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Complex physico-chemical characterization and kinetic studies on the reduction and activity of catalyst for ammonia synthesis regenerated by electric-arc plasma

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Abstract

A comprehensive physico-chemical characterization is carried out and the reduction kinetic and activity are studied of samples of CA-1-type catalyst for ammonia synthesis regenerated in quasi-equilibrium electric-arc low-temperature plasma. The experimental conditions are described for the plasma-chemical regeneration of a spent catalyst for ammonia synthesis. The samples regenerated are characterized by means of determining: the specific surface (using the Klyatchko-Gurvich technique); the size of the finely-dispersed particles (electron microscope analysis); and the phase content (X-ray phase analysis, Möessbauer spectroscopy, chemical analysis, derivatographic analysis). A mechanism is proposed for the plasma-chemical regeneration of the samples. The reduction process is studied and the activity, the relative degree of transformation, the activation energies, the rate constants, the relative activity and the degree of thermal deactivation of the regenerated samples are determined. It is found that the samples are reduced three to five times as fast as the standard ones. The increased reduction rate and the high catalytic activity are due to the increased pre-exponent factor in the Arrhenius equation at constant activation energy. The causes for the high activity and thermal stability of the samples are explained. The advantages of the plasma-chemical technique are outlined as compared with the conventional methods for activation of spent catalysts for ammonia synthesis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma-chemical regeneration of catalysts; Ammonia synthesis; Powder technology; Nanomaterials

1. Introduction

The problem of plasma-chemical regeneration (PCR) of spent (deactivated) catalysts has not been discussed in the periodic scientific literature. The conventional techniques for catalysts regeneration consist in: feeding of a gas with reducing action into columns containing a deactivated catalyst [1], or melting the catalyst in an oxidizing or neutral medium followed by re-granulation [2]. A disadvantage of the first method is the impossibility to restore the catalyst's activity if irreversible changes in its structure and content have taken place, while the second is only applicable to fused catalysts; moreover, in the latter case the activity cannot be restored fully, while the energy consumption is high.

It is the author's believe that the plasma-chemical technique for synthesis of oxide catalysts [3], in particular those employed in the synthesis of ammonia [4], can be used to carry out through investigations on the PCR [5,6] of spent catalysts.

The purpose of the present work is to characterize physico-chemical activity of CA-1-type ammonia-

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synthesis catalyst regenerated in quasi-equilibrium electric-arc low-temperature plasma (LTP) and to study the kinetic of its reduction.

2. Experimental

The PCR investigation of the CA-1-type ammonia-synthesis catalyst was carried out on an electric-arc plasma-chemical installation with power of up to 150 kW and output of 150 g h^{-1}; it was described in [7]. The raw material was deactivated CA-1-type catalyst (of Russian make, widely used in the last 20 years in the east European nitrogen industry), ground and fractioned down to a particle-size of less than 50 μm. The plasma-forming gas was Ar (flow rate of 3 $m^3 h^{-1}$), and Ar or pure N_2 were used as a powder-carrying gas (flow rate of 0.8 $m^3 h^{-1}$). The plasma-chemical process (PCP) took place in a “warm” wall (WW) reactor (diameter of 2 cm, length of 10 cm) made of heat-resistant ceramics (ZrO_2) and placed in a water-cooled metal housing [7]. The quenching was performed at a rate of $dT/d\tau \cong 10^{-5}\,K\,s^{-1}$ by means of injecting cold jets of technical-grade nitrogen (mixed with 5% of oxygen), and on the water-cooled metal walls of the quenching chamber. The time of residence of the micron-size particles in the plasma-chemical reactor (PCR) was 1–5 ms, while the temperature in the reactor vessel was 1100–3400 K, depending on the electric power consumption. The filter and the cold walls of the powder-trapping chamber accumulated a finely-dispersed catalyst fraction with particle size of 100–300 nm and specific surface of 3–10 $m^2 g^{-1}$. The particle size was determined by electron microscope analysis on a transmission electron microscope (Philips EM-301); the specific surface was measured by means of the Klyatchko-Gurvich technique [8]; the phase content was evaluated via X-ray analysis on a TUR-M62 equipment; the Fe^{2+}/Fe^{3+} ratio was obtained by chemical analysis; finally, the average plasma temperature in the PCR was measured calorimetrically. One cm^3 of the finely-dispersed powder produced was subjected to reduction in the flow installation shown schematically in Fig. 1. Hydrogen was used as a reducing agent with flow rate of 40,000 h^{-1} in isothermal reduction mode at 673, 723, 773 and 823 K. The reduction process was monitored each half hour by weighing the amount of moisture released; fused KOH was used as an adsorber. The activity was determined on a flow installation at a pressure of 30 MPa and flow rate of a stoichiometric nitrogen–hydrogen mixture of 30,000 h^{-1}.

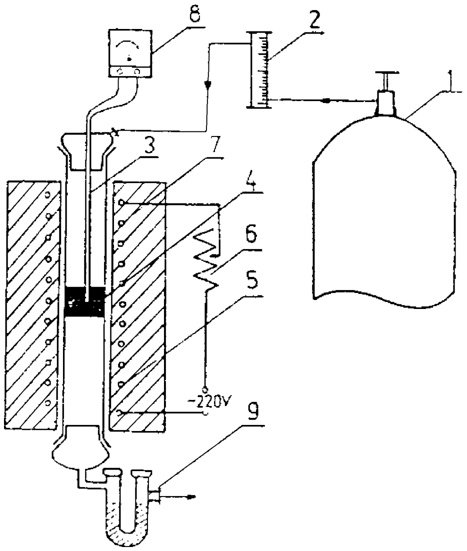

Fig. 1. Schematic diagram of a flow installation for dynamic and kinetic studies of reduction processes: (1) hydrogen bottle; (2) flow-rate meter; (3) quartz reactor vessel; (4) catalyst; (5) electric furnace; (6) auto-transformer; (7) thermocouple; (8) milivoltmeter; (9) U-shaped tube filled with fused KOH.

