LOW-TEMPERATURE PLASMA AS APPLIED TO PREPARATION AND RECOVERY OF A CATALYST FOR AMMONIA SYNTHESIS*

G. P. Visokov and G. P. Georgiev

UDC 546.171.1:544-44:539.9...15

Results of a physicochemical study of the properties of catalysts for ammonia synthesis prepared and (or) recovered in an electric-arc plasma are reported.

Introduction. High-energy parameters of low-temperature plasma (LTP) and high hardening rates ($dT/d\tau = 10^5$-10^6 K/sec) predetermine obtainment (regeneration) of ammonia synthesis catalysts with a highly developed specific surface [1, 2] and numerous defects in a crystalline structure of condensed phases [1-11]. The regeneration of spent deactivated catalysts used in the chemical industry and, in particular, in ammonia production is an especially urgent problem. The available methods of catalyst regeneration are reduced to the supply of a regeneration gas into reactors with a reversible-deactivated catalyst [12] or to their melting in an oxidizing or neutral gaseous medium and regranulation [13]. A drawback of the former method lies in the impossibility of recovering the activity in the presence of irreversible changes in the structure and a chemical composition of the catalysts, while of the latter – in the fact that it is applicable only for plasma catalysts, whose the activity does not recover to the full extent, but whose energy consumption is high. The plasma-chemical method of regeneration of deactivated oxide catalysts [6] and, in particular, of ammonia synthesis catalysts provides the recovery of the catalytic activity of deactivated catalysts to values commensurable with parameters of fresh catalysts.

The conducted experiments concerned with preparation [1-3, 5, 7, 9-11] and regeneration [1, 2, 4, 6, 8, 10] of ammonia synthesis catalysts, using solid ingredients [1-11] (metals, oxides, carbonates or their mixtures) in a neutral or oxidizing medium (OM) [5] and in a redox medium (RM) [9], are a prerequisite for kinetic studies (determination of the extent of recovery, activity, relative degree of transformation, rate constants, activation energy, thermal stability, relative activity, etc.).

The present work is aimed at investigation of the physicochemical characteristics of the kinetics of recovery and the ammonia synthesis kinetics of plasma-chemically synthesized and (or) regenerated catalysts of the type SA-1.

1. Experimental Studies. Synthesis and (or) regeneration of catalysts for ammonia synthesis have been carried out on a plasma-chemical constant-current electric-arc plant with a regulated electric power up to 15 kW and output up to 150 g/h. A schematic diagram of the experimental plant is given in [1, 2].

For regeneration, we used as initial raw material, the ammonia synthesis catalyst SA-1, preliminarily ground to particles less than 50 μm. Argon at a flow rate of 3 m^3/h was used as the plasma-forming gas, while argon or pure nitrogen at a flow rate of 0.8 m^3/h was used as the transport gas. The plasma-chemical process was conducted in a reactor with "hot" walls [8]. Hardening at a rate $dT/d\tau \cong 10^5$ K/sec was accomplished by cold jets of technical nitrogen (containing 5% O_2) and on water-cooled metallic walls of a hardening unit. The residence time of the deactivated catalyst particles in the plasma-chemical reactor was 1-5 msec and the temperature in the reaction space of the plasma-chemical reactor was 1100-3400 K depending on the consumed electric power. On the filter and on the cold walls of the dust-catching chamber, a fraction of the ultradispersed ammonia synthesis catalyst (UC) of the type SA-1 was accumulated, with the particles sized to 100-300 nm and the UC specific surface 3-10 m^2/g. The catalyst SA-1 ultradispersed powder (UP) in a volume of 1 cm^3 was regenerated on a flow-type plant. As the regenerating agent, hydrogen with a volume velocity of 40,000 h^{-1} was used in isothermal modes of regeneration at 673, 723,

---

*All-Union Conference on Physics of Low-Temperature Plasma (Minsk, September 1991).

Institute of Electronics, Bulgarian Academy of Sciences, Sofia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 63, No. 2, pp. 165-171, August, 1992. Original article submitted November 12, 1991.

