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Plasma–chemical preparation and properties of catalysts used in synthesis of ammonia

G. P. VISSOKOV
Institute of Electronics, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee Blvd., Sofia 1784, Bulgaria
E-mail: ie@bgearn.bitnet

Thorough investigations, including thermodynamic calculations, were carried out on the plasma–chemical preparation of ammonia-synthesis catalysts in a quasi-equilibrium electric-arc low-temperature plasma. Obtaining samples with maximal catalytic activity and thermal stability necessitated that the plasma–chemical process take place in a "cold wall" plasma–chemical reactor within the 1000–3000 K temperature interval; the activity of the "plasma" catalysts thus produced was higher by 15%–20% than that of their conventional industrial analogues. Various physicochemical and kinetic techniques were applied to characterize in detail the catalysts synthesized. Some considerations are given concerning the possible future development of plasma–chemical production of catalysts. © *1998 Kluwer Academic Publishers*

1. Introduction

The theory and practice of heterogeneous catalysis have demonstrated that the activity of solid-phase catalysts is determined by their chemical and phase content, crystal structure and active specific surface. A similarity of slopes is usually observed between the catalysts' active and total specific surface dependencies. On the other hand, it is also known that one can use low-temperature plasma (LTP) to produce condensed-phase compounds (metals, oxides, nitrides, spinels, etc.) that have a highly developed specific surface with the size of ultradispersed particles (UDP) of the order of a few tens of nanometres and also manifest a high catalytic activity [1]. When the plasma–chemical synthesis (PCS) of ultradispersed (UD) powders is accompanied by chemical reactions, and when an effective quenching of the reaction products takes place at a rate $dT/d\tau = 10^5$–10^6 K s^{-1}, then conditions are created for condensation of UDPs with an unusual distribution of the additives [2], degenerated crystal structure [2, 3] and numerous defects in the crystal lattice; these also exhibit a high catalytic activity in heterogeneous catalytic processes [1–4]. The plasma–chemical technique (PCT) thus turns out to be efficient in synthesizing highly active catalysts.

Although at present the investigations on the preparation of highly active catalysts are still at the laboratory, pilot-plant, or patenting stages, reports can be found in the specialized literature on the synthesis and activation of catalysts under LTP conditions [1–6]. By analysing and summarizing the existing modest amount of experimental data, the studies on the plasma–chemical synthesis and activation of catalysts can be classified into two main groups: (1) plasma–chemical fabrication and activation of catalysts in the condensed phase, and (2) plasma deposition of catalytically active compounds and mixtures on substrates [4, 7, 8].

The manner of catalyst preparation affects such important properties as its specific surface, porosity, density, mechanical strength, thermal stability, etc. This is why the preparation procedure is sometimes as important as the catalyst's chemical composition.

According to Roginskiy's theory of oversaturation [9], catalysts obtained under the conditions of energy oversaturation must possess an increased activity. The extent of energy oversaturation of a system increases with the increase of the rate of heat transfer to it

$$\frac{dQ}{d\tau} = \alpha(T_1 - T_2)\,dF_1 \qquad (1)$$

which is proportional to the difference between the temperature, T_1, of the heat carrier (plasma in the case considered here) and T_2 of the substance heated (micrometre-size particles), as well as to the surface, dF, separating them. If one assumes that the material treated is of spherical shape with radius R, then the specific surfaces of particles belonging to different fractions will be inversely proportional to their radii

$$\frac{F_1}{F_2} = \frac{R_2}{R_1} \qquad (2)$$

or, the smaller the particles, the higher will be their specific surface. However, decreasing the particles size is only reasonable to a certain limit, defined by Biot's criterion

$$B_i = \frac{\alpha R}{\lambda} = \frac{R/\lambda}{1/\alpha} \qquad (3)$$

where λ is the particle coefficient of heat conductivity and α is the coefficient of heat transfer from the heat carrier to the particle.

The numerator in Equation 3 characterizes the resistance to heat propagation from the surface to the centre of the particle, and the denominator, that to transfer of heat from the heat carrier to the particle surface. When R is large, the heat-transfer process is limited by the heat resistance of the particle, and inversely, for small R, by the heat resistance of the phase interface. There obviously exists a value of R for which the two quantities are equal ($B_i = 1$)

$$R = \frac{\lambda}{\alpha} \tag{4}$$

To create maximal energy oversaturation, the raw materials must be predispersed to a particle size as close as possible to that defined by Equation 4. The calculations for the case of catalysts used in the synthesis of ammonia (mainly iron oxides or elemental iron) yield a value of approximately 50 μm.

Industrial catalysts must comply with the following requirements.

1. Activity – the catalyst should provide a sufficient reaction rate under the specific technological conditions.
2. Stability – the catalyst should not lose its activity over a long period of time.
3. The catalyst should exhibit a lack of sensitivity to catalytic poisons, mostly clorine and sulfur compounds.
4. Selectivity – the catalyst should accelerate the desired reaction only, and not affect side reactions.
5. It should have good mechanical strength.
6. Most of the catalysts are produced as oxides and have to be reduced before use – the reduction period should be as short as possible in order to avoid a decrease in the production efficiency.

The requirements listed are quite contradictory. Thus, a high activity cannot always be combined with a sufficient stability, while a stable catalyst is difficult to reduce. A high mechanical strength is usually inherent to catalysts with high density and, therefore, with low activity. One has to conclude, therefore, that a certain compromise is to be accepted in the development of conventional industrial catalysts with particular properties.

The authors believe that applying the PCT [10] allows the preparation of catalysts complying with all requirements listed above. For instance, the large specific surface and high dispersity of the catalysts, the defective crystal structure, the phase content, the homogeneous distribution of the catalytic active components among the promoters (and vice versa), all determine the high catalytic activity of "plasma" catalysts. The fact that following this technique, the catalysts are synthesized in the gaseous phase at high temperatures and then removed as solid-state high-temperature modifications of the respective compounds [3] determines their increased thermal stability and durability under intensive use. The specific distribution of the components in the "plasma" catalysts content contributes to a drop in their sensitivity to poisons, while the possibility strictly to control their composition is a guarantee for selectivity. The large specific surface of UD "plasma" catalysts, together with the numerous defects in their crystal structure, are conducive to their fast reduction. Pressing or depositing these compounds on substrates ensures high mechanical strength.