3. Results and discussion

Table 1 presents some of the technological parameters characteristic for the PCP: the average temperatures of the plasma and the reactor, the specific surface before and after reduction, the size of the particles, the main phases, the Fe^{2+}/Fe^{3+} ratio, and the bulk mass of the samples. As one can see, the dispersity of the catalyst and, within certain limits, its content can be controlled by varying the PCP parameters.

To widen the scope of physico-chemical characterization of the PC-regenerated samples, Möessbauer spectroscopy analysis was performed at a range of 9 mm s^{-1} and 300 K. The conditions for regeneration and activation of the samples in the “WW” PCR were as follows: (a) argon atmosphere, PCR temperature of 1300 K (sample V-2), 1800 K (sample V-3), and 6800 K (sample V-4); (b) nitrogen atmosphere,

Table 1
Some physico-chemical properties of samples of a regenerated CA-1-type ammonia-synthesis catalyst as functions of the PCP temperature in PCR at plasma-forming gas (Ar) flow rate of $1.19\,g\,s^{-1}$

Number	T_{pl} (K)	T_{PCR} (K)	Specific surface ($m^2\,g^{-1}$)		Particle size (nm)	Main phases	Fe^{2+}/Fe^{3+}	Bulk mass ($kg\,m^{-3}$)
			Before reduction	After reduction				
1	1400	600	3.5	9.4	100–300	Fe_3O_4, Fe_2O_3	0.45	555
2	2000	700	3.1	7.1		FeO, $FeO{\cdot}Al_2O_3$	0.42	620
3	2500	1200	3.2	7.9		α-Fe, γ-Fe	0.42	550
4	6300	2800	6.9	10.6			0.41	560
5	3600	1200	5.9	8.4	80–250	Fe_3O_4, Fe_2O_3	0.42	550
6	4400	1800	3.6	7.8		FeO, $FeO{\cdot}Al_2O_3$	0.41	520
7	7000	3200	4.7	6.7		Fe_xN_y, α-Fe, γ-Fe	0.41	530
8	–	–	1.6	7.9	50 μm	Fe_3O_4, FeO, Al_2O_3	0.45	750

plasma temperature of 7000 K (sample V-11). Sample V-1 was a standard CA-1-type catalysts for ammonia synthesis deactivated and passivated under industrial conditions.

The catalyst samples thus obtained ($100\,cm^3$) were pressed at a pressure of $5000\,kg\,cm^{-2}$ and subsequently ground and fractioned. The specimens were then reduced for 60 min in the installation shown in Fig. 1 as follows:

Sample V-2 at 673 K ⇒ sample V-5
Sample V-2 at 773 K ⇒ sample V-6
Sample V-3 at 673 K ⇒ sample V-7
Sample V-3 at 773 K ⇒ sample V-8
Sample V-4 at 673 K ⇒ sample V-9
Sample V-4 at 823 K ⇒ sample V-10
Sample V-11 at 673 K ⇒ sample V-12
Sample V-11 at 723 K ⇒ sample V-13

The reduced samples were passivated in a nitrogen–hydrogen mixture containing 1 vol.% O_2. The Möessbauer spectra of the regenerated (Fig. 2) and the reduced (Fig. 3) samples were used to identify the α-Fe, γ-Fe, Fe_3O_4 and $Fe_{1-x}O$ phases. Based on the location of the central singlet, one could claim that superparamagnetic α-Fe_2O_3 was present, or one could prefer the existence of γ-Fe in the reduced samples due to the short reduction time. In some samples (e.g. V-4 and V-7) the presence of 3–7% of γ-Fe_2O_3 could be assumed. Finally, it is the author's belief that the γ-Fe_2O_3 lines overlapped with those of Fe^{3+} at the tetrahedral magnetite sites.

The contents of the separate phases in the catalyst samples are proportional to the respective partial spectral areas; their values in percent are given in Table 2. The initial deactivated catalyst contained 89 mass% metallic α-Fe and 11 mass% Fe_3O_4. However, as the data in Fig. 2 and Table 2 demonstrate, after regeneration in argon atmosphere the oxide-phases content increased substantially with the temperature (due to the ab- and adsorption of O_2 present in the argon). Thus, sample V-4 (6800 K) contained about 25% elemental Fe (α-Fe, γ-Fe), while in sample V-11, regenerated in nitrogen atmosphere, the amount of metallic Fe was about 55%. To shorten the reduction time, one should lower the oxide amount in the catalyst to the maximal possible extent—regeneration, therefore, should be carried out at a low temperature, e.g. 1300 K, in argon atmosphere.

From Fig. 3 and Table 2, one can deduce the degree of reduction of the samples regenerated using the percentage content of elemental iron as a criterion. As a rule, this degree was lower at low temperatures; it was the lowest for sample V-9 and for the initial material (V-4) which contained predominantly an oxide phase. The best results in this respect were achieved at 773 K with samples V-6 and V-8. The Möessbauer analysis of these samples revealed the presence of only α-Fe and about 5–6% of γ-Fe, since the reduction had been complete and passivation precluded the formation of Fe_3O_4. Magnetite and FeO were also present in the samples. In all reduced samples, with the exception of V-6 and V-8, the amount of elemental Fe was below 90%.

