

Propane Oxidation on Nickel in a Self-Oscillation Mode

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Abstract—The kinetics of the catalytic oxidation of propane with oxygen on nickel in a self-oscillation mode was studied. A comparative analysis of changes in reaction rate oscillations with time in the presence of nickel wire and foil was performed. It was found that the reaction medium influenced the morphology of the catalyst surface. With the use of X-ray photoelectron spectroscopy, it was demonstrated that a NiO layer no less than 100 nm in thickness was formed on the catalyst surface in the course of the reaction of propane oxidation. The mechanism of the appearance of self-oscillations in the test system is discussed.

INTRODUCTION

Interest in the phenomena of multiple steady states and reaction rate oscillations in various catalytic processes has quickened in the past decades [1–7]. In homogeneous catalysis, these phenomena were discovered in 1951 by Belousov, who found that, in the oxidation of citric acid with bromate in the presence of cerium ions as catalysts, the solutions changed colors at regular intervals (Belousov–Zhabotinskii reaction) [8]. Early in the 1970s, self-oscillations were also detected in the heterogeneous catalytic reactions of CO and H₂ oxidation on platinum and nickel [9–11]. Analogous phenomena were found later in the reactions of ammonia, ethylene, and methanol oxidation; CO hydrogenation; NO reduction; etc. By now, more than two dozen heterogeneous reactions that occur in a self-oscillation mode on various catalysts (bulk and supported metals, oxide catalysts, zeolites, etc.) are known [3].

The study of reactions under non-steady-state conditions opens up wide opportunities for obtaining information on detailed reaction mechanisms: the nature and rate constants of elementary steps, short-lived reaction intermediates, and their role in the overall chemical reaction [12]. From this standpoint, it is of current interest to find new examples of oscillating reactions and to reveal the nature of critical phenomena. An undoubted advantage of studying reactions in a self-oscillation mode consists in the possibility of determining the surface composition of the catalyst in the course of a single experiment on both active and inactive branches of reaction rate curves. This study provides an opportunity to understand which changes in the system are responsible for its transition between these states. We can say that the study of reactions in a self-oscillation mode is a new tool for examining the mechanisms of catalytic reactions.

Previously, we found that propane oxidation with oxygen in the presence of nickel wire can occur in a

self-oscillation mode over the temperature range 650–750°C [13, 14]. The period of oscillation of the rate of this reaction was tens of seconds at a pressure of ~1 Torr in the reaction mixture. The appearance of self-oscillations was preceded by an induction period, during which the catalyst did not exhibit a detectable activity in propane oxidation, and the duration of this period depended on the pretreatment of the sample. In this work, we report the results of an experimental study of the mechanism of catalytic propane oxidation on nickel under the specified conditions. We compared the dynamics of reaction rate oscillations in the presence of nickel wire and foil. We studied changes in the chemical composition of the surface layer of the catalyst in the course of propane oxidation by X-ray photoelectron spectroscopy with the use of a procedure for layer-by-layer analysis. Based on the experimental data, we proposed a mechanism for the formation of self-oscillations in the test system.

EXPERIMENTAL

The kinetic studies of propane oxidation were performed in a flow reactor made of fused silica [15]. Figure 1 shows a simplified diagram of the experimental setup. A mixture of propane and oxygen was supplied immediately to the inlet of the reactor with a nickel catalyst. The reaction was studied over the temperature range 600–850°C. The flow rate of the gas mixture at the reactor inlet was 1 cm³/s (NTP). In this case, the pressure measured at the reactor outlet was 1 Torr. To determine the dependence of the period of oscillation on the composition of the reaction mixture, the ratio $P_{\text{C}_3\text{H}_8}/P_{\text{O}_2}$ in the mixture was varied within a range from 50 : 1 to 1 : 1. In particular experiments, water vapor was added to the reaction mixture in the ratio $P_{\text{C}_3\text{H}_8}/P_{\text{O}_2}/P_{\text{H}_2\text{O}} = 10 : 1 : 6$. The temperature of a gas phase in the reactor was monitored using a Chromel–Alumel thermocouple arranged along the axis of the

[†] Deceased.