The erroneous notion is quite common that the plasma–chemical catalysts are expensive. If one takes into account the main characterics of PCPs, namely, one-stage production, high temperatures and rates, miniaturization of the equipment, simplicity in the modelling, optimization and control, similarity of the technological installations, etc., it can be safely claimed that PCTs will soon prove their indisputable advantages. Further, it must be bourne in mind that the cost of catalysts is a small fraction of the total cost of industrial ammonia production (2%–3%) and is not, therefore, a decisive factor.

The lack of data on the problem in the available patent and periodic scientific literature, taken in the context of the above a priori considerations regarding the LTP synthesis of highly active thermally stable catalysts, prompted the author to begin the studies reported here on the processes of PC preparation of a catalyst used in ammonia production and, furthermore, to characterize thoroughly its physicochemical and, most of all, its catalytical properties as compared with its conventional counterpart CA-1.

2. Experimental procedure

The preparation of catalysts for ammonia synthesis took place in a plasma–chemical d.c. electric arc installation with power adjustable up to 15 kW and output of up to 150 g h^{-1}; its design was described elsewhere [11]. The "cold wall" (CW) PCR was made of copper and was water-cooled; the "warm wall" (WW) PCR was made of heat-resistant ceramics (ZrO_2) and was placed in a water-cooled copper housing. The average temperature of the plasma and the PCR were measured calorimetrically. During the working cycle, the wall temperature of the latter reactor was kept close to 1500 K. The samples were produced in either an oxidizing or a redox atmosphere. In both cases, technical-grade argon was used as a plasma-forming gas at a flow rate of 1.7 m^3 h^{-1} (0.792 g s^{-1}); the powder-carrying gas in the former case was air (oxygen) at a flow rate of 0.5 m^3 h^{-1}(0.16 g s^{-1}), and in the latter, hydrogen with a flow rate of 0.5 m^3 h^{-1} (0.012 g s^{-1}). Quenching in both cases was achieved through injection of cold air at a flow rate of up to 30 m^3 h^{-1} and on the cold water-cooled walls of the powder-trapping chamber. The initial batch (fraction below 50 μm) for synthesis in an oxidizing atmosphere consisted of Fe, Al, K_2CO_3, $CaCO_3$ and SiO_2 in such a mass proportion as to obtain, after PC oxidation, a catalyst mixture containing 94 mass % ($Fe_3O_4 + Fe_2O_3 + FeO$), 3 mass % Al_2O_3, 0.8 mass % K_2O, 2 mass % CaO and 0.2 mass % Si_2O – a composition similar to the conventional industrial analogue CA-1. In a redox atmosphere, the initial batch contained Fe_3O_4, Al_2O_3, K_2CO_3, $CaCO_3$ and SiO_2 in a mass proportion, allowing the production of a catalyst with a components' mass ratio analogous to that of the industrial catalyst CA-1. The specific surface of the samples was determined by means of the Klyatchko-Gourvitch technique [12], while their mass content was established via chemical analysis. Reduction of the samples was carried out in the isothermal mode (673, 723, 773, and 823 K) on a flow installation using hydrogen with a volumetric velocity of $40\,000\,h^{-1}$. The amount of moisture released as a result of the reduction process was weighed, with molten KOH used as adsorbent. The process was monitored by measuring the amount of moisture released every half hour. The activity was determined on a flow installation at a pressure of 30 MPa and a volumetric velocity of the stoichiometric nitrogen–hydrogen mixture (NHM) of $30\,000\,h^{-1}$.

Finally, the UDPs were characterized by means of electron microscopy, X-ray structural and phase analyses, derivatographic analysis and Mössbauer spectroscopy.

3. Results and discussion

The phase diagram of the Fe–O system indicates that, above 1713 K, Fe_2O releases oxygen according to the reaction [8]

$$Fe_2O_3 \rightleftharpoons 0.667\ Fe_3O_4 + 0.1670\ O_2 \qquad (5)$$

i.e. above this temperature the haematite lattice is transformed into that of magnetite, and oxygen is released. A further rise in the temperature up to 3200 K results in thermal destruction of the magnetite

$$Fe_3O_4 = 3FeO + O \qquad (6)$$

Thermodynamic studies of the Fe–O–Al system have revealed the presence of Fe_3O_4 and $FeO{\cdot}Al_2O_3$ at temperatures over 1700 K. The Fe–Al–K–O is much less studied at high temperatures, but the data available [13] show that K_2O in concentrations up to 0.6 mass % dissolves in the magnetite. At such temperatures, K_2O forms ferrites of the $K_2O{\cdot}11Fe_2O_3$ and $K_2O{\cdot}Fe_2O_3$ types [14], CaO binds the iron oxides in a triple ferrite $CaO{\cdot}Fe_3O_4$, while SiO_2 forms complex compounds with the iron oxides. A review of the specialized scientific literature revealed no data on the equilibrium parameters of the multicomponent heterogeneous system Fe–Al–K–Ca–Si–O; this system is used to produce the conventional catalyst CA-1 which is widely exploited for ammonia production in Eastern Europe. This is why we applied a universal programme for determination of the equilibrium parameters of multicomponent heterogeneous systems. The calculation of thermodynamic equilibria in multicomponent systems relies on the fact that the free enthalpy (FE) of a system reaches an extremum at equilibrium. It is assumed that the system does not exchange matter with the ambient medium, i.e. it is isolated and closed. Under these conditions, the problem of finding the equilibrium thermodynamic characteristics is solved by first setting the values of two thermodynamic parameters (usually the pressure, P, and the temperature, T); to calculate chemical equilibrium parameters, the initial quantitative elemental content also has to be defined. A set of parameters $(P, T, M_1, M_2, \ldots, M_k)$ is thus formed, where k is the number of chemical elements present in the initial composition, and M_i is the initial number of moles of the ith element. The calculation is performed within the bounds of the set of system components; the reduced molar FE, G_j, is known for each jth component at a given temperature. All condensed components form separate phases with constant composition; their volume is neglected. The gaseous components make up a single gaseous phase where the ideal-gas law and Dalton's law hold true

$$P_jV = x_jRT \qquad (7)$$

$$P = P_1 + P_2 + P_3 + \cdots + P_m \qquad (8)$$

where P_j is the partial pressure of the jth component, x_j is the number of moles of the jth component, and m is the number of the components forming the gaseous mixture. Finally, an initial mass of 1 kg is adopted for the mixture.