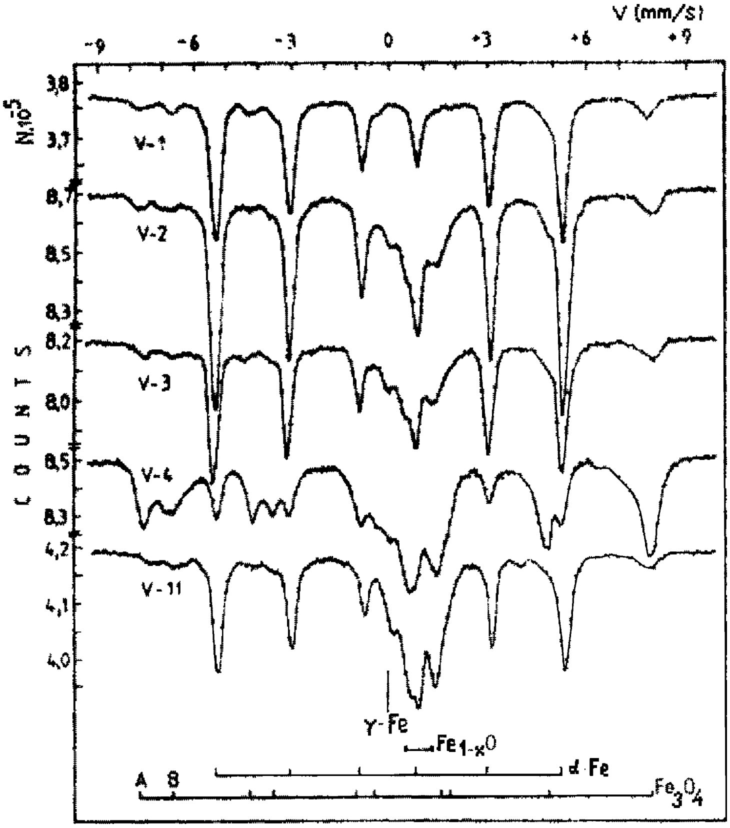

Fig. 2. Möessbauer spectra at room temperature of samples V-1, V-2, V-3, V-11.

On the other hand, a comparison of the Möessbauer spectra of plasma-chemical prepared ammonia-synthesis catalysts [9] with those of the samples discussed above shows a certain difference in the phase content; moreover, the values of the specific surface and the bulk mass are also different. These discrepancies arise because in plasma-chemical synthesis in a PCR (as in oxidation of elemental Fe) the metal vaporizes and then condenses; as the process takes place in the presence of oxygen, Fe_3O_4 is also oxidized to α-Fe_2O_3—this is precisely the oxide found in the final ultra-dispersed product. In contrast, only vaporization and condensation occur during the regeneration process.

The existence of a bi-dispersive size distribution of the ultra dispersed particles (Fig. 4) in some samples of a plasma-chemical regenerated catalyst, as predicted by a numerical experiment, was confirmed by the electron microscopy data. This is an interesting experimental fact whose explanation, it is the author's belief, lies in the following. A significant portion of the mass of the regenerated catalyst particles in a PCR is in the gaseous phase. Since the boiling temperature of Al_2O_3 (3803 K) is considerably higher than that of elemental Fe (3023 K), those Al_2O_3 particles that have not been completely vaporized act as condensation nuclei for the formation of nanocrystals in the newly condensed phase—this is observed as the appearance of new particles with equivalent diameter larger than that of the particles formed via condensation from a homogeneous gas phase. In other words, when spent ammonia-synthesis catalysts are regenerated, the formation of the new phase takes place beginning from both homogeneous and unhomogeneous phases.

The possible mechanism of regeneration (activation) of the spent catalyst is as follows. The

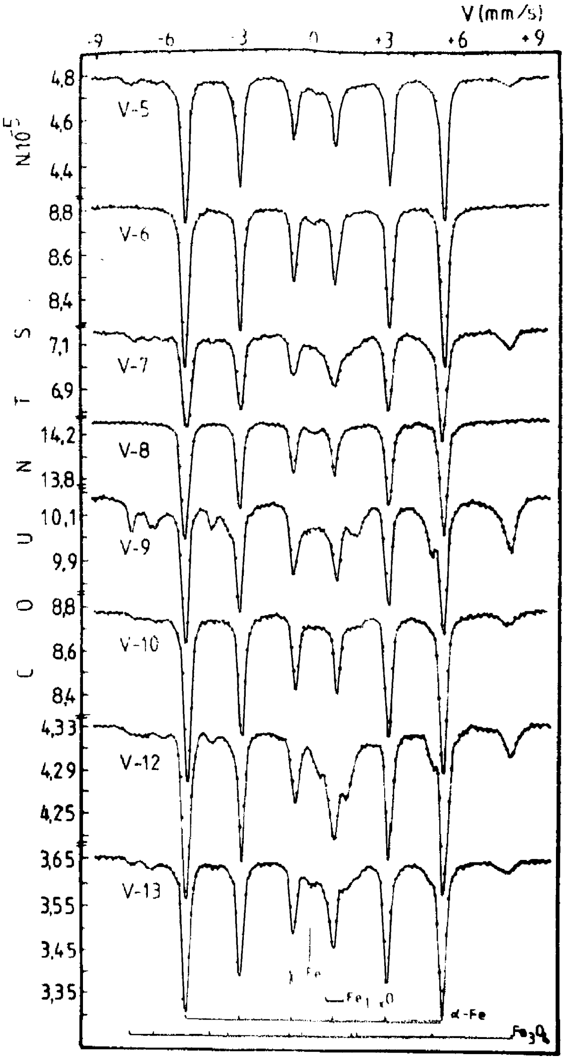

Fig. 3. Möessbauer spectra of the regenerated and reduced samples V-5–V-13.

gaseous-phase portion of the catalyst is quenched efficiently at a rate of $dT/d\tau = 10^5/10^6\,K\,s^{-1}$—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 Möessbauer spectra in Table 2) 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-type catalyst (Table 1), 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.