TABLE 1. Some Physicochemical Properties of Regenerated Samples of the Ammonia Synthesis Catalyst SA-1 as a Function of the Plasma-Chemical Process Temperature at a Carrier-Argon Flow Rate 1.19 g/sec in a Reactor with "Cold" Walls

Test No.	T_{th}, K	T_r, K	Specific surface m^2/g prior to regen.	Specific surface m^2/g after regen.	Particle size, nm	Basic phases	$\frac{Fe^{2+}}{Fe^{3+}}$	Bulk density, kg/m^3
In technical argon at its flow rate 1.49 g/sec								
1	1400	600	3,5	9,4	100—	Fe_3O_4, Fe_2O_3	0,45	550
2	2000	700	3,1	7,1	—300	FeO, FeO·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
In pure nitrogen at its flow rate 0.26 g/sec								
5	3600	1200	5,9	8,4		Fe_3O_4, Fe_2O_3	0,42	550
6	4400	1800	3,6	7,8	80—	FeO, FeO·Al_2O_3	0,41	520
7	7000	3200	4,7	6,7	—250	Fe_xN_y, α, γ-Fe	0,41	530
The standard catalyst SA-1								
8	—	—	—	—	< 50 μm	Fe_3O_4, FeO Al_2O_3	0,45	750

TABLE 2. Specific Surface (m^2/g) of the Plasma-Chemically Regenerated Catalysts (numeration of tests corresponds to Table 1) as a Function of the Isothermal Regeneration Temperature

Test No.	Unregenerated catalyst	Catalyst regenerated at temperatures, 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	—

773, and 823 K. The amount of moisture released during the regeneration process was determined by a weighing method; a melt potassium base served as an adsorbent. The regeneration process was controlled by the amount of moisture released every 30 min.

In the synthesis of catalyst samples, two approaches are implemented: the processes have been conducted in an OM or RM. As the plasma-forming gas, technical argon with a flow rate 3 m^3/h was used in both cases, while as carrier gas—air (O_2) with a flow rate of 0.8 m^3/h in the former case and hydrogen with a flow rate of 0.5 m^3/h in the latter case were taken. Hardening in both cases was implemented by injecting cold air jets with a flow rate up to 30 m^3/h and on cold walls of the dust-catching chamber. When we conducted the synthesis in an oxidizing medium, the initial charge (a fraction lower than 50 μm) with the composition Fe, Al, K_2CO_3, $CaCO_3$, and SiO_2 was used in such a mass ratio as to produce, after the oxidizing process, the catalyst mass with the composition (wt. %): Fe_3O_4 + FeO + Fe_2O_3 – 94; Al_2O_3 – 3; K_2O – 0.8; CaO – 2; SiO_2 – 0.2, i.e., similar to that of the composition of the standard commercial catalyst SA-1. With the synthesis conducted in the RM, we used the charge of Fe_3O_4, Al_2O_3, K_2CO_3, $CaCO_3$, and SiO_2 in such mass ratio as to obtain, after air hardening, the catalyst with the mass ratio of the components analogous to the commercial catalyst SA-1. The activity was determined on the flow-type plant at the pressure of 30 MPa and a volume velocity of 30,000 h^{-1} of the stoichiometric nitrogen–hydrogen mixture.

2. Experimental Results and Discussion. *Kinetic Studies of the Ammonia Synthesis Catalyst Regenerated in an Electric-Arc LTP.* Table 1 lists some technological parameters of the plasma-chemical process: the mean-mass temperature of the plasma T_p and plasma-chemical reactor T_r (determined by the calorimetric technique), the specific surface before and after the recovery (determined by the Klyachko-Gurvich method [14]), particle sizes (determined from electron-microscopic photos of the UC), basic phases (determined from the x-ray analysis), the ratio (from the chemical analysis) and the bulk density of the samples.

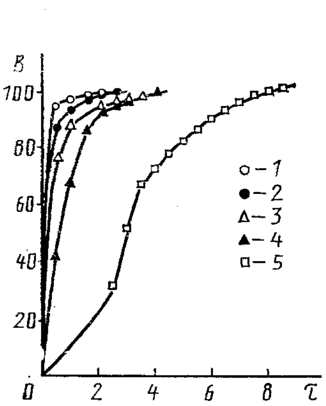

Fig. 1

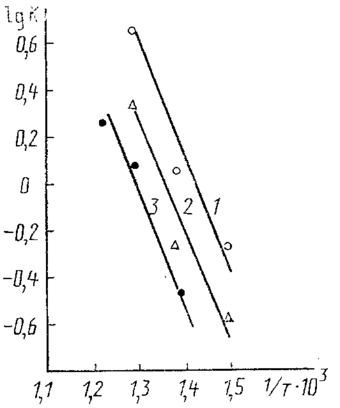

Fig. 2

Fig. 1. Degree of the recovery of samples vs time at 773: 1) sample No. 1; 2) No. 2; 3) No. 3; 4) No. 4; 5) No. 8 (numeration of the samples corresponds to Table 1). B, %; τ, h.