The above assumptions reduce the problem of finding the equilibrium chemical content to solving the following non-linear optimization problem

$$G^*_{(x)} = \sum_{j=1}^{m} (G^*_j - R\ln P_j)x_j + \sum_{j=m+1}^{n} G^*_j x_j \rightarrow \max \qquad (9)$$

under the conditions

$$\sum_{j=1}^{n} a_{ij}x_j = b_i \quad (i = 1, 2, \ldots, k) \qquad (10)$$

$$x_j > 0 \quad (j = 1, 2, \ldots, m) \qquad (11)$$

$$x_j \geqslant 0 \quad (j = m+1, \ldots, n) \qquad (12)$$

where $G^*_{(x)}$ is the reduced FE of the system, n is the total number of components in the system with the first m forming the gaseous phase and the rest being in the solid phase, and a_{ij} is the stoichiometric coefficient of the ith element in the chemical formula of the jth component.

Equation 10 represents the material balance for each of the initial materials. Inequalities 10 and 11 reflect the necessity of having positive condensed-phase concentration.

Returning to the specific case discussed here, the equilibrium parameters of the multicomponent heterogeneous system Fe–Al–K–Ca–Si–O were calculated for a pressure of 0.1 MPa within the temperature interval 1000–3700 K (step of 300 K) at the following initial composition ($mol\ kg^{-1}$)

I variant: Fe, 12.084 $mol\ kg^{-1}$ (67.48 mass %); Al; 0.584 87 $mol\ kg^{-1}$ (1.58 mass %); K, 0.168 52 $mol\ kg^{-1}$ (0.66 mass %); Ca, 0.356 87 $mol\ kg^{-1}$(1.43 mass %); Si, 0.327 13 $mol\ kg^{-1}$ (0.92 mass %); O, 16.961 $mol\ kg^{-1}$ (27.14 mass %); Ar, 0.198 26 $mol\ kg^{-1}$ (0.79 mass %).

II variant: Fe, 3.5186 $mol\ kg^{-1}$ (19.65 mass %); Al, 0.1703 $mol\ kg^{-1}$ (0.46 mass %); K, 0.049 07 $mol\ kg^{-1}$ (0.19 mass %); Ca, 0.103 91 $mol\ kg^{-1}$ (0.42 mass %); Si,

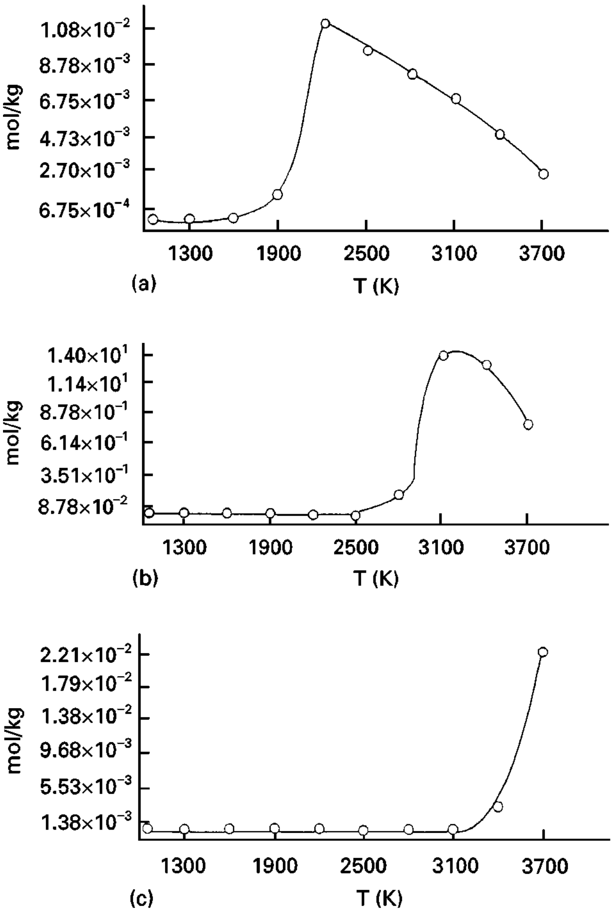

Figure 1 Concentration of (a) K_2O, (b) FeO and (c) CaO (mol kg^{-1}) in the gaseous phase for the equilibrium composition of the Fe–Al–K–Ca–Si–O system as a function of the temperature (variant I).

0.095 253 mol kg^{-1} (0.27 mass %); O, 49.387 mol kg^{-1} (79.02 mass %).

The data calculated are used to plot the concentration of the respective component in condensed or gaseous phase versus the temperature (e.g. Fig. 1). Similarly, the concentration curves of Fe_3O_4, Fe_2O_3, Al_2O_3, CaO, SiO_2, and the possible combination compounds in the gaseous and condensed phase at equilibrium composition of the Fe–Al–K–Ca–Si–O system, are also constructed as functions of temperature [2].

Four series of experiments were carried out: series 1 and 2 in a CW PCR, and 3 and 4 in a WW PCR. Argon at a flow rate of 0.792 g s^{-1} was used as a plasma-forming gas; the powder-carrying and oxidizing gas was either air (0.16 g s^{-1}, series 1), or technical-grade nitrogen containing 5% oxygen (0.135%, series 2, 3, and 4). Throughout the investigations, the PCR temperature was maintained mainly in the 1000–3000 K range. The well-homogenized powder material (fraction below 50 μm) was introduced radially in the PCR mixer by means of a piston powder feeder in order to prevent separation of the ingredients. Quenching took place at the cold water-cooled walls of the powder-trapping chamber (series 1, 2, 3); series 4 was carried out without quenching. Part of the results obtained during the four series are shown in Table I.

The data presented in Table I show an increase of the specific surface and a decrease of the bulk mass of the material, both brought about by the rise of the average PCR temperature. It is known that molten catalysts that in the unreduced form are composed of magnetite (i.e. have a Fe^{2+}/Fe^{3+} ratio of $\cong 0.5$), exhibit the highest activity. The Fe^{2+}/Fe^{3+} ratio in the samples of series 1 varied from 0.26–0.30, i.e. magnetite and haematite were in comparable amounts; in series 2 it was found that this ratio was in the 0.32–0.41 interval, indicating a magnetite predominance; finally, in series 3 and 4, $Fe^{2+}/Fe^{3+} = 0.09$–0.16, the probes, therefore, consisted mainly of haematite. The values of this ratio were affected by the partial pressure of oxygen in the PCR, the temperature regime of the process, and by the use and efficiency of the quenching. Furthermore, the defects in the magnetite packing, when brought into contact with the oxygen in air, led to a rearrangement of the magnetite lattice to that of a haematite, as proven by the Fe^{2+}/Fe^{3+} ratio and the X-ray structural analysis. The X-ray analysis revealed the main phases in the catalyst, namely Fe_3O_4, Fe_2O_3, FeO and $FeO{\cdot}Al_2O_3$. At higher temperatures, α-Fe_2O_3 was transformed into the ferromagnetic γ-Fe_2O_3 which is characterized by a spinel lattice with parameter $a = 833$ pm. A continuous series of interim oxides is known to exist between γ-Fe_2O_3 and Fe_3O_4 that can be considered as solid solutions of γ-Fe_2O_3 in Fe_3O_4. Dissolving of γ-Fe_2O_3 in Fe_3O_4 is manifested as a slight shift of the latter compound's lines in the X-ray patterns, while the Fe_3O_4 lattice parameter is lower by about 0.17%–0.25% [3].