After the reduction process was completed at the isothermal modes cited above, the H_2 flow was terminated and N_2 containing 0.1–0.2 vol.% of O_2 was introduced in the reactor to passivate the pyroforic samples. Table 3 presents the specific surface of the samples after a 100% reduction and passivation. One can observe a tendency for a decrease of this parameter as the temperature of the isothermal reduction is raised—this is due to the fact that the recrystallization processes are accelerated as the temperature is increased. This assumption is supported by the electron microscope photographs of PC-regenerated samples (Fig. 5) and of PC-regenerated samples of a CA-1-type catalyst for ammonia synthesis (Fig. 6) that were reduced isothermally at 773 K and then passivated by technical-grade nitrogen (containing 0.5 vol.% O_2). One can observe the well developed crystalline structure of metallic Fe, as well as the distribution of the promoting oxides on the surface.

Table 4 shows the variation of the degree of reduction during reduction at 773 K. No induction period was observed for the regenerated samples, while in the case of the industrial CA-1-type catalyst, it was well expressed during the first 2 h of the process. It is in this period when the new α-Fe phase is formed which catalyses the synthesis of ammonia. During the second period, the autocatalytic one, α-Fe nuclei are already present so that the reduction process is considerably eased and its rate rises with the time due to the increase of the boundary surface between the two phases (Fig. 7). Evidently, since the regenerated samples consist predominantly of α-Fe, there is no induction period in their case and the autocatalytic one is very short—in the order of minutes (Fig. 7). At the end of the process, the amount of moisture released drops down to zero and the degree of reduction reaches a constant value ($B = 100\%$).

The reduction dynamics of the regenerated samples was investigated at several isothermal modes (673, 723, 773 and 823 K). At 673 K, the process proceeded

Table 2
Area (%) of the individual phases in the samples studied

Sample	Origin of the sample	Area (%) of the partial spectra			
		α-Fe	Fe_3O_4	$Fe_{1-x}O$	γ-Fe
V-1	CA-1-type standard, deactivated	89	11	–	–
V-2	From V-1, 1300 K, argon	70	9	14	7
V-3	From V-1, 1800 K, argon	66	12	12	10
V-4	From V-1, 6800 K, argon	19	50	26	5
V-11	From V-1, 7000 K, nitrogen	44	10	35	11
V-5	From V-2, reduced at 673 K	85	8	4	3
V-6	From V-2, reduced at 773 K	94	–	–	6
V-7	From V-3, reduced at 673 K	73	13	12	2
V-8	From V-3, reduced at 773 K	96	–	–	4
V-9	From V-4, reduced at 673 K	55	30	10	5
V-10	From V-5, reduced at 823 K	86	8	3	3
V-12	From V-11, reduced at 673 K	65	12	16	7
V-13	From V-11, reduced at 723 K	82	7	8	3

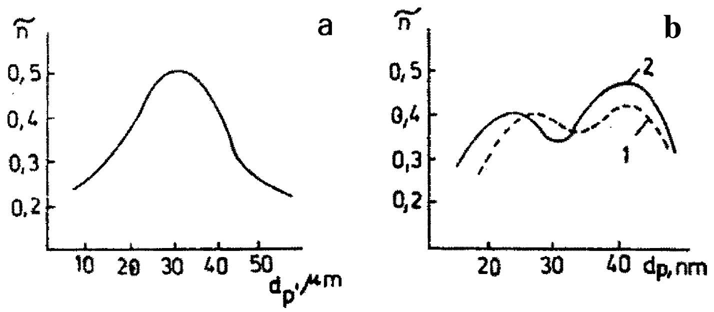

Fig. 4. Particle-size distribution of spent CA-1-type catalyst for ammonia synthesis (a) and of plasma-chemically regenerated CA-1-type catalyst (b): (1) numerical experiment; (2) electron microscope analysis.

Table 3
Specific surface of samples of a plasma-chemically regenerated catalyst as a function of the temperature of isothermal reduction (sample numbering refers to Table 1)

Number	Unreduced catalyst (m^2/g)	Catalyst reduced at temperature (K)			
		673	723	773	823
1	3.5	9.4	7.5	6.3	–
2	3.1	7.1	6.1	5.5	3.7
3	3.2	7.9	4.3	3.3	–
4	6.9	10.6	10.0	8.6	7.5
5	5.9	8.4	6.0	5.9	5.6
6	3.6	7.8	7.4	–	4.5
7	4.7	6.7	4.9	4.8	–
8	1.6	7.9	7.8	7.6	–

very irregularly—the amount of H_2O released per unit time varied in a wide range, which was an indication for the complex mechanism and kinetic of the reduction at lower temperatures. Performing the isothermal reduction at 723 K resulted in a more regular course of the process: the moisture was released mainly in the first hours of the process—this became more pronounced as the temperature rose. Hydrogen interacts first with the surface of the unreduced catalyst particles; at these temperatures the process is constrained by the rate of H_2 interaction with the iron-oxides, i.e. it takes place in the kinetic region. As the process proceeds into the depth of the micron-size standard CA-1-type catalyst particles, its rate diminishes because the reverse diffusion of water vapor towards the particles surface is hindered.