Fig. 2. Temperature dependence of the recovery rate constants: 1) sample No. 1; 2) No. 3; 30 No. 8 (numeration of the samples corresponds to Table 1).

The regeneration (activation) mechanism of deactivated spent catalysts in an LTP is as follows: a larger portion of the catalyst particles is in a gaseous phase in the plasma-chemical reactor. Effective hardening at dT/dτ ≅ 10^5 K/sec brings the catalyst mass into a condensed phase with imperfect crystalline lattices of components forming it. Catalyst poisons leave the system as volatile gaseous products.

With the recovery process having been performed in the mentioned thermal regimes, hydrogen supply is ceased and a nitrogen flow with 0.1-0.2 vol.% oxygen content is delivered for passivation of pyrophore regenerated samples. Table 2 lists the specific surfaces of the samples after recovery of up to 100% and passivation. As is seen, with increasing temperature of the plasma-chemical recovery, a tendency is observed to decreasing the specific surface of the samples. This is a consequence of enhancement recrystallization processes with increasing the temperature.

Figure 1 shows the degree of recovery of the samples versus the process duration at 773 K. For the regenerated samples, there is no induction period, while for the commercial catalyst SA-1 it is well observed for the first 2 h of the process.

The dynamics of the recovery of regenerated samples has been investigated for four isothermal regimes (673, 723, 773, and 823 K). The process is highly irregular at 673 K; the amount of released water per unit time varies in a wide range, thus testifying to a complicated kinetic mechanism of the recovery at low temperatures. The basic amount of moisture is released within the initial hours of recovery, the more so, the higher the temperature.

The deactivated catalyst contains elemental iron which, as a result of thermal impact, is fixed into the metastable gamma-modification along with α-Fe [8]. The obtained catalyst has almost the same ratio of Fe^{2+}/Fe^{3+}(see Table 1), its specific surface is high, and there are many defects in the crystalline lattice of iron oxides with complete binding of Al_2O_3 in the form of $FeO \cdot Al_2O_3$, which indicates the high thermal stability of the regenerated samples. In the regenerated samples in the recovered and unrecovered forms, a free γ-Fe phase is observed [8]. Apparently, thermal impact at a hardening rate of dT/dτ ≅ 10^5 K/sec fixed the high-temperature gamma-modification in a metastable state in an amount up to 10 wt.%.

The equation recommended in [15, 16] describes well the kinetic data well. The calculated rate constants K are used to draw the Arrhenius dependences. From Fig. 2 it is seen that these three straight lines are parallel. With the recovery of all the samples (Nos. 1-8 in Table 1), equal activation energies 77.8 ± 6 kJ/mole are observed. This means that the difference in the rate constants is due to the preexponential factor. The recovery rate of the regenerated samples is 3-5 times higher than that of the standard catalyst; a sample regenerated at higher temperatures recovers more quickly. We can say that the regenerated samples generate a larger number of active sites in the LTP than a classical catalyst. The excess free energy on the surface of the catalyst particles increases, there exist structural supersaturations and defects in the lattice of catalytically active phases and this facilitates a transition of ions via an interface between solid phases formed during the recovery.

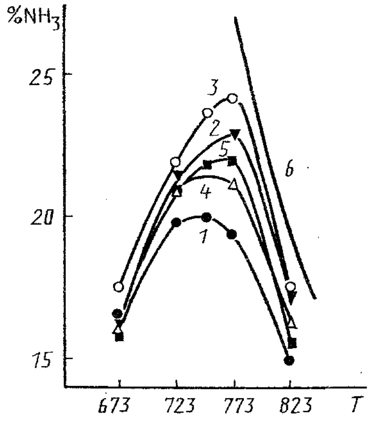

Fig. 3

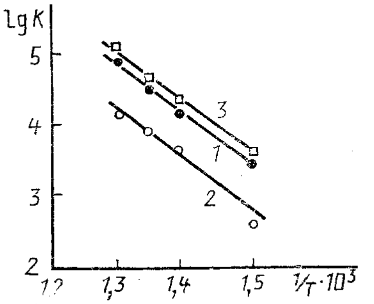

Fig. 4

Fig. 3. Catalyst activity vs temperature at P = 30 MPa, W = 30,000 h^{-1}, and H_2:N_2 = 3:1: 1) commercial catalyst SA-1 (experiment of the present authors); 2) plasma-chemically synthesized catalyst in the oxidizing medium — SA-PSO; 3) plasma-chemically synthesized catalyst in the redox medium — SA-PSVO; 4) plasma-chemically regenerated catalyst in the oxidizing medium — SA-PRO; 5) plasma-chemically regenerated catalyst in the redox medium — SA-PRVO; 6) equilibrium curve. T, K.