In analogy with samples obtained in LTP based on the Fe–O–Al system [2], the derivatograms (Fig. 2) showed only an insignificant endothermic effect at 843 K; above this temperature, the reaction

$$Fe_3O_4 + Fe \rightarrow 4FeO \qquad (13)$$

takes place. No other effects could be discerned on the DTA curve taken in the 300–1200 K range in a neutral medium. For this temperature interval, the rate of sample mass variation was negligible.

Electron microscopy (Fig. 3) showed that the size of the UD catalyst particles falls within the 20–60 nm range. In some cases, the high degree of dispersity of PC-obtained CA-1-type catalysts made the X-ray phase analysis difficult. It then seemed appropriate to employ Mössbauer spectroscopy, a technique with proven capabilities in the study of heterogeneous catalysts [15]. Thus, such an analysis was carried out on four samples (Table II, V-16, V-17, V-14 and V-19). The spectra obtained are presented in Fig. 4 – they overlap with the those of magnetite, haematite, α-Fe, and of the paramagnetic part containing wüstite and γ-Fe, and are an indication of the complexity of the compounds produced through plasma-chemical treatment. The areas of the partial Mössbauer spectra are proportional to the relative content of the phases, if one assumes equality of the Debye–Waller factors.

Table III presents the relative area of the peaks of the different phases. It is seen that the content of the

TABLE I PCP technological parameters and some results of the physicochemical studies: series 1 (nos 1–7); series 2 (nos 8–15); series 3 (nos 16–21); and series 4 (nos 22–28)

No	T_{pl} (K)	T_{PCR} (K)	Content (mass %)			S (m^2g^{-1})	ρ ($kg\,m^{-3}$)	Fe^{2+}/Fe^{3+}
			Fe_2O_3	Fe_3O_4	Al_2O_3			
1	2400	800	28	65	3.1	21	320	0.30
2	2600	1100	33	60	3.1	23	320	0.28
3	3800	1400	35	58	3.2	25	310	0.28
4	4500	1800	38	55	3.1	27	300	0.27
5	7100	2300	43	50	3.1	23	310	0.26
6	7500	2500	44	49	3.0	30	300	0.26
7	7400	2500	44	49	3.0	33	300	0.26
8	2500	900	11	82	3.0	20	420	0.41
9	2700	1000	13	80	3.0	21	420	0.40
10	3500	1300	15	78	3.1	22	410	0.37
11	4200	1700	18	74	3.0	25	400	0.35
12	6000	2000	21	72	3.1	24	400	0.33
13	7200	2300	22	71	3.2	27	400	0.33
14	7300	2400	23	70	3.1	29	400	0.32
15	8100	2700	23	70	3.1	30	390	0.32
16	2400	1300	75	18	3.0	29	310	0.16
17	2800	1600	76	18	2.9	30	320	0.16
18	3300	1800	75	18	3.0	30	310	0.16
19	4500	2400	78	15	3.0	35	300	0.13
20	6000	2900	78	15	2.8	33	310	0.13
21	6700	3000	80	13	2.9	35	300	0.11
22	2500	1400	81	12	2.9	32	300	0.11
23	2700	1500	81	12	2.8	35	300	0.11
24	3000	1700	81	12	2.8	36	300	0.11
25	4300	2300	82	11	2.9	40	290	0.10
26	6200	2900	83	10	2.9	38	290	0.10
27	7800	3100	83	10	2.9	39	290	0.10
28	10500	3400	85	8	2.9	40	290	0.09

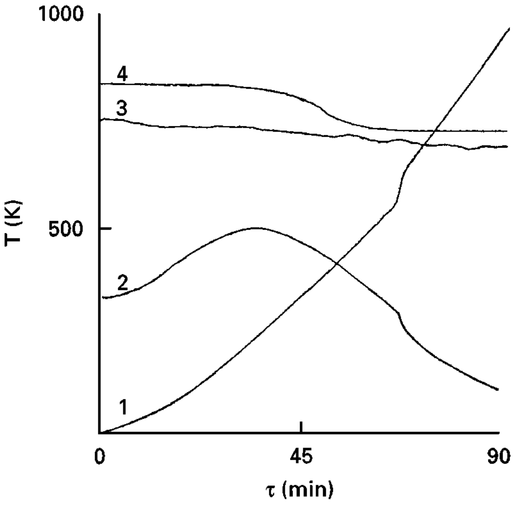

Figure 2 Derivatogram of sample 18, Table I: 1, heating curve; 2, differential curve (DTA); 3,4, thermogravitograms (DTG and TG).

oxidized iron state is the lowest in sample V-17 (obtained at 1000 K in a CW PCR). The Fe and FeO contents (35.2 and 32.8 mass %, respectively) are the highest in sample V-17. The high α-Fe concentration determines the large bulk-mass value (700 $kg\,m^{-3}$) and the relatively small specific surface (21 m^2g^{-1}) of the same sample. The Fe_3O_4 and α-Fe_2O_3 contents are the highest in sample V-19 (42 and 25.4 mass %, respectively). Sample V-15 contains less Fe_3O_4 and more γ-Fe_2O_3 and Fe_xO than sample V-19. The α-Fe_2O_3 content in samples V-14 and V-17 is minimal, while γ-Fe is altogether lacking in V-19.

One should note that the samples obtained at high temperatures in the presence of a limited amount of oxygen are similar to those prepared in a hydrogen atmosphere, where the processes of Fe_3O_4, and other iron oxides formation, take place. The qualitative data on the samples content, obtained via Mössbauer spectra processing, are in good agreement with the quantitative X-ray analysis results (e.g. sample V-17, Fig. 5).

Summarizing the results of the studies on the PC preparation of catalysts with composition similar to the conventional CA-1 catalyst, as well as the data from the physicochemical analyses, it is recommended that, in order to produce a magnetite phase only, the PCP should take place in a CW PCR with quenching and an oxygen content not exceeding 5%. In addition, the temperature interval 1300–3000 K is optimal for obtaining samples with maximal specific surface, spherical-particles dispersity and defects in the active-phase crystal lattice – prerequisites for the formation of a highly active surface.

In addition, preliminary studies were carried out to determine the activity of the synthesized samples at a pressure of 0.1 MPa in a flow installation. They

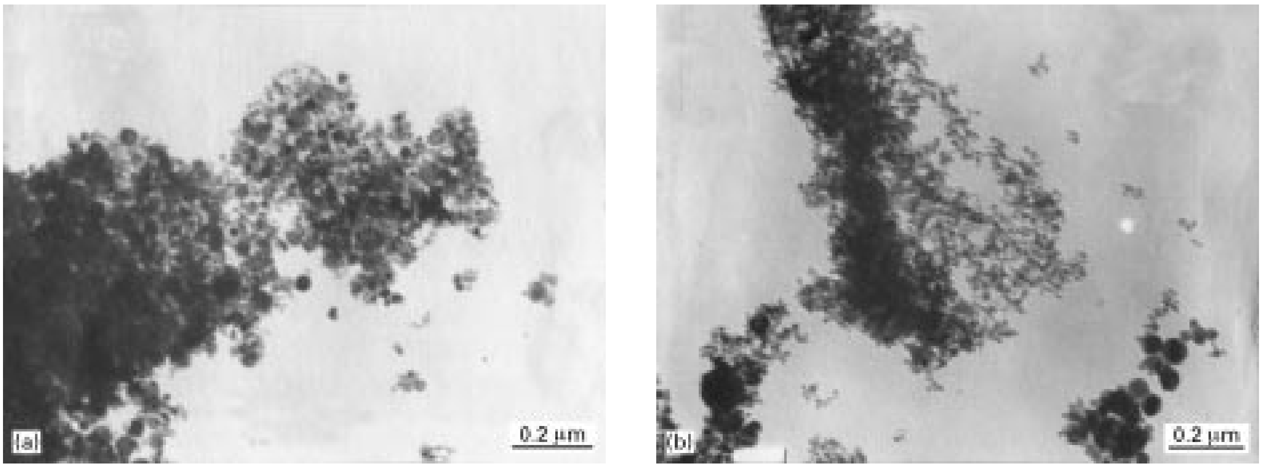

Figure 3 Electron micrographs of UD particles of a CA-1-type catalyst for ammonia synthesis prepared in LTP: (a) sample 5, Table I; (b) sample 11, Table I.

TABLE II Technological parameters of the process and physicochemical properties of the samples

Samples	PCR type	Temperature (K)		Gas medium flow rate[a] ($g s^{-1}$)			S ($m^2 g^{-1}$)	Bulk mass ($kg m^{-3}$)	Particle size (nm)
		Plasma	Reactor	Ar	Air	N_2, 5% O_2			
V-16	CW	7400	2400	0.9	0.14	–	33	300	10–40
V-17	CW	2400	1000	0.9	0.14	–	21	700	10–40
V-14	WW	5500	2800	1.84	–	0.33	29	230	10–50
V-14	WW	2500		1.61	–	0.33	32	300	10–40

[a] The flow rate is measured at 300 K.

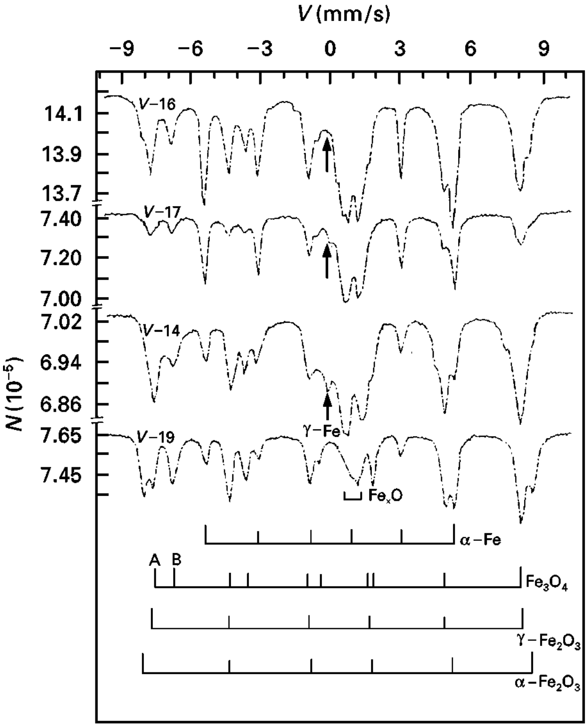

Figure 4 Mössbauer spectra at room temperature of samples V-16, V-17, V-14 and V-19.

TABLE III Relative areas of the partial Mössbauer spectra

Sample	α-Fe	Fe_3O_4	α-Fe_2O_3	γ-Fe_2O_3	Fe_xO	γ-Fe
V-16	25.4	25.3	9.7	12.1	25.5	2
V-17	35.2	18.2	2	8.3	32.8	4.5
V-14	12.1	29.8	5	23.1	24.5	5.5
V-19	11.8	42.0	25.4	9.2	11.6	–

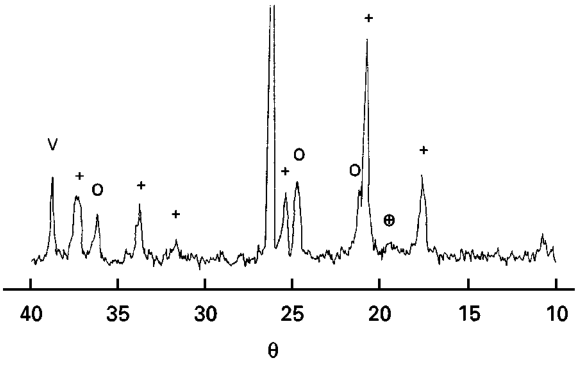

Figure 5 X-ray pattern of sample V-17 produced in a CW PCR ($T_{PCR} = 1000$ K). The intensive iron peaks confirm the incomplete oxidation of elemental metal iron. V, Fe; +, Fe_3O_4; O, FeO; ⊕, Fe_2O_3.