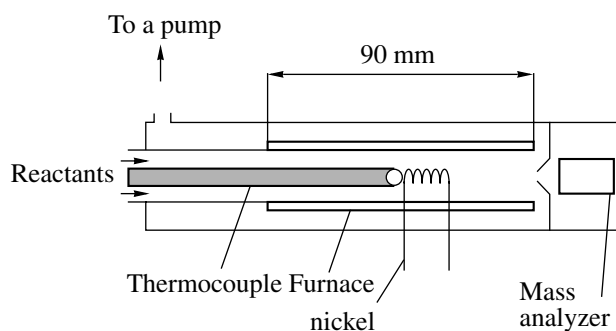


Fig. 1. Schematic of the experimental setup.

reactor. The thermocouple was placed in a fused-quartz case in order to exclude side reactions due to the contact of the thermocouple material with the reaction mixture. The chemical analysis of mixtures at the reactor outlet was performed with the use of an MS-7303 quadrupole mass spectrometer (Russia). The gas phase was sampled through a quartz diaphragm 0.2 mm in diameter. The sampling time was no longer than 0.1 ms [15].

Nickel metal as wire (99.98%) 0.1 mm in diameter and 70 cm in length or foil (99.98%) 0.1 mm in thickness and 8×12 mm in size was used as a catalyst for propane oxidation. The wire was coiled around a mini bobbin of fused silica [13]. In the experiments with nickel foil, the foil plane was oriented parallel to the reactor axis.

The chemical composition of the near-surface layers of catalysts was studied with a VG ESCALAB HP electron spectrometer with the use of AlK_{α} radiation ($h\nu = 1486.6$ eV). The scale of binding energies (E_b) was calibrated against the lines due to the Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.7 eV) inner levels in the spectra of gold and copper surfaces, respectively. A procedure of layer-by-layer analysis was used for determining depth concentration profiles. The layer-by-layer etching of catalyst surfaces was performed immediately in the chamber of the electron spectrometer using 3-keV argon ions at a current density of $10 \mu A/cm^2$. The rate of etching was 1–2 nm/min [16].

The electron micrographs of nickel surfaces were obtained using a BS-350 scanning electron microscope (Tesla).

RESULTS

In the course of experiments, we found that propane oxidation on nickel can occur in a self-oscillation mode at 650–750°C. Figure 2 demonstrates a typical time dependence of the partial pressures of oxygen and main reaction products. The dynamics of reaction rate oscillation was practically identical on nickel wire and foil. For comparison, Fig. 3 shows the time dependence of the concentration of oxygen in the course of propane oxidation in the presence of nickel foil and wire under identical conditions. The main reaction products were

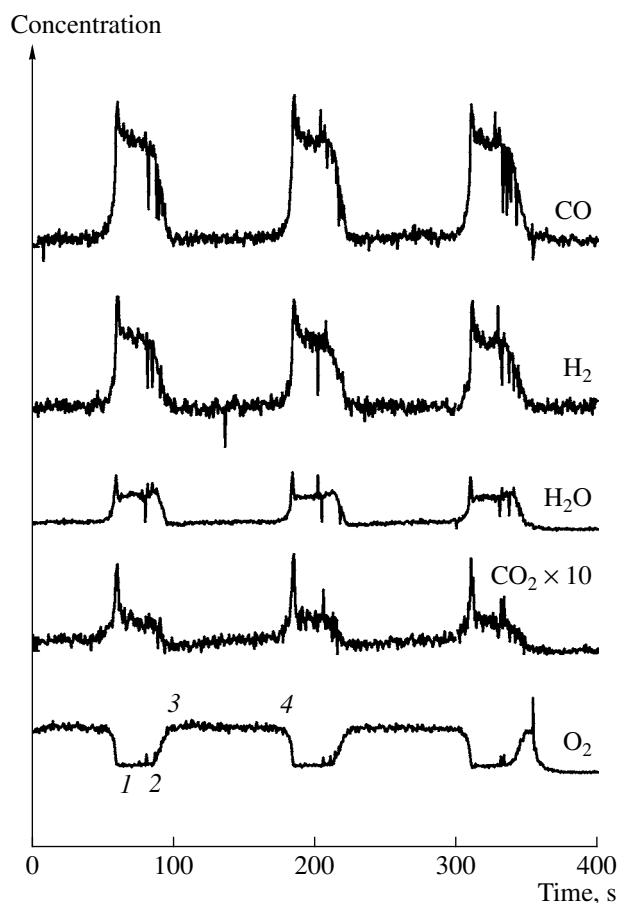


Fig. 2. Typical concentration oscillations of oxygen and the products of propane oxidation on nickel foil. The temperature of the gas phase was $T_{g,p} = 700^\circ C$; the ratio between the partial pressures of propane and oxygen at the reactor inlet was $P_{C_3H_8}/P_{O_2} = 10$; 1–4 refer to critical points (see the text).