Fig. 4. Rate constant vs temperature: 1) commercial catalyst SA-1 (experiment of the authors); 2) commercial catalyst SA-1 deactivated for 3 h at 1073 K; 3) plasma-chemically synthesized catalyst in the redox medium — SA-PSVO.

Kinetic Studies of the Activity of Plasma-Chemically Synthesized Catalysts for Ammonia Synthesis. Figures 3 and 4 show some results of kinetic studies of six catalyst samples. The activity was determined at the following five temperatures in a catalytic reactor: 673, 723, 748, 773, and 828 K. After temperature determination, the temperature was increased to 1073 K and maintained for 3 h, i.e., thermal deactivation of the samples was performed and then the activity was determined again.

The activity values as NH_3 percents as a function of temperature before and after superheating (Fig. 3) show that sample No. 3, plasma-chemically synthesized in the RM, displays the highest activity. Thus, for instance, the relative degree of transformation x at 773 K (at this temperature x is maximum) for the SA-PSVO is 91.5%, while for the standard catalyst SA-1 it is equal to 73.0%. After superheating the SA-PSVO, x = 82.8%, while for the SA-1, x = 41.2%, i.e., the plasma-chemically synthesized catalyst is much more stable. Also, we have calculated the rate constants in the Arrhenius equation as a function of the ammonia synthesis temperature. The ammonia synthesis rate is described by the Temkin and Pyzhev equation [17]. The activation energy of the ammonia synthesis process for three different temperature ranges is calculated by the slope of Arrhenius straight lines (Fig. 4). The Arrhenius equation $K = K_0 \exp(-E/kT)$ is applicable for the temperature ranges in which the ammonia synthesis proceeds in the kinetic region. With grinding of the catalyst particles, the kinetic region broadens toward higher temperatures. This is demonstrated by activation energies in different temperature ranges. For the standard catalyst SA-1, the activation energy decreases in the temperature range 748-773 K (100 kJ/mole), while within 673-723 K it is equal to 148.2 kJ/mole; for the plasma-chemically synthesized samples in the oxidizing or redox medium within the temperature range 673-723 K it is 152.0 and 163.2 kJ/mole, respectively, while for the 748-773 K range, it is 185.8 and 135.7 kJ/mole.

Inspection of the dependence log K = f(1/T) (Fig. 4) for the standard and synthesized or (and) regenerated samples in the quasi-equilibrium LTP reveals that the logarithmic straight lines within the kinetic control domain of the process are parallel, i.e. the activation energy within the frame of exact activity determination is constant. According to the theory of active sites, an increase in the rate constant of the process at the constant activation energy is indicative of the fact that the activation is a result of increasing the number of the active sites. If the activation energy decreases in the kinetic region of the process, then it is a consequence of increasing the activity of the available active sites. Apparently, the plasma-chemically regenerated catalysts and, primarily, the plasma-chemically synthesized catalysts possess a larger number of active sites per unit mass as compared to the commercial catalyst SA-1 and, as a result, a relative increase of the catalytic activity is realized by 15-25% (depending on the temperature).

The relative activity ($Y_a = 100 K_2/K_1$, %) of the deactivated catalysts is especially high at low temperatures (673 and 723 K). Thus, for instance, for sample No. 4 at 673 K it makes up 94.1%, while for the standard catalyst SA-1 it is 12.9% (according to literature data, 15%). At superheating of the samples, recrystallization of catalytically active phases occurs. In this case, the cubic space-centered lattice of α-Fe acquires a normal structure (for plasma-chemically synthesized catalysts, the lattice parameter Y_a of magnetite decreases up to 0.25 rel.%). Structural defects on account of thermal fluctuations of interstitial crystal atoms (the Taman temperature is $0.52T_{melt}$ of iron) decrease and the catalytic activity deteriorates. Obviously, with superheating up to 1073 K, the plasma-chemically synthesized and (or) regenerated samples undergo relatively smaller changes in their phase composition and crystalline structure of the phases and, as a result, deactivation processes are less pronounced in the conditions examined, compared to the commercial catalyst SA-1.

The degree of deactivation of the catalyst SA-1 ($Y_d = 100 (K_2 - K_1)/K_1$, %) is severalfold higher, according to our data and literature data than in the case of standard or regenerated samples under LTP conditions.