showed that 773 K the PCS samples were reduced at two to four times as fast as the standard CA-1 catalyst, and, furthermore, were substantially more active and thermally stable (Fig. 6). After passivation, the X-ray analysis revealed the presence of α- and γ-Fe phases. The high dispersity, the defects in the crystal structure

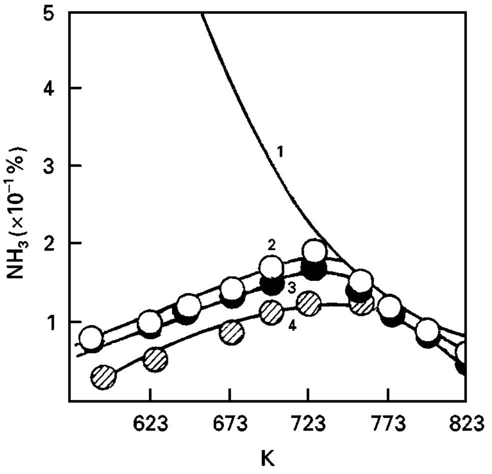

Figure 6 Catalytic activity (% NH_3) as a function of the temperature (T, K) at pressure 0.1 Mpa: 1, equilibrium curve; 2, activity of a catalyst prepared in LTP; 3, activity of a catalyst prepared in LTP and heat-treated for 3 h at 1073 K; 4, activity of type CA-1 industrial catalyst.

TABLE IV Activity (z, % NH_3) as a function of the temperature (T, K) before and after overheating[a] of PCS ammonia-synthesis catalysts, $P = 30$ MPa, $W = 30\,000\ h^{-1}$

No.	Catalyst type	Activity Z (% NH_3)				
		673 K	723 K	748 K	773 K	823 K
1	Industrial catalyst CA-1 (present experiment)	16.6	19.8	20.0	19.3	14.9
		6.0[a]	10.8[a]	11.0[a]	10.9[a]	10.2[a]
2	Industrial catalyst CA-1 (literature data) [16]	16.8	20.7	20.8	19.7	15.5
		7.1[b]	13.4[b]	15.6[b]	16.5[b]	14.0[b]
3	Plasma chemically synthesized in oxidizing media CA-PSO	16.5	21.4	22.0	22.9	17.0
		15.0[a]	18.7[a]	19.5[a]	19.8[a]	15.4[a]
4	Plasma chemically synthesized in redox media CA-PSRO	17.5	21.9	23.7	24.2	17.5
		16.8[a]	20.3[a]	21.5[a]	21.9[a]	17.0[a]

[a] Overheating at 1073 K for 3 h.
[b] Overheating at 973 K for 20 h.

TABLE V Relative degree of transformation ($x = (z/z_p)$, 100 %) as a function of the temperature (T, K) before and after overheating of PCS ammonia-synthesis catalysts. $P = 30$ MPa, $W = 30\,000\ h^{-1}$ (sample numbering is the same as in Table IV)

No.	Relative degree of transformation $x = Z/Z_p \cdot 100(\%)$				
	673 K	723 K	748 K	773 K	823 K
1	35.3	55.3	61.5	73.0	77.9
	12.8[a]	30.2[a]	33.9[a]	41.2[a]	53.3[a]
2	35.7	57.8	64.0	74.5	81.0
	15.1[b]	37.4[b]	48.0[a]	62.4[b]	73.2[b]
3	35.1	59.7	67.7	86.6	88.9
	31.9[a]	52.2[a]	60.0[a]	74.9[a]	80.5[a]
4	37.2	61.1	72.9	91.5	90.7
	35.7[a]	56.7[a]	66.2	82.8[a]	88.9[a]

[a] Overheating at 1073 K for 3 h.
[b] Overheating at 973 K for 20 h.

TABLE VI Rate constant of the ammonia-synthesis process (K, $Pa^{1/2}\,h^{-1}$) as a function of the temperature (T, K) before and after overheating of PCS catalysts. $P = 30$ MPa, $W = 30\,000\ h^{-1}$ (sample numbering is the same as in Table IV)

No.	(Rate constant, $Pa^{0.6}h^{-1}$)			
	673 K	723 K	748 K	773 K
1	2780 (360[a])	15720 (4320[a])	31440 (7920[a])	56270 (14290[a])
2	2810 (420[b])	17320 (4430[b])	34030 (17028[b])	57440 (37035[b])
3	2760 (2240[a])	18870 (14070[a])	38990 (28890[a])	93770 (57730[a])
4	3150 (2970[a])	20316 (16990[a])	47630 (38110[a])	125020 (81320[a])

[a] Overheating at 1073 K for 3 h.
[b] Overheating at 973 K for 20 h.

TABLE VII Activation energy (E, kJ mol^{-1}) for various temperature ranges before and after overheating[a] of PCS ammonia-synthesis catalysts, $P = 30$ MPa, $W = 30\,000\ h^{-1}$ (sample numbering is the same as in Table IV)

No.	Activation energy, E (kJ mol^{-1})		
	673 – 723 K	748 – 773 K	673 – 773 K
1	141.3 (202.9[a])	112.1 (113.7[a])	130.3 (159.6[a])
2	148.2 (191.8[b])	100.8 (149.6[b])	130.7 (193.9[b])
3	156.6 (149.8[a])	168.9 (133.3[a])	152.7 (140.7[a])
4	152.0 (142.4[a])	185.8 (145.9[a])	159.5 (143.4[a])

[a] Overheating at 1073 K for 3 h.
[b] Overheating at 973 K for 20 h.

of the catalytically active phases, the existence of a mixture of α-and γ-Fe, the optimal Fe^{2+}/Fe^{3+} ratio, and the mode of forming the active surface via reduction, all determine the high activity of the PCS samples – 15%–20% higher than the standard.

Tables IV–IX and Figs 7 and 8 present the results of the kinetic studies of six samples. The activity was measured at five temperatures in the catalytic reactor, namely, 673, 723, 748, 773 and 823 K. Subsequently, the temperature was raised to and maintained for 3 h at 1073 K, i.e. overheating and deactivation of the samples was achieved; the catalytic activity was then measured once again.

The activity as percentage of NH_3 as a function of the temperature before and after overheating of the samples is presented in Table IV and Fig. 7. As seen, the highest activity (with the chemical composition being practically the same) is exhibited by sample 4 which was prepared using PCS in a redox medium.

As the temperature rises, the relative degree of transformation x also rises (Table V). Thus, at 773 K, $x = 91.5\%$ for CA-PCRO, and $x = 73\%$ for CA-1; after overheating $x = 82.8\%$ for CA-PCRO, and $x = 41.2\%$ – i.e. the PCS catalyst is much more thermally stable.

$$W = k_1 P_{NA}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right) - k_2\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{1-\alpha} \qquad (14)$$

TABLE VIII Relative activity of deactivated catalysts ($y_a = (k_2/k_1)$, 100 %) as a function of the working temperature (T, K). Deactivation performed at 1073 K for 3 h (sample numbering is the same as in Table IV)

No.	Relative activity, $y_a = (k_2/k_1)\cdot 100$ (%)			
	673 K	723 K	748 K	773 K
1	12.9	27.5	25.2	25.4
2	15.0[a]	25.6[a]	50.0[a]	64.5[a]
3	81.1	74.6	74.1	61.6
4	94.1	83.6	80.0	65.0

[a] Overheating at 973 K for 20 h.

TABLE IX Degree of deactivation of the catalysts ($y_d = (k_1 - k_2)/k_1$ 100, %) as a function of the working temperature (T, K). Deactivation performed at 1073 K for 3 h (sample numbering is the same as in Table IV)

No.	Degree of deactivation, $y_d = (k_1 - k_2)/k_1 \cdot 100$ (%)			
	673 K	723 K	748 k	773 K
1	87.1	72.5	74.8	74.6
2	85.0[a]	74.4[a]	50.0[a]	35.5[a]
3	18.9	25.4	25.9	38.4
4	5.9	16.4	20.0	35.0

[a] Overheating at 973 K for 20 h.

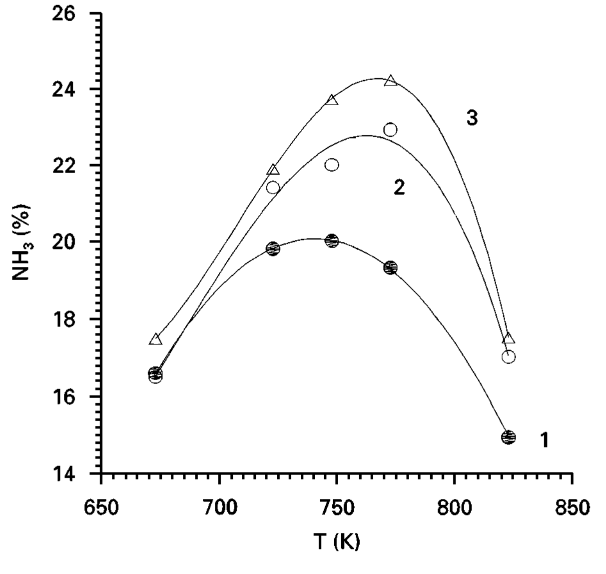

Figure 7 Activity of catalysts for ammonia synthesis (% NH_3) as a function of the temperature at $P = 30$ MPa and $W = 30\,000$ h^{-1}: 1, CA-1 industrial catalyst (our experiment); 2, catalyst plasma-chemically synthesized in an oxidizing atmosphere – CA-PSO; 3, catalyst plasma-chemically synthesized in a redox atmosphere – CA-PSRO.

Where W is the observed reaction rate, equal to the difference between the rates of formation and disintegration of ammonia; k_1, k_2 are the rates of formation and disintegration of ammonia ($k_1/k_2 = k_p$, k_p being the equilibrium constant); P_{H_2}, P_{N_2}, P_{NH_3} are the partial pressures of hydrogen, nitrogen and ammonia; and α is a constant, $0 < \alpha < 1$.

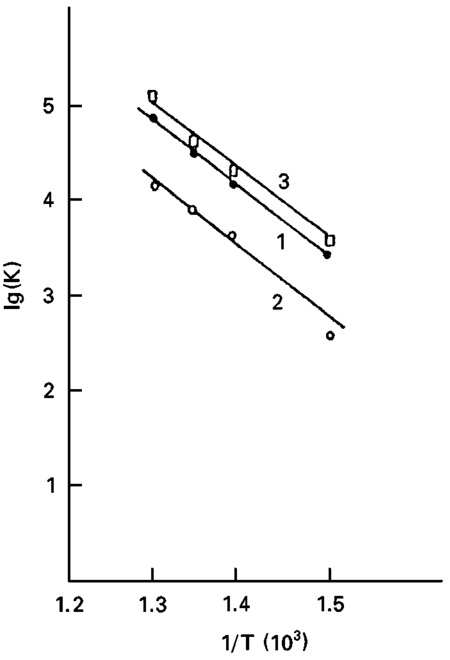

Figure 8 Rate constant ($\log k$) of the ammonia-synthesis process as a function of the temperature, 10^3 T^{-1}. 1, CA-1 industrial catalyst (our experiment); 2, CA-1 industrial catalyst deactivated at 1073 K for 3 h; 3, catalyst plasma-chemically synthesized in a redox medium – CA-PSRO.

The value of α describes the extent of covering the catalyst surface with ammonia during the synthesis process. For an industrial catalyst in the 673–823 K range, where the investigations were carried out, this value can be assumed to be 0.5; the rate constant in a flow system under isothermic conditions is then calculated using the equation [16]

$$k = (10.2P)^{0.5} W_0 \int_{z_1}^{z_2} \frac{z(1-z)^{1.5}}{(1+z)^2[L^2(1-z)^4 - z^2]} \mathrm{d}z = W_0(10.2P)^{0.5} I(z) \quad (15)$$

where k is the rate constant in the Arrhenius equation ($Pa^{1/2}h^{-1}$), P is the pressure in the catalytic reactor (MPa), W_0 is the volumetric flow rate of the stoichiometric NHM (h^{-1}), z_1, z_2 are the ammonia concentrations at the reactor input and output (molar parts), and $L = z_p(1 - z_p)^2$, z_p being the equilibrium ammonia concentration. The values of $(10.2P)^{0.5}I(z)$ were taken from [16].

The activation energy of the ammonia-synthesis process was calculated for three different temperature intervals (Table VII) using the slope of the Arrhenius lines (Fig. 8)

$$E = R(\ln k_1 - \ln k_2) \Big/ \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (16)$$

where k_1, k_2 are the rate constants in the Arrhenius equation at temperatures T_1 or T_2, E is the activation energy (kJ mol^{-1}), $R = 8.316\,96$ is the gas constant (kJ mol^{-1} K^{-1}).

The Arrhenius equation

$$k = k_0 \exp(-E/RT) \qquad (17)$$

is applicable to temperature intervals where the ammonia-synthesis process takes place in the kinetic region. As the temperature rises, the rate of the process begins to be limited by macrokinetic factors so that it takes place in the diffusion region. For smaller catalytic particles, the kinetic region broadens towards the higher temperatures. This is illustrated by the values of the activation energy in different temperature ranges (Table VII): for the conventional CA-1 catalyst the activation energy begins to drop in the 748–773 K range (100.8 kJ mol^{-1}), while in the 673–723 K range its value is 148.4 kJ mol^{-1}; in contrast, for samples plasma-chemically synthesized in an oxidizing or redox atmosphere, the activation energy has values of 152.0 and 163.3 kJ mol^{-1}, respectively, in the latter temperature range, and 185.8 and 135.7 kJ mol^{-1}, in the former.

If the dependences $\log k = f(1/T)$ (Fig. 8) is studied for conventional catalysts and for those prepared under LTP conditions, it can be seen that the lines in the kinetic region are parallel, i.e. the activation energy is constant within the limits of the accuracy of measurements. According to the active centres theory, when the process rate constant rises (as in this case – Table VI) at constant activation energy, the activation is due to an increase of the active centres number. Inversely, if the activation energy decreases in the kinetic region, activation results from an increase in the activity of the existing active centres. Obviously, the PCS catalysts possess a greater number of active centres in unit mass compared to the CA-1 industrial catalyst; this is the cause of the 15%–20% rise (depending on the temperature) in the their catalytic activity.

Table VIII presents the values of relative activity of thermally deactivated catalysts. It was especially high at lower temperatures (673–723 K), e.g. at 673 K for sample 4 it was 91.4%, while for the conventional CA-1 catalysts it was only 12.9% (15% according to [16]). Clearly, overheating gives rise to processes of recrystallization of the catalytically active phases, whereby the cubic body-centred crystal lattice of α-Fe assumes a normal structure (in PCS catalysts a 0.25% drop is observed in the lattice parameter [2, 3]). Also, the structural defects diminish as a result of the atoms thermal vibration in the crystallites interstitials (Taman's temperature is $\sim 0.52\, T_{\text{melting}}$ of iron). All this leads to a decrease in the catalytic activity. In the case of PCS samples, overheating at 1073 K leads to relatively less phase and structural changes, so that the deactivation processes are less strongly expressed, as compared with the industrial CA-1 catalyst under similar conditions. At 773 K, the relative activity of the deactivated PCS catalysts differs to a lesser degree from that of the conventional (according to the data in [14], the activity is even the same). The reason for this is that diffusion processes begin to exert a limiting influence on the rate of the ammonia-synthesis process – the activity is no longer determined by the chemical kinetics (i.e. the number and activity of the active centres on the catalyst surface), but rather by the diffusion of nitrogen molecules in the catalyst bulk.

According to both the present data and that of Kuznetsov and Dmitrenko [14] (Table IX), the deactivation degree of the CA-1 catalyst is several times higher than that of the "plasma" samples.

It is natural to ask the question: what is the reason for the increased activity and thermal stability of PCS catalysts? To obtain catalysts with magnetite phase only, synthesis must take place in a CW PCR with quenching and with the oxygen content in the gas mixture not exceeding 5 vol%. Preparation of samples with maximal specific surface, particles dispersity and lattice defects in the catalytically active phases – prerequisites for the formation of a highly active surface – requires operation in the optimal 1300–3000 K temperature range. The PCS samples are reduced three to five times as fast as the standard CA-1 catalyst; their specific surface reaches 40 $\text{m}^2\,\text{g}^{-1}$, while that of CA-1 in unreduced form does not exceed 1 $\text{m}^2\,\text{g}^{-1}$. We believe that the causes determining the increased catalytic activity of PCS samples as compared with the standard catalysts should be sought in the high dispersity, the defective crystal structure of the catalytically active phases, the existence of a mixture of α- and γ-Fe, the optimal $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio ($\cong 0.45$), and, finally, by the formation of active surfaces on these samples through reduction.

4. Conclusion

Based on a universal computer code, the equilibrium parameters were found for the first time of the multicomponent Fe–Al–K–Ca–Si–O system for a pressure of 0.1 MPa in the 1000–3700 K temperature range and for various initial compositions.

The technological conditions were established for producing samples with maximal catalytic activity and thermal stability; these can be summarized as follows.

1. The PCP must take place in a CW PCR with quenching; the oxygen content in the gas phase must not exceed 5 vol% – these are the conditions for obtaining a magnetite phase only.
2. The optimal temperature range is 1000–3000 K which ensures samples with maximal specific surface, respectively, dispersity of the particles and crystal lattice defects.
3. The dispersity of the catalysts synthesized and, within certain limits, their content, can be controlled via variation of the PCP parameters.

The PCS specimens are reduced two to five times as fast as the CA-1 catalyst; their specific surface can reach 40 m^2g^{-1}, while that of CA-1 is 1 m^2g^{-1}. Catalysts for use in the synthesis of ammonia produced under the conditions of electric-arc quasi-equilibrium LTP exhibit catalytic activity that is higher by 15%–20% in comparison with the conventional CA-1 catalyst. Furthermore, they are much more resistant to overheating and deactivation.

Kinetic studies were also carried out on PCS catalysts for conditions similar to industrial ones. They proved that the increased catalytic activity is due to an increase in the pre-exponential factor in the Arrhenius equation at a constant activation energy, i.e. to a rise in the number of active centres in unit catalytic mass.

The PCT is, therefore, efficient in the preparation of catalysts for ammonia synthesis. Its advantages are: finely dispersed catalysts are obtained with a high specific surface; the homogeneous distribution of the components in the specimens contributes to a lowering of their sensitivity to catalytic poisons; the possibility of forming a strictly constant composition is a guarantee for selectivity; the dispersity and composition of the samples can be controlled within wide limits via variation of the PCP parameters; the 0.25% decrease of the lattice parameter of the main phases (Fe, Fe_3O_4) determining the catalytic activity probably determines the high rate of reduction and, to a certain degree, increases the catalytic activity; overheating affects to a substantially lesser extent the activity of PCS catalysts; pressing or deposition on a substrate can ensure high mechanical strength; the energy consumption for PCS catalysts production is comparable to, and sometimes even lower than, that associated with the other two thermal processes. The process comprises only two stages: PCS of catalysts and formation of granules or tablets.

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