CO and H_2 . The period of oscillation was about 120 s. The half-periods of maximum activity, during which the intense consumption of oxygen and the violent release of both the main products and complete oxidation products occurred, alternated with the half-periods of low activity, during which the rate of formation of all products reached a minimum. The period and shape of oscillations only slightly depended on temperature in the range 650–750°C; however, a considerable dependence of the period of oscillation on the mole fractions of propane and oxygen in the reaction mixture was observed (Fig. 4).

The observed self-oscillations were simple in shape: intense relaxation-type oscillations with a weak quasi-periodic structure occur in the half-periods of maximum activity (see Fig. 3). It is well known that the shape analysis of self-oscillations provides an opportunity to draw important conclusions on the mechanism of reaction [4]. For example, the appearance of relaxation oscillations indicates that at least two metastable

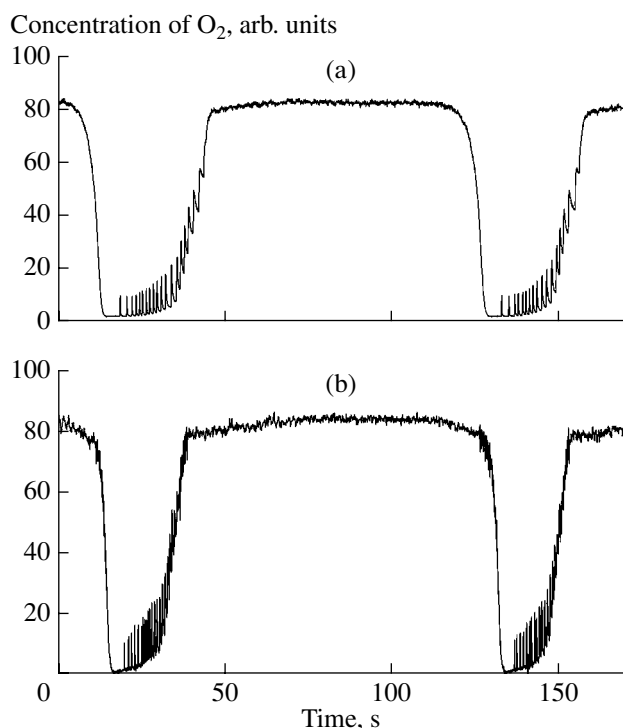


Fig. 3. Changes in the concentration of oxygen in the course of the catalytic oxidation of propane on (a) nickel foil and (b) nickel wire. The dimensions of the foil were chosen so that the surface area corresponded to the surface area of the wire. $T_{g,p} = 700^{\circ}\text{C}$; the ratio between the partial pressures of propane and oxygen at the reactor inlet was $P_{\text{C}_3\text{H}_8}/P_{\text{O}_2} = 10$.

states of the catalyst can exist in the system under the same conditions (the temperature of the catalyst or the reaction medium, the total pressure, and the partial pressures of reactants). It is believed that, in the presence of oxygen in the reaction mixture, the catalyst surface in one of these states is a nickel oxide. On the other hand, because the reaction is performed in an excess of propane, neither the reduction of nickel to the metal nor the formation of nickel carbide can be excluded.

The controllable change of the state of a system by varying external parameters is an informative method for studying the mechanisms of chemical reactions. Note that the system examined is characterized by periodic passage through four critical points, at which the behavior of the reaction changed considerably. In Fig. 2, these points are marked by figures 1–4. It was found that, on changing external parameters at the instant the system passed through these critical points, different responses of the system could be detected.

The abrupt termination of the supply of reactants to the system is one of these external actions. Figure 5 shows the kinetic curves of water and hydrogen release, which were measured on stopping the supply of a propane–oxygen mixture at the instants the system passed through points 3 and 4, respectively. Evidently, the

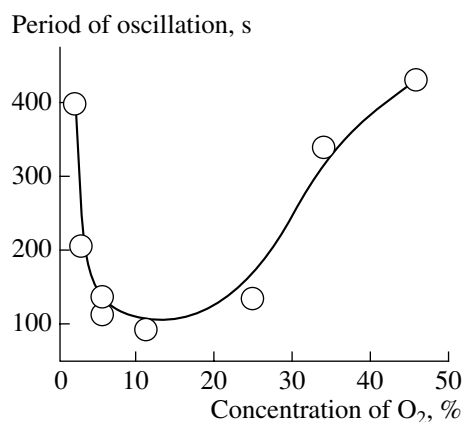


Fig. 4. Dependence of the period of oscillation of the rate of propane oxidation on nickel wire upon the mole fraction of oxygen in the starting mixture. $T_{g,p} = 700^{\circ}\text{C}$.

release of a large amount of hydrogen and only a small amount of water was observed when the supply of the reactants was stopped at point 3 (Fig. 5a). However, to the contrary, if the supply of the reactants was stopped point 4 (Fig. 5b), a much smaller amount of hydrogen and a much greater amount of water were released. Based on these data, we can assume that the complete oxidation products of propane accumulated on the surface in the course of the half-periods of low catalytic activity, which are time intervals between points 3 and 4.