Synthesis must be conducted in plasma-chemical reactors with "cold" walls and accompanied by hardening. The oxygen content in a gaseous mixture must not exceed 5% by volume in order to obtain only the magnetite phase in catalysts [2, 10]. To form a highly active surface, it is necessary to have samples with the maximum specific surface, dispersity of particles, and defects in a crystal lattice of catalytically active phases. The optimal temperatures for obtaining such samples are 1300 to 3000 K.

Conclusion. It is established that the plasma-chemical method is an effective tool for regeneration (activation) of spent deactivated catalysts in ammonia synthesis. The process consists of two stages: plasma-chemical regeneration (dispersion) of catalysts and formation of granules or pellets. A mechanism of catalyst regeneration is proposed. Plasma-chemically regenerated catalysts are found to recover 3-5 times faster than the standard catalyst. The recovery rate increases with the preexponential factor in the Arrhenius equation at a constant activation energy.

Plasma-chemically synthesized samples also recover 3-5 times faster than the standard catalyst SA-1 [7]. Their specific surface attains 40 m^2/g, while for the standard catalyst it does not exceed 1 m^2/g. The synthesized and (or) regenerated catalyst samples for ammonia synthesis in an electric-arc LTP display a 15-25% higher relative catalytic activity in comparison with the standard catalyst of the SA-1-type. The increased catalytic activity is attributed mainly to the large number of active sites per unit catalyst mass. The "plasma" samples are much more resistant to superheating and deactivation.

The physicochemical properties of the samples [4], the defective structure of catalytically active phases, the presence of α- and γ-Fe after recovery [7, 8] as a result of the effective thermal impact of hardening at $dT/d\tau \approx 10^5$ K/sec [2], the finely dispersed composition, the uniform distribution of promoters in the samples, the optimal ratio Fe^{2+}/Fe^{3+} in the unregenerated catalysts, and the complete spinel formation of Al_2O_3 to $FeO \cdot Al_2O_3$ underlie the observed high catalytic activity and thermal stability of plasma-chemically synthesized and (or) regenerated samples of catalysts for ammonia synthesis.

LITERATURE CITED

1. G. P. Vissokov, Applied Plasma Chemistry [in Bulgarian]. Pt. 1. Low-Temperature Plasma as Applied to Inorganic Chemistry Technology, Sofia (1984).
2. G. P. Vissokov, Applied Plasma Chemistry [in Bulgarian]. Pt. II. Low-Temperature Plasma as Applied to Organic Chemistry Technology and Metallurgy, Sofia (1987).
3. G. P. Vissokov, Trans. of Chemistry of the Bulgarian Acad. of Sciences, **16**, Nos. 1/2, 114-121 (1983).
4. G. P. Vissokov and G. P. Georgiev, Annual Collected Papers of VKhTI, **29**, No. 2, 186-189. Sofia (1984).
5. G. P. Vissokov, Inventor's Certificate (Bulgaria) No. 35353. Method of Obtaining Oxide Catalysts; October 26 (1982).
6. G. P. Vissokov, Inventor's Certificate (Bulgarian) No. 35481, Method of Regeneration of Oxide Catalysts, January 12 (1983).
7. T. M. Peev, G. P. Vissokov, I. Czako-Nagy, and A. Vertes', Appl. Catal., **19** 301-305 (1985).
8. G. P. Vissokov, T. M. Peev, I. Czako-Nagy, and A. Vertes', Appl. Catal., **27**, 257-264 (1986).
9. G. P. Vissokov, Proc. VI Int. Symp. Heterogeneous Catalysis, Sofia (1987). Pt. 2, 303-308.
10. G. P. Vissokov, Plasma Chemistry-89, Collected Papers of the Petrochemical Catalysis of the USSR Acad. of Sciences, Moscow (1989), pp. 33-68.
11. V. N. Men'shov, E. A. Boevskaya, and V. L. Gartman, Abstracts of the All-Union Symp. on Plasma Chemistry (Moscow, November 1979), Moscow (1979), Pt. II, pp. 40-43.
12. Ch. Tomas, Industrial Catalytic Processes and Effective Catalysts [in Russian], Moscow (1973).
13. I. P. Mukhlenov (ed.), Technology of Catalysts [in Russian], Moscow (1989).

14. A. L. Klyachko-Gurvich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 10, 1884-1886 (1961).
15. V. K. Skarchenko, M. T. Rusov and O. A. Strel'tsov, Ukr. Khim. Zh., **24**, 443 (1958).
16. O. A. Strel'tsov, M. T. Rusov, and V. K. Skarchenko, Zh. Fiz. Khim., **33**, 2521 (1959).
17. Handbook of Nitrogen Worker [in Russian], Moscow (1986).