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Some peculiarities of nano-dispersed catalysts synthesized or regenerated in an arc plasma conditions

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Abstract

In this review we present our considerations and investigations about:

- The thermodynamic and kinetic peculiarities of plasma-chemical processes (PCPs) for the preparation or regeneration of nano-dispersed catalysts (NDC).
- The mechanism of evaporation of micron-size particles under the conditions of powder-carrier high enthalpy chemically reactive plasma jets and the mechanism of condensation of NDC phases upon quenching.
- The correlation between the parameters of PCPs occurring in powder carrier chemically reactive high-enthalpy flows and the dispersity of the desired condensed NDC.
- The optimal PCPs parameters (average mass temperature, type and geometry of plasma-chemical mixing chambers and reactors, quenching, trapping of condensed phases, etc.) in neutral, reducing, oxidizing and reducing–oxidizing (redox) media, leading to the obtaining of the desired condensed catalysts with controlled dispersity, chemical activity, phase composition, crystal lattice defects, etc.
- The characterization of some properties of plasma-chemically synthesized and/or regenerated NDC (chemical, physicochemical, physical, catalytic, etc.).

Keywords: Nano-structured catalysts; Plasma-chemical preparation—activation, regeneration; Properties

1. Introduction

Three main directions are developed worldwide at present in the field of plasma-chemical synthesis, activation and regeneration of catalysts [1–4], namely: (a) plasma-chemical synthesis and/or regeneration of spent catalysts under the thermal plasma conditions, (b) deposition of catalitically active compositions on carriers by means of thermal plasma, and (c) catalysts activation under the high-frequency discharge, during their heterogeneous catalytic action. Our work has been carried out mainly in the first direction, namely to produce highly active, thermally stable and selective catalysts and/or to regenerate spent catalysts for the ammonia production, such as catalysts for methane steam conversion, catalysts for natural gas reforming, catalysts for low-temperature steam conversion of carbon monoxide and catalysts for the ammonia synthesis.

Taking into account first and foremost the features of the physical and chemical properties of the dispersed materials, including catalysts we consider the following classification (depending on the mean diameter of the particles) to be expedient—nano-particles: NP (ultra-dispersed: UD, including clusters) 1–50 nm; high-dispersed: HD (finely dispersed: FD) 50–500 nm; powders of micrometer sizes: 0.5–100 μm; roughly dispersed: RD >0.1 mm [4].

This review paper is aimed at summarizing the results of the original investigations of the author and his collaborators on the synthesis and/or regeneration of nano-dispersed catalysts under the conditions of thermal quasi-equilibrium arc plasma.

In this article we have presented our considerations and investigations about:

- The thermodynamic and kinetic peculiarities of plasma-chemical processes (PCPs) for the preparation or regeneration of nano-dispersed catalysts (NDC).
- The mechanism of evaporation of micron-size particles under the conditions of powder-carrier high enthalpy

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chemically reactive plasma jets and the mechanism of condensation of NDC phases upon quenching.
- The correlation between the parameters of PCPs occurring in powder carrier chemically reactive high-enthalpy flows and the dispersity of the desired condensed NDC.
- The optimal PCPs parameters (average mass temperature, type and geometry of plasma-chemical mixing chambers and reactors, quenching, trapping of condensed phases, etc.) in neutral, reducing, oxidizing and redox media, leading to the obtaining of the desired condensed catalysts with controlled dispersity, chemical activity, phase composition, crystal lattice defects, etc.
- The characterization of some properties of plasma-chemically synthesized and/or regenerated NDC (chemical, physicochemical, physical, catalytic, etc.).

2. Methods and models

For the first time in practice, worldwide:

- The equilibrium compositions of the multi-component heterogeneous systems Ni–Al–O–Ca–Mg, Cu–Zn–Al–O and Fe–Al–K–Ca–Si–O have been established in gaseous and condensed phase, starting from different proportions of the ingredients, at a pressure of 0.1 MPa in the temperature range of 1000–3700 K, by means of universal program [4,5]; a method has been developed for the calculation of the changes in the Gibbs (free) energy during the phase transitions [4,5].
- One- and two-dimensional models of the motion, heating, melting and evaporation of micron-size particles in the plasma jet [4–8] and of the condensation of nano-sized catalyst particles from the gaseous phase have been proposed, describing the experimental results with an accuracy sufficient for engineering purposes. In order to obtain nano-dispersed powders (NDP) with the highest possible dispersity and purity, conditions should be established in the plasma-chemical reactor (PCR), under which the time of evaporation of the raw material should be equal to or shorter than the contact time of the reagents.
- A method has been proposed and developed, for plasma-chemical regeneration of exhausted, deactivated catalysts (and for synthesis of mentioned catalysts, in some cases) used in ammonia production processes, in natural gas reforming (steam conversion of CH_4 (SCM)), in low-temperature steam conversion of CO (LTSCCO) and in NH_3 synthesis (AS). These catalysts revealed in numerous cases higher catalytic activity, selectivity and thermal stability than their commercial analogues.

3. Experimental

The plasma-chemical synthesis (PCS) of nano-dispersed powders (NDP) comprises the following main stages:

1. *Reagents introduction and their mixing with the plasma jet.*
2. *Heating, melting and evaporation of reagents*: Duration of the above-mentioned stages determines the residence time of reagents in the plasma-chemical reactor (PCR). The residence time decreases when turbulent high-enthalpy plasma is used, and size of powder reagents is less than 50 μm. Condensed phase evaporation is the process rate-determining step in heterogeneous PCP [9].
3. *Chemical reaction*: Conducting the chemical reaction in gaseous phase ensures high purity of the product. The reaction of gaseous reagents and not-evaporated solid particles causes changes in the chemical composition of particles surface layer. This is due to the slow diffusion of reagents to the core of the particle. In some cases the slow diffusion limits the entire evaporation of the particles.
4. *Reaction of plasma flow with cooling reagents (quenching) aimed at*: (a) Fixing the chemical composition of desired products, (b) obtaining highly dispersed condensed phase and (c) (sometimes) partially caring out additional chemical reactions. Product with desired nano-dispersed particles is obtained at fast cooling of reaction mixture, i.e. at quenching rate $dT/d\tau \cong 10^4$ to 10^5 K/s. All mentioned above grounds the necessity of models for condensation.
5. *Trapping of NDP*: This stage is carried out mainly in cyclones with mechanical (bag, cartridge), electrical, etc. filters. Depending on the process conditions (temperature, reagents' concentration, condensation conditions, etc.) the final product is obtained as epitaxial film, fiber-crystals, poly-crystals, amorphous or NDP. To obtain nano-disperse particles (NDPs) it is necessary to ensure process conditions leading to high rate of crystal nucleation and low rate of crystals growth.

The peculiarities of quasi-equilibrium PCP used in the technologies for the production of NDC have been developed and constructed for the first time in Bulgaria. They are intended to the processing of ingredients of a definite purity, with a capacity of up to 5 t per year and power of up to 100 kW. These investigations started in 1970s of the 20th century in the University of Chemical Technology and Metallurgy, Sofia. They continued in the Institute of Electronics at Bulgarian Academy of Sciences.

Different variants have been designed and constructed: plasma-chemical mixing chambers and PCR (cylindrical, conical, with "cold" or "warm" walls [4,9,10]; powder-feeding devices (with fluidized bed, with pistons, with pneumatic transportation); powder-carrier chambers (chamber-like, with partitions, settlers); filters (mechanical and electrical, cyclones), etc.

Generalized scheme of the laboratory installation designed and built by us, for plasma-chemical production of catalysts and/or regeneration of spent catalysts has been presented in some of our papers [4,11,12].

4. Results and discussion

High dispersity, respectively high specific surface represents the characteristic feature of the NDPs obtained under conditions of low-temperature plasma (LTP). Conditions of NDP formation in gaseous phase allow to obtain very small particles, including particles with size of critical crystal nucleus following the scheme:

1. Association of molecules of the substance's vapors—basic process that is typical for each condition of the vapor.
2. The association is due to the van der Waals interactions of gaseous (vapor) molecules. Because the van der Waals bonds are weaker compared to the covalent chemical bonds in molecules entering the complex, the molecules keep their structure and properties.
3. Complexes are formed when at least three molecules collide. As a result, some of the colliding molecules form relatively stable aggregates and the other carry away the heat as a kinetic energy of translation.
4. It is assumed that complex associates are in thermodynamic equilibrium with the separate molecules and possess the same energy of translation. The average lifetime of complexes exceeds many times the time of molecules' collision. At temperature below the critical temperature of evaporation, the bond-energy is much higher than the thermal energy. That is why dimers and trimers are stable. Bond-energy of each molecule from the complex is increased with increase in the complex size.
5. Real vapor is assumed as mixture of simple gases consisting of single molecules, dimers, trimers, etc. When the system is in equilibrium, decomposition of any of gaseous complexes is compensated by formation of more simple complexes of other gases. Processes that take place are similar to the reversible chemical reactions.