The addition of reaction products to the reaction mixture was the other version of an external action on the system used in this study. We found that the addition of water vapor to the reaction mixture considerably changed the character of oscillations. Figure 6 demonstrates the results of these experiments. Initially, a mixture of $\text{C}_3\text{H}_8 + \text{O}_2 + \text{H}_2\text{O}$ in a ratio of 10 : 1 : 6 was supplied to the reactor; next, at the point $t = 1130$ s in time, which is marked with an arrow in Fig. 6, the supply of water vapor was completely terminated, while the flows of propane and oxygen remained unchanged. It can be seen that the presence of water as a constituent of the reaction mixture resulted in the consumption of water simultaneously with the consumption of oxygen. If only propane and oxygen were the constituents of reactants, the consumption of oxygen coincided in time with the formation of water (periods from 60 to 90 s and from 180 to 210 s in Fig. 2). The addition of water also increased the yield of hydrogen. In other words, in this case, a water-gas shift reaction occurred in the system. It is well known that this reaction is catalyzed by metals in a reduced state [17]. Based on these data, we can conclude that nickel metal was present on the surface of the catalyst during the half-periods of maximum activity.

The appearance of self-oscillations was preceded by an induction period, during which the catalyst did not exhibit noticeable activity in propane oxidation. Previously [13], it was found that the induction period for a

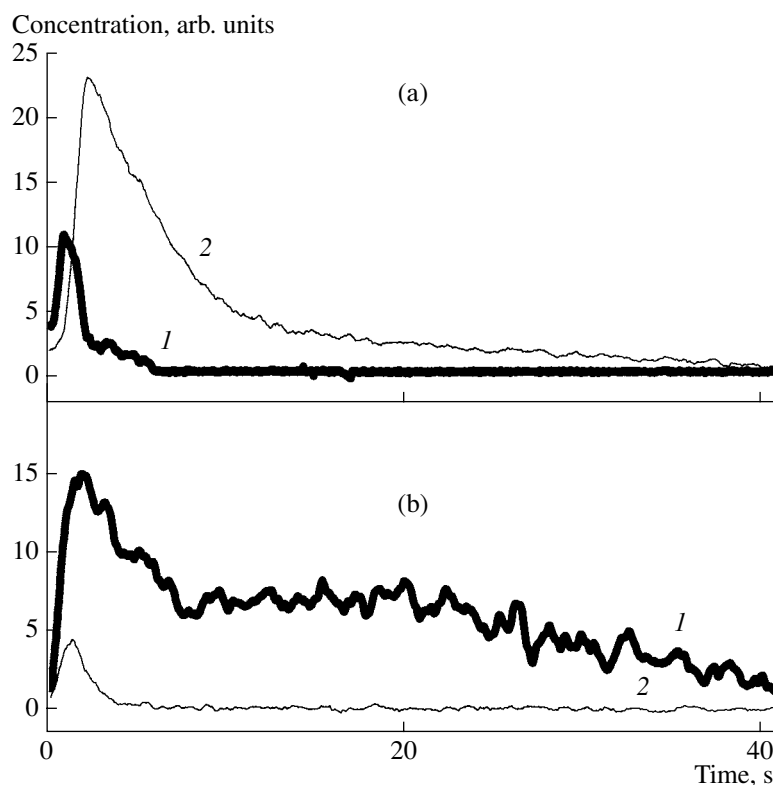


Fig. 5. Kinetic curves of release of (1) water and (2) hydrogen measured upon stopping the reaction at time points (a) 3 and (b) 4 (see Fig. 2), respectively. $T_{g,p} = 700^{\circ}\text{C}$.

fresh sample was ~ 1.5 h. After activation, the catalyst placed in the reaction atmosphere can initiate self-oscillations without an induction period even after long

storage in air. This is indicative of the formation of an activated catalyst surface which is stable to the action of air. This activated surface is responsible for the observed instability of the steