, Cu, ZnO, Al_2O_3, $CuAl_2O_4$, $ZnAl_2O_4$ [2, 3, 7-10, 12, 18]; for synthesis of ammonia, up to 40 m^2/g (the main fraction is within 100 nm, in the case of regeneration, 10–300 nm), Fe_3O_4, Fe_2O_3, Fe_2O, $FeO \cdot Al_2O_3$, α-Fe, and γ-Fe [2, 3, 7-21].

The above described phase composition is recorded by x-ray diffraction analysis of the specimens and Mössbauer spectra of catalyst specimens for synthesis of ammonia of the type SA-1 produced by PCS [16].

A comprehensive physicochemical analysis of specimens produced and/or regenerated by the PCM was carried out with x-ray diffraction, x-ray phase, electron microscopic, divertographic chemical, and other methods. The dynamics and kinetics of formation of the active surface area by reduction are studied and the activity of the specimens as catalysts is determined: for reforming of natural gas (reduction and conversion degrees, output and efficiency are determined [2, 7-10, 12, 18]; for low-temperature catalysis of carbon oxide by steam with the use of a model gas that stimulates commercial gas at temperatures and volume rates of the vapor–gas mixture similar to those used in industry (we determined the activity, i.e., the conversion degree, residual content of carbon oxide, and thermal stability [2, 3, 7-10, 12, 18]); for synthesis of ammonia with the use of a stoichiometric nitrogen-hydrogen mixture at a volume rate of 30,000 h^{-1} and pressures of 0.1 and 30 MPa (we determined the activity (it appeared 15–20% higher than it is in a CA-1 catalyst), the relative conversion degree, rate constants, activation energy, specific activities, conversion degrees in deactivation, etc. [2, 3, 7-21]).

It is found experimentally that the optimal temperature range for the PCR that was used for synthesis of specimens with the highest degree of fineness and activity is 2000–3000 K with catalysts for reforming of natural gas, 2000–3800 K with catalysts for LTC of a carbon oxide by steam, and 1300–3000 K with catalysts for synthesis of ammonia.

The procedure of regeneration (activation) of dead catalysts is as follows [2, 9, 18]. In a PCR a substantial part of catalyst particles is in the gas phase. Effective hardening at the rate $dT/d\tau \cong 10^5-10^6$ K/sec removes the catalytic mass from the system in the condensed phase at a rate that provides a normal structure of crystal lattices of the components that form the system. Catalyst poisons, for example, oils, leave the system in the form of volatile gaseous products. Together with α-Fe, a dead deactivated catalyst for synthesis of ammonia also contains elemental iron (according to Mössbauer spectroscopy its content may be up to 90%), which is transformed into a metastable γ-modification as a result of hardening-induced heat shock. The catalyst is produced with the ratio Fe^{2+}/Fe^{3+} identical to the ratio contained in a fresh specimen, with an extensive specific surface area (10–30 m^2/g), and numerous defects in crystal lattices of iron oxides with completely bound Al_2O_3 in the $FeO \cdot Al_2O_3$ matrix. This is a reason for the high thermal stability of the regenerated specimens.

It seems to the point to mention that in reduction of iron oxides, in particular Fe_2O_3, by hydrogen in an electric arc LTP in a pilot plant, almost complete reduction was achieved, and the specific surface area of pyrophoric UF iron powder was 160 m^2/g. X-ray diffraction analysis and Mössbauer spectra show that the product contains α-Fe and superparamagnetic γ-Fe. As the hardening rate increases from 10^6 to 10^7 K/sec, the contents of γ-Fe increases from about 50% to almost 100%, respectively. Thus, the PCM can be used to produce UF high-temperature γ-Fe.

Results on the dynamics and kinetics of PCS-produced and/or regenerated catalyst specimens show [2, 9, 13-15, 21] that LTP treatment creates preconditions for production of catalytic composites that are reduced two to five times more rapidly in comparison with their commercial analogs.

The logarithmic straight lines in the curves $\log K = f(1/T)$ [9, 13, 15, 21] are parallel to one another, and, consequently, in the range of kinetic control of the processes (with the accuracy of determination of regeneration and activity) the activation energy is constant. According to the theory of active sites, if the process rate constant is higher at a constant activation energy, the activation is a consequence of an increase in the number of active sites per unit surface area, and if the activation energy decreases in the kinematic region of the processes, the activation results from an increase in the activity of the active sites. It is evident that PC-regenerated catalysts, especially those produced by PCS have more active sites per unit surface area as compared with commercial SA-1 catalysts, because of which the reduction rate is 2–5 times higher, and in synthesis of ammonia the catalytic activity is 15–20% higher, depending on temperature. Thus, the higher catalytic activity of PCS-produced and/or regenerated specimens is determined by the defective crystalline structure of catalytically active phases, the UF composition of particles that comprise the catalytic specimens (the crystallite size of catalytically active phases is in the range 10–40 nm), the distribution of UF components (promoters with a lower melting temperature are located predominantly on the surface of UF catalytic particles), high porosity, specific surface area, and dispersity of the phases, and optimal chemical composition of the specimens.

Specimens produced and/or regenerated by PCS exhibit higher thermal stability than commercial specimens as a result of formation of compounds with a high Taman temperature, for example, $NiAl_2O_4$ with catalysts for reforming of natural gas, $CuAl_2O_4$ with catalysts for LTC of carbon oxide by steam, and $FeO \cdot Al_2O_3$ with catalysts for synthesis of ammonia.

Dalmon's method of layer-by-layer dissolution of the surface of UFP shows that element impurities are distributed in accordance with the *a priori* concepts of successive condensation of the components, depending on condensation (boiling) temperatures. High-temperature impurities are located inside the UFP and low-temperature impurities are on the surface (for example, potassium oxide in the composition of UFP of the catalyst for synthesis of ammonia) [9].

The compensatory ballistic method was used to perform thermographic analysis of the catalyst specimens for synthesis of ammonia. At low magnetizing fields the Hopkinson effect is observed. The Curie temperature of the regenerated ferromagnetic catalysts depends on their composition and reduction degree and the Curie temperature of nonregenerated catalysts depends on the formation of solid solutions with iron oxides. Thermomagnetic hysteresis of catalysts depends on the regeneration degree, the highest heating temperature of specimens, and the heating and cooling rates. It should be noted that chemical interactions and crystallographic transformations in the catalysts have a significant effect [9]. A correlation was found between electronic interactions and magnetization in the ferromagnetic catalysts in the synthesis of ammonia.

Conclusion. The extensive specific surface area of PCS-produced and/or regenerated catalysts, their chemical composition, high rates of formation of the active surface by reduction, the defective crystal lattice of catalytically active phases and, to the greatest extent, the catalytic activity and thermal stability made these catalysts competitive with conventional commercial specimens for probable production in catalytic workshops.

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