The particles' size is quite bigger compared to the size of critical nucleus, because it is difficult to realize condensation in the entire volume of the system, which condensation leads to the over-saturation decrease only due to nucleation. Coagulation takes place along with the condensation.

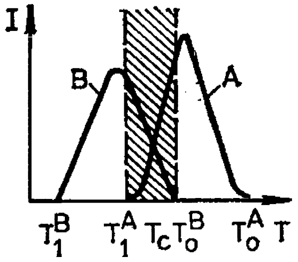

Fig. 2. Probability distribution of formation of different crystalline modifications as function of temperature.

The scheme of formation of nano-particle structures is the following (Fig. 1).

In our opinion, the mechanism of NDP production under the conditions of LTP is the following: as a result of the chemical reaction and in conformity with the system's thermodynamics, a certain level of saturation is reached in the flow at which level nuclei appear. The nuclei are able to grow to small drops both independently or through coagulation, if quenching is not carried out at exact time and place.

Changing the temperature conditions of reagents and residence time of reagents into the flow can control the crystallization process. Different crystalline modifications of the same plasma-chemically synthesized powders (PCSP) can be obtained.

A system is shown in Fig. 2, in which system the crystallization could lead to formation of a high-temperature modification, B. The crystallization starts at temperature T_0, when it is characterized by the bond energy of the corresponding crystalline lattice, passes through a maximum and ends at temperature T_1, when the liquid particles are already unable to migrate to vacancies in the crystalline lattice. Parameters of A and B curves, as well as curves mutual situation, are determined by the particularities of each individual system. A high-temperature modification A is formed during the initial crystallization stage, at $T > T_c$. Predominately phase

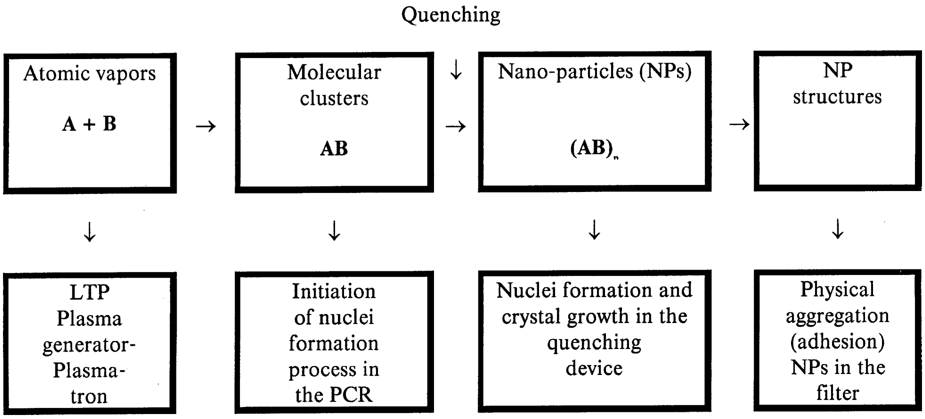

Fig. 1. Scheme of formation of nano-particle structures.

B is crystallized at temperature $T < T_c$. Both phases are formed in the temperature interval T_1^A–T_0^B. The rate of crystallization is lower than the rate of condensation when the temperature is decreased because the condensation process is monotonously speeded up by the temperature decrease, while the rate of crystallization is initially increased and then sharply decreased by the temperature decrease. Due to this delay, that is enhanced when the NDP is obtained under conditions of LTP by the high quenching rate, large portion of aggregates formed in the temperature range T_0^A–T_1^A are crystallizing, using the way A with formation of defective crystalline structures. The quenching rate is also a factor that determines the size of particles formed. This is due to the fact that the probability for kinetic collisions of nuclei formed in the reagents' stream during the condensation is higher at high temperatures compared to the probability at low temperatures. That is why at high temperatures, i.e. at low rates of quenching, the probability of formation of particles with larger size is higher than the probability of formation of particles with smaller size. And vice versa—at high quenching rate the probability of NDPs formation is high. At more effective quenching, i.e. with higher rate, the quality of the nano-dispersed product in state A is higher—the fact that is in conformity with experimental results.

On the basis of developed plasma-chemical processes for preparation and/or regeneration of nano-dispersed catalysts in a condensed state [2–25], performed in neutral (Ar, He), reducing (H_2, C, CO, NH_3, CH_4, C_3H_8 and C_4H_{10}), oxidizing (O_2, air, CO_2) and redox media, the respective optimal parameters have been determined (average mass temperature—Tables 1 and 2, type and geometry of plasma-chemical mixing chamber and reactors, mode and rate of quenching, specific surface, powder trapping, etc.), leading to the obtaining of the desired condensed NDC of controlled dispersity (specific surface), catalytic activity, morphology, structure (crystal lattice defects) and phase composition.

The possible mechanism of regeneration or activation of the spent catalyst for ammonia synthesis, for example, is as follows: the gaseous-phase portion of the catalyst is quenched efficiently at rate of $dT/d\tau = 10^5$ to 10^6 K s^{-1}—this is so fast as not to allow the normal build-up of the catalyst-components crystal lattices. Poisons (such as oil) deposited on the surface of the deactivated catalyst particles leave the system as volatile gaseous products. The deactivated catalyst contains elemental Fe (up to 90%, according to the Mössbauer spectra [4,17–20]) which, as a result of the thermal shock during quenching, is frozen in the metastable γ-modification (up to 10 mass%), besides the α-Fe. Thus, a catalyst is produced that is characterized by almost the same Fe^{2+}/Fe^{3+} ratio as in the CA-1 catalyst, a large specific surface, numerous defects in the iron-oxides crystal lattice, and a complete bonding of Al_2O_3 in $FeO \cdot Al_2O_3$; the latter determines the high thermal stability of the samples regenerated.

For the first time in practice worldwide we have developed a PCP for the production of ND γ-Fe with specific surface of up to 160 m^2/g by reduction of iron oxides with hydrogen under the conditions of electric arc LTP. A possibility has been ensured for controlling the α- to γ-Fe ratio in the desired catalytically active product by the quenching rate applied.

Various properties of the ND or FD catalysts have been determined, i.e. physical (morphology, structure, mechanical properties, specific surface (dispersity), loose mass, magnetic, thermal, electric properties, etc.), chemical (chemical activity, pyrophoric properties, viscosity, pH, hydrophility, phase composition), physicochemical (catalytic activity and

Table 1
Plasma-chemical processes developed for NDP production in oxidizing medium—synthesis or regeneration of catalysts

Basic reaction	NDP specific surface (m^2/g)	Temperature range (K)
$(Ni, Al) + O_2 = NiO + Al_2O_3 + NiAl_2O_4$	Catalysts for steam conversion of CH_4; up to 110	2000–3000
$(Cu, Zn, Al) + O_2 = CuO(Cu_2O) + ZnO + Al_2O_3$	Catalysts for steam conversion of CO; up to 45–51	Up to 5100
$3Fe + 2O_2 = Fe_3O_4$	Catalysts for ammonia synthesis; up to 20–30	1100–3400
$4Fe + 3O_2 = Fe_2O_3$		1100–3400
$2Fe + O_2 = 2FeO$		1500–3500

Table 2
Plasma-chemical processes developed for NDP production in reduction-oxidizing medium

Basic reaction	NDP specific surface (m^2/g)	Temperature range (K)
(I) $NiO + H_2 = Ni + H_2O$	Catalysts for steam conversion of CH_4; up to 40	$(1–4) \times 10^3$
(II) $2Ni + O_2 = 2NiO$		$(4–1) \times 10^3$
(I) $(CuO, ZnO, Al_2O_3) + H_2 = (Cu, Zn, Al) + H_2O$	Catalysts for lower temperature steam conversion of CO; up to 50	$(1–4) \times 10^3$
(II) $(Cu, Zn, Al) + O_2 = CuO(Cu_2O) + ZnO + Al_2O_3$		4×10^3 to 300
(I) $Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$	Catalysts for ammonia synthesis; up to 10–30	$(1–4) \times 10^3$
(II) $3Fe + 2O_2 = Fe_3O_4$		4×10^3 to 300

reduction degree of the oxides in the catalysts' composition, impurities' distribution in the bulk or on the surface of NDC), by means of different methods: X-ray phase and structural analysis, electron microscopy, IR and Mössbauer spectroscopy, emission-spectral, derivatographic, thermomagnetic methods, by studying the dynamics and kinetics of formation of the active surface upon reduction (the "plasma" catalysts undergo reduction two to five times faster than their respective commercial analogues), etc. [2–25].

The following determinations have been performed for some catalysts:

- A catalysts for natural gas reforming [4–7,12,15,16,20]—degree of CH_4 conversion, productivity and efficiency.
- A catalysts for low-temperature steam conversion of CO [4,20] (using a model gas, simulating the commercial one, for temperatures and volume rates of the steam–gas mixture similar to those applied in commercial processes)—activity (degree of conversion, residual CO content, thermal stability).
- A catalysts for ammonia synthesis [4,17–20] or regenerated catalysts [4,8,11,13,18,20] (using a stoichiometric nitrogen–hydrogen mixture, volume rate of 30,000 h^{-1} and pressures of 0.1 and 30 MPa)—activity (by 15–29% higher than that of the CA-1 catalyst), rate constants, activation energy, relative activities, degree of conversion upon deactivation, etc.

Concepts have been developed of the relationship between some properties (dispersity, respectively specific surface, crystal lattice parameters) of NDC and the plasma-chemical processes (PCPs) parameters: electric potential and electric current of the discharge, electric power consumed, coefficient of efficiency, consumption, proportion of the reagents and place of feeding, type and consumption of plasma-forming and powder-carrier gases, average mass temperature and enthalpy of the active part of the arc as well as in the plasma-chemical reactor (PCR), temperature profile and gradients in the reactor space, contact time of the reagents, type, rate and place of quenching of the reaction products, way of trapping of NDC, etc. The establishment of the relationships between the unique properties of the NDC and the PCPs enable the production of catalysts under conditions close to the optimum ones.

The various kinetic studies carried out on the above-listed plasma-chemically synthesized (PCS) and/or regenerated catalysts used in the technologies of ammonia production and the explanation of the PCS and/or regeneration create a basis for the development of a concept concerning the enhanced catalytic activity and thermal stability of "plasma" catalysts, as compared to those of traditional commercial marks. The increased relative catalytic activity is due to the rise of the pre-exponential multiplier in Arrhenius equation at a constant activation energy [4,17–20], i.e. the plasma-chemical treatment results in the generation of a relatively higher number of active centers per unit area of the catalyst, as compared to conventional commercial catalysts. The enhanced thermal stability of "plasma" specimens is due to the incorporation of structure-stabilizing promoters in the crystal lattice of the catalytically active phases (e.g. Al_2O_3 in the crystal lattice of Fe_3O_4, included in the composition of the non-reduced catalyst of ammonia synthesis).

Thus, the enhanced catalytic activity of the PCS and/or regenerated specimens is due to: the defective crystalline structure of the catalytically active phases; the crystallite size of the catalytically active phases (within the limits from 10 to 40 nm); the distribution of the ND components (the lower melting promoter additives are situated predominantly on the surface of the catalytic NDP); the high porosity, specific surface and dispersity of the phases; the appropriate chemical composition of the specimens.

Within the framework of the complex physicochemical analysis the compensation ballistic method has been performed [4,20]. For low values of the magnetizing field, the Hopkinson effect was observed for a catalyst for ammonia synthesis. The Curie temperature of the reduction ferromagnetic catalysts for ammonia synthesis depends on the composition and their reduction degree, and that of unreduced catalysts is determined by the formation of solid solutions with the ferrous/ferric oxides. The thermal magnetic hysteresis of the catalysts depends on the reduction degree, the highest heating temperature of the samples, as the chemical interaction and the crystallographic conversion in the catalysts have a significant impact. A correlation is observed between the electron interactions and the magnetism of the ferromagnetic catalysts for ammonia synthesis [4,20]. PCS NDC are characterized by a large specific surface (from several m^2/g to several tens m^2/g), i.e. by a high dispersity (the average diameter of the particles is usually below 100 nm, and in some cases is even below 50 nm); the particle size is usually characterized by a normal logarithmic distribution [26], but some times—by bi-dispersed distribution [27]. Spherical and spheroidal shape is characteristic for many of NDPs. It is clear that plasma-chemical processes obtain condensed particles with spherical shape, where the rate of phase transitions is very high. This includes transitions with liquid phase participation, where the naturally formed solid phase should be drop-shaped. But the phase transition rate is so high that the particles are unable to obtain the shape characteristic for their crystal state. At slower quenching of the gaseous phase crystals with different degree of perfection are obtained.

Low loose mass (0.5–0.05 g/cm^3), tendency to aggregation, crystalline structure (with defects either on the surface or in the bulk) or amorphous one (mainly with a spherical or spheroid shape), increased chemical activity (pyrophoric activity), are among the important peculiarities of NDC.

In the case when the respective metal in the composition of catalysts is present in more than one oxidation degrees (e.g. iron oxides), the chemical composition of the ND metal depends on the average mass temperature in the plasma-chemical reactor (PCR) (the temperature profile of the reactor), on the stoichiometric excess of the oxidant and on the reaction duration.

Table 3
Some technological parameters and physicochemical properties of NDC synthesized in LTP

Nano-dispersed substance	Particle size (nm)	Passivation agent	Composition of the protection layer
Mo	<100	CO	$Mo(CO)_6$
α-Fe, γ-Fe	10–100	N_2, CO (0.5% O_2)	Fe_xO_y, $Fe(CO)_5$
CA-1 type catalyst for AS	20–60	CO_2, N_2 (0.5–1% O_2)	Fe_xO_y
Catalyst for LTSCCO	10–40	N_2 (1% O_2)	CuO, Cu_2O
Catalysts for SCM	10–30	N_2 (1–2% O_2)	NiO

Appropriate sorbates have been found that were able to decrease the high chemical activity of some NDC, expressed in some cases as pyrophoric activity. They are as follows: CO for Mo, N_2 or CO containing 0.5 vol.% O_2 for Fe; CO_2 or N_2 containing 0.5–1% O_2 for CA-1 type catalyst for ammonia synthesis (AS); N_2 with 1% O_2 for catalyst for LTSCCO and N_2 containing 1–2% O_2 for catalyst for SCM (Table 3).

Plasma-chemically synthesized mono-component NDP (metals or oxides) with size not exceeding 50 nm are characterized by a relative decrease a of the period of the crystal lattice by up to 0.9%:

$$a\,(\%) = \frac{(a_{\mathrm{MS}} - a_{\mathrm{NDPs}}) \times 100}{a_{\mathrm{MS}}}$$

where a_{MS} is the period of the crystal lattice of monolithic sample and a_{NDPs} the period of the crystal lattice of nano-dispersed particle. The relative decrease a gives a quantitative notion for the relative change of the crystal lattice parameter in NDPs. If $a > 0$, $a_{\mathrm{NDPs}} < a_{\mathrm{MS}}$; if $a < 0$, $a_{\mathrm{NDPs}} > a_{\mathrm{MS}}$. In the case of impurity containing NDP (as in catalysts for example), the period of the crystal lattice can decrease under the action of Laplace pressure P [$P = \alpha(1/R_1 + 1/R_2)$], where R_1 and R_2 are the bending radius of the surface in a given point in two mutually perpendicular planes, α is the surface tension or increase due to incorporation of promoters in the basic phase.

After effective quenching of the desired products, phases are formed, which are usually high-temperature modifications with minimum free surface energy, i.e. with maximum densely packet crystal lattice, and which could be without analogues in the bulky specimens. Using the method of Delmon [4,20] for layer gradual dissolution of the NDC surface, it is shown that the elemental impurities (as a promoters) are distributed in conformity with the a priori concept of consecutive condensation of the components, depending on the respective values of the condensation (boiling) temperature. Higher-boiling impurities are situated in the bulk of NDC (e.g. W) while impurities (promoters) condensing at lower temperature are found on the surface (e.g. K_2O) in NDP of the catalyst for ammonia synthesis.

In our opinion, further investigations in the field of NDC obtaining under the conditions of thermal LTP have to be aimed at solving the following problems:

- Creation of effective plasma-chemical devices (installations) able to ensure entire evaporation of raw materials.
- Studying the peculiarities of the condensation and crystallization of nano-dispersed phases that proceed simultaneously with chemical reactions under non-equilibrium conditions (i.e. at quenching).

5. Conclusions

The plasma-chemical method offers unique advantages in the case when alternative methods for the production of NDC with specific properties are not available. The experimental results concerning PCP parameters can be used in the design of pilot-production plants by taking into account the criteria for their modeling and, in some cases, of commercial-scale-installations. For practicable applications, some of developed PCP for preparation of NDC should be adapted to production-scale conditions. This could be realized in any chemical or metallurgical plant, interested in the production of NDC with unique properties.

The large specific surface of PCS and/or regenerated catalysts, their chemical composition, the high rates of formation of their active surface by reduction, the defective crystal lattice of the catalytically active phases and, what is most important, their high catalytic activity and thermal stability make them potentially competitive to traditional commercial catalysts upon their eventual production in specialized work-rooms.

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