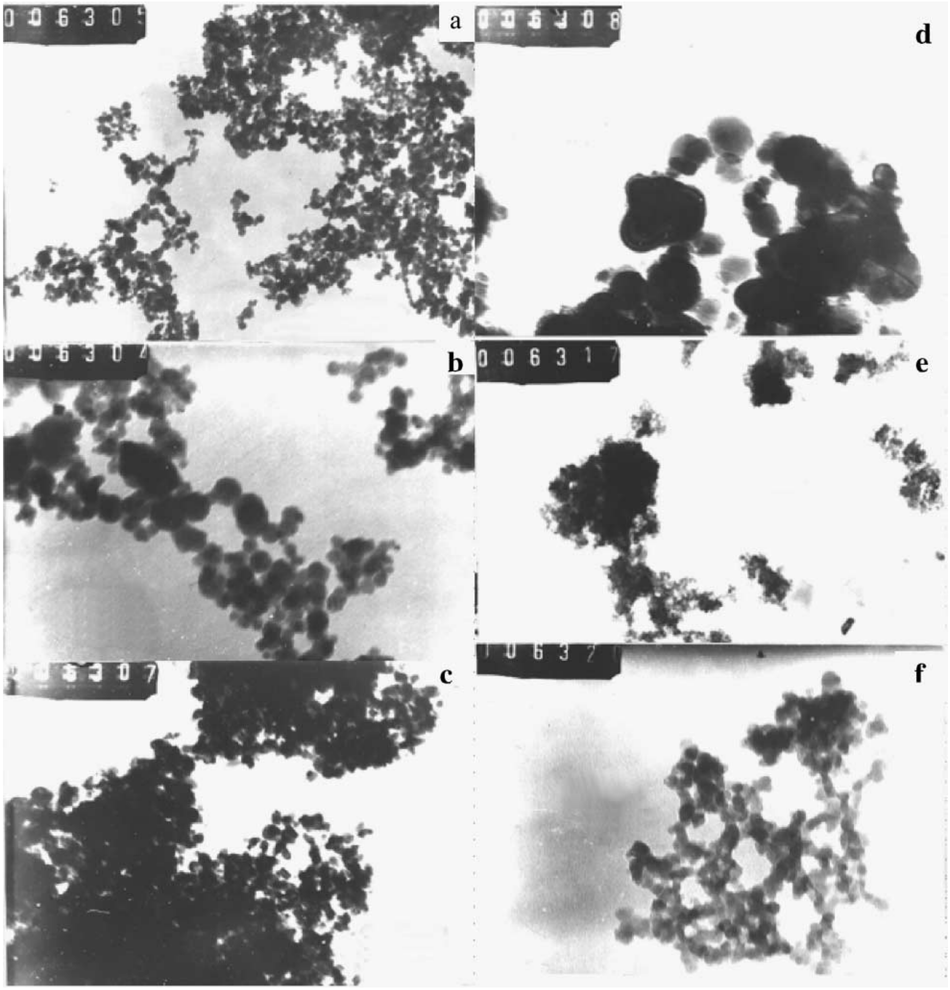

Fig. 5. Electron microscope photographs of plasma-chemically regenerated samples of CA-1-type catalyst for ammonia synthesis: (a) sample 4 (Table 1), magnification 36,000, 1 mm = 28 nm; (b) sample 4 (Table 1), magnification 98,000, 1 mm = 10.2 nm; (c) sample 4 (Table 1), reduced at 723 K and passivated, magnification 36,000, 1 mm = 28 nm; (d) sample 4 (Table 1), reduced at 723 K and passivated, magnification 98,000, 1 mm = 10.2 nm; (e) sample 1 (Table 1), magnification 36,000, 1 mm = 28 nm; (f) sample 1 (Table 1), reduced at 723 K and passivated, magnification 98,000, 1 mm = 10.2 nm.

Skarchenko, Strel'tsov and Rousov's first-order equation is written as [10,11]

$$K = \frac{2.303}{\tau} \log\left(\frac{m}{m_0 - m_x}\right) \qquad (1)$$

where K is the rate constant of the reduction process (h^{-1}); m_0 the maximal amount of water that can be released (g) and m_x is the amount of water released for 1 h ($\mathrm{g\,h}^{-1}$).

The rate constant K is used to calculate the Arrhenius activation energy for reduction:

$$\begin{aligned} &E = 4.58 \frac{\log(K_{T_2}/K_{T_1})}{(1/T_1) - (1/T_2)}; \quad T_2 > T_1; \\ &K = K_0 \exp(-E/RT); \quad K_\mathrm{r} = K_{0\mathrm{r}}(-E/RT); \\ &E = E_\mathrm{r} = 77.8 \pm 6\,\mathrm{kJ\,mol}^{-1} \end{aligned} \qquad (2)$$

where E is the activation energy for reduction of the CA-1-type catalyst ($\mathrm{kJ\,mol}^{-1}$); E_r the activation

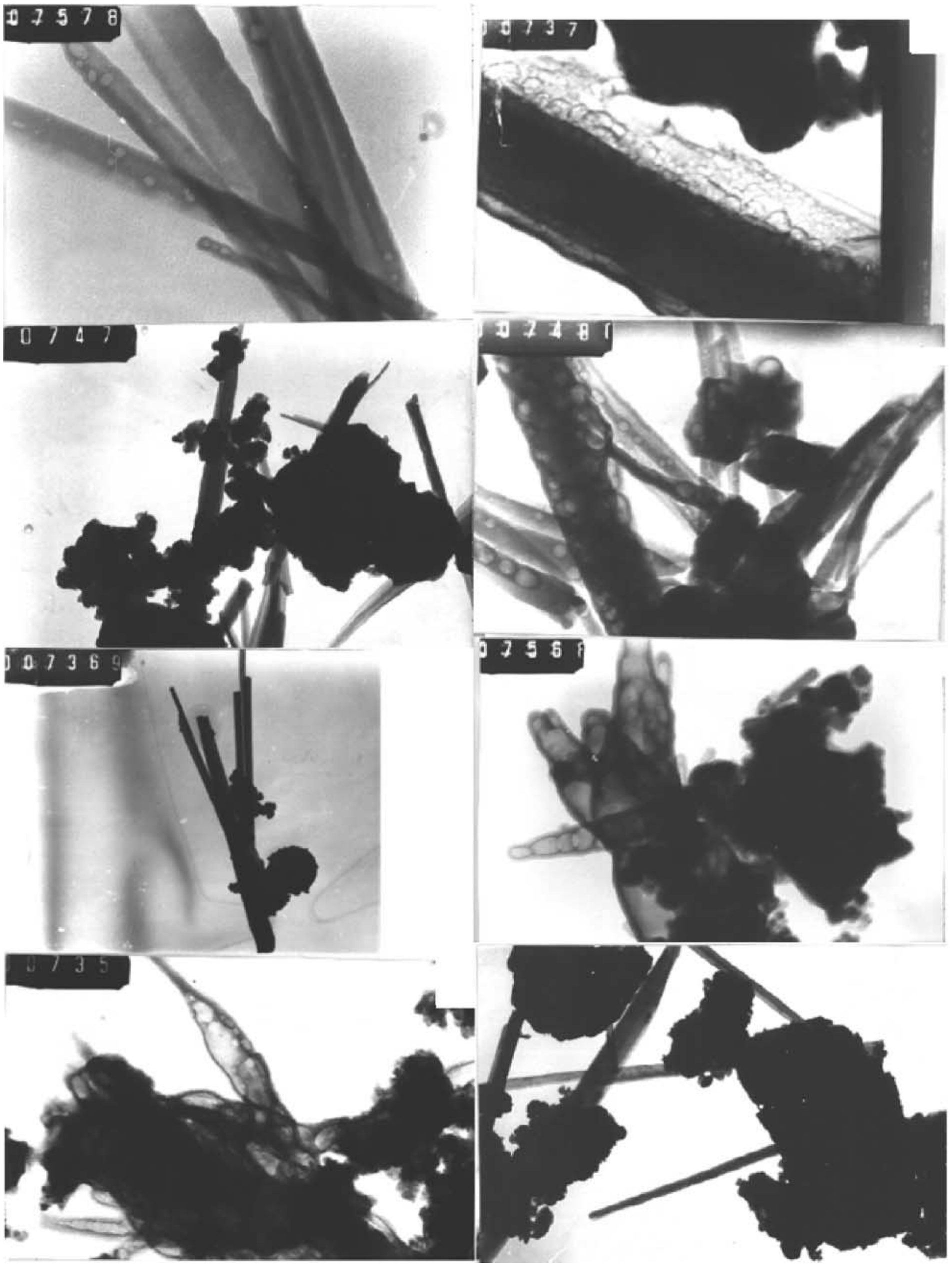

Fig. 6. Electron microscope photographs of plasma-chemically regenerated CA-1-type catalysts for ammonia synthesis isothermally reduced at 773 K and passivated with technical-grade nitrogen (oxygen content of 0.5%), magnification 91,000, 1 mm = 10.9 nm.

energy for reduction of a PC-regenerated CA-1-type catalyst (kJ mol^{-1}); K_0 the pre-exponential factor in the Arrhenius equation for the standard CA-1-type catalyst and $K_{0\mathrm{r}}$ is the pre-exponential factor in the Arrhenius equation for a PC-regenerated CA-1-type catalyst.

As the dependence $\log K = f(1/T)$ (Fig. 8) demonstrates, the logarithmic straight lines constructed for

Table 4
Degree of reduction (B, %) of catalyst sample isothermally reduced at 773 K (samples numbering refers to Table 1)

Time (h)	Sample						
	1	2	3	4	5	6	8
0.5	95.5	86.9	71.9	42.4	68.6	40.1	–
1.0	98.0	93.8	89.3	69.6	92.2	61.4	–
1.5	99.8	99.0	96.5	86.9	94.3	75.6	–
2.0	99.9	100.0	97.2	94.9	98.6	91.1	–
2.5	100.0	–	98.5	96.5	100.0	100.0	31.1
3.0	–	–	99.0	98.2	–	–	52.3
3.5	–	–	100.0	100.0	–	–	66.5
4.0	–	–	–	–	–	–	72.4
4.5	–	–	–	–	–	–	78.0
5.0	–	–	–	–	–	–	82.4
5.5	–	–	–	–	–	–	86.2
6.0	–	–	–	–	–	–	90.4
6.5	–	–	–	–	–	–	93.3
7.0	–	–	–	–	–	–	95.7
7.5	–	–	–	–	–	–	98.2
8.0	–	–	–	–	–	–	100.0

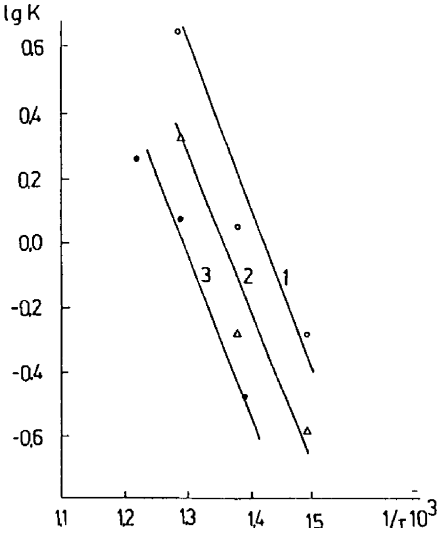

Fig. 8. Rate constant of the reduction process as a function of the temperature: (1) sample 1; (2) sample 2; (3) sample 8 (sample numbering refers to Table 1).

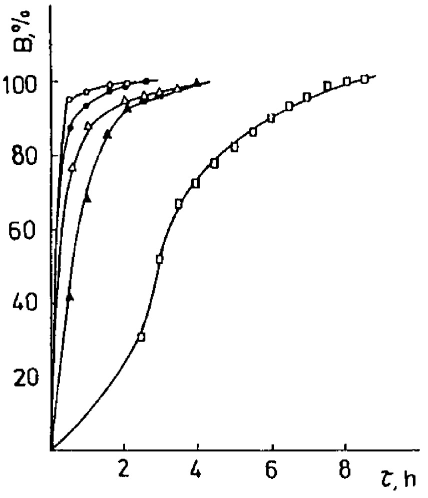

Fig. 7. Degree of reduction (B, %) of fresh and of regenerated samples of CA-1-type catalyst for synthesis of ammonia as a function of the time (τ, h) at 773 K: (○) sample 1; (●) sample 2; (△) sample 3; (▲) sample 4; (☐) sample 8 (sample numbering refers to Table 1).

the different plasma-chemical conditions (Table 1, numbers 1–7) are parallel. Moreover, the line corresponding to sample 1 (regenerated at the lowest temperature) is at the top. The calculated activation energy has identical values ($77.8 \pm 6\,\mathrm{kJ\,mol^{-1}}$). According to the active centers theory, a rise in the rate of reduction of catalysts with the activation energy remaining constant has to do with the presence of a larger number of active centers at the catalyst's surface. On the other hand, an increase of the rate of reduction accompanied by a decrease of the activation energy is due to a growth in the activity of already existing active centers. The experimentally observed rise (a factor of 3–5, Fig. 7) in the rate of reduction of samples regenerated under LTP conditions was, therefore, the result of an increase of the number of active centers. Thus, the active centers theory supports the assumption that LTP-regenerated samples possess a larger number of active centers compared with conventional catalysts. In addition, in LTP-regenerated catalysts, the excess free energy at the particles' surface is released, and structural saturation and lattice defects exist in the catalytically-active phases; this eases the transition of ions through the boundaries between the solid phases formed during the reduction, i.e. the reaction diffusion is facilitated.

Tables 5–10 and Fig. 9 summarize the results of kinetic studies of four catalyst samples. The activity was determined at five reactor temperatures: 673, 723, 748, 773, and 823 K. After the first measurements, the

Table 5
Activity (Z, %NH_3) as a function of the temperature (T, K) before and after overheating[a] of PCR ammonia-synthesis catalysts, $P = 30$ MPa, $W = 30{,}000\ h^{-1}$

Number	Catalyst type	Temperature (K)				
		673	723	748	773	823
Activity, Z (%NH_3)						
1	Industrial catalyst CA-1-type (present experiment)	16.6 (6.0[a])	19.8 (10.8[a])	20.0 (11.0[a])	19.3 (10.9[a])	14.9 (10.2[a])
2	Industrial catalyst CA-1-type (literature data) [12]	16.8 (7.1[b])	20.7 (13.4[b])	20.8 (15.6[b])	19.7 (16.5[b])	15.5 (14.0[b])
3	Plasma-chemical regenerated in (oxidizing media CA-PRO)	15.8 (14.5[a])	21.0 (18.0[a])	21.4 (18.2[a])	21.2 (18.1[a])	15.5 (14.0[a])
4	Plasma-chemical regenerated in (redox media CA-PRRO)	16.1 (15.6[a])	21.1 (19.8[a])	21.5 (20.0[a])	22.0 (18.7[a])	16.2 (14.1[a])

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

Table 6
Relative degree of transformation ($x = (Z/Z_{eq}) \times 100$, %) as a function of the temperature (T, K) before and after overheating of PCR ammonia-synthesis catalysts, $P = 30$ MPa, $W = 30{,}000\ h^{-1}$ (samples numbering same as in Table 5)

Number	Temperature (K)				
	673	723	748	773	823
Relative degree of transformation, $x = Z/Z_{eq} \times 100$ (%)					
1	35.3 (12.8)[a]	55.3 (30.2)[a]	61.5 (33.9)[a]	73.0 (41.2)[a]	77.9 (53.3)[a]
2	35.7 (15.1)[b]	57.8 (37.4)[b]	64.0 (48.0)[a]	74.5 (62.4)[b]	81.0 (73.2)[b]
3	33.6 (30.9)[a]	58.6 (50.3)[a]	65.9 (56.0)[a]	80.2 (68.5)[a]	81.0 (73.2)[a]
4	34.3 (33.2)[a]	58.9 (55.3)[a]	66.2 (61.5)[a]	83.2 (70.7)[a]	84.7 (73.7)[a]

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

temperature was raised to, and maintained for 3 h at 1073 K, i.e. an overheating was performed to deactivate the samples; the activity was then measured once again. The activity values in %NH_3 as a function of the temperature before and after overheating are given in Table 5. One can see that the highest activity was exhibited by sample 4 prepared by PC-reduction in a redox medium.

Table 7
Rate constant of the ammonia-synthesis process (K, $Pa^{0.5}\ h^{-1}$) as a function of the temperature (T, K) before and after overheating of PCR catalysts, $P = 30$ MPa, $W = 30{,}000\ h^{-1}$ (samples numbering same as in Table 5)

Number	Temperature (K)			
	673	723	748	773
Rate constant, K ($Pa^{0.5}\ h^{-1}$)				
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	2500 (2170[a])	18510 (12830[a])	35720 (22940[a])	72290 (45650[a])
4	2700 (2470[a])	18590 (15720[a])	38110 (31440[a])	81710 (50440[a])

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

Table 8
Activation energy (E, kJ mol^{-1}) for various temperature ranges before and after overheating[a] of PCR ammonia-synthesis catalysts, $P = 30$ MPa, $W = 30{,}000\,h^{-1}$ (samples numbering same as in Table 5)

Number	Temperature range (K)		
	673–723	748–773	673–773
Activation energy, E (kJ mol^{-1})			
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	163.3 (145.0[a])	135.7 (124.3[a])	145.7 (139.0[a])
4	154.4 (151.0[a])	146.8 (92.8[a])	147.8 (130.9[a])

[a] Overheating at 1073 K for 3 h.

[b] Overheating at 973 K for 20 h.

Table 9
Relative activity of deactivated catalysts ($y_a = (k_2/k_1) \times 100$, %) as a function of the working temperature (T, K)[a]

Number	Temperature (K)			
	673	723	748	773
Relative activity, $y_a = (k_2/k_1) \times 100$ (%)				
1	12.9	27.5	25.2	25.4
2	15.0[b]	25.6[b]	50.0[b]	64.5[b]
3	86.7	69.3	67.0	63.2
4	91.5	84.6	82.5	62.0

[a] Deactivation performed at 1073 K for 3 h (samples numbering same as in Table 5).

[b] Overheating at 973 K for 20 h.

Table 10
Degree of deactivation of the catalysts ($y_d = (k_1 - k_2)/k_1 \times 100$, %) as a function of the working temperature (T, K)[a]

Number	Temperature (K)			
	673	723	748	773
Degree of deactivation, $y_d = (k_1 - k_2)/k_1 \times 100$ (%)				
1	87.1	72.5	74.8	74.6
2	85.0[b]	74.4[b]	50.0[b]	35.5[b]
3	13.3	30.7	33.0	36.8
4	8.5	15.5	17.5	38.0

[a] Deactivation performed at 1073 K for 3 h (samples numbering same as in Table 5).

[b] Overheating at 973 K for 20 h.

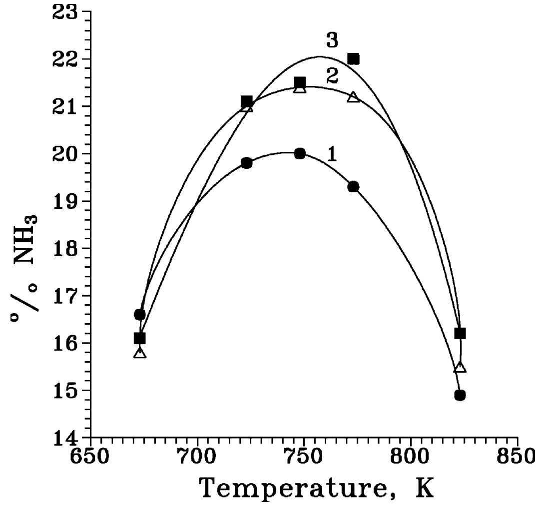

Fig. 9. Activity of catalysts for ammonia synthesis (%NH$_3$) as a function of the temperature (T, K) at pressure $P = 30$ MPa and flow rate $W = 30{,}000\,h^{-1}$: (1) industrial CA-1-type catalyst (present experiment); (2) catalyst plasma-chemically regenerated in oxidizing atmosphere (CA-PRO); (3) catalyst plasma-chemically regenerated in redox atmosphere (CA-PRRO).

As the temperature was raised, the relative degree of transformation x increased (Table 6). Thus, the value of this parameter at 773 K for a PC-regenerated and reduced in a redox medium CA-1-type (CA-PRRO) catalyst was 83.2%, while for the conventional CA-1-type catalyst $x = 73.0\%$; after overheating these values were 70.7 and 41.2%, respectively. In other words, the PC-regenerated catalyst had a much better thermal stability. The values of the rate constant in the Arrhenius equation were also calculated as a function of the temperature of the ammonia-synthesis process. These results were discussed in [9].

When the temperature was raised, the rate of the process began to be limited by macrokinetic factors. If the catalyst particles were ground down to a smaller size, the kinetic region widened towards the higher temperatures. This was indicated by the values of the activation energy in the different temperature intervals (Table 8). Table 9 presents the values of the relative activity of thermally deactivated catalysts. It was especially high for the lower temperatures, 673 and 723 K. For example, for sample 4 at 673 K it was 91.5%, while for the conventional CA-1-type catalyst the value was 12.9% (a value of 15% was cited in [2]). According to our data (Table 10) and that in [13], the degree of deactivation of the CA-1-type catalyst was several times as high as that of the regenerated samples.

4. Conclusion

Summarizing the results of the investigations on PCR of spent catalysts for synthesis of ammonia and of the physico-chemical and kinetic studies, one can point out that the following factors.

1. The plasma-chemical technique is efficient in regeneration of spent ammonia-synthesis catalysts.
2. The advantages of using this technique are as follows: (a) a regenerated finely-dispersed catalyst is obtained with specific surface of $40\,\mathrm{m}^2\,\mathrm{g}^{-1}$; (b) the dispersity of the regenerated catalyst and, within certain limits, its content, can be controlled via varying the PC-process parameters; (c) the energy consumption associated with PC-regeneration of spent catalysts are lower compared with the other thermal techniques, while the process comprises two steps only: PCR (dispersing) of the material, and preparation of granules and tablets.

A mechanism describing the regeneration process is proposed. The PC-regenerated catalysts are reduced three to five times as fast as the standard—the increased rate of reduction is due to an increase of the pre-exponential factor in the Arrhenius equation at constant activation energy.

The physico-chemical properties of the PC-regenerated samples, the defects in the crystal lattices of the catalytically-active phases, the presence after reduction of α-Fe and γ-Fe as a result of the efficient thermal shock associated with the quenching at a rate of $\mathrm{d}T/\mathrm{d}\tau = 10^5\,\mathrm{K\,s}^{-1}$, the finely dispersed product obtained, the optimal $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$ ratio in the unreduced catalysts, are all reasons for the observed high rate of formation of an active surface during the reduction, and determine the high catalytic activity and thermal stability of the samples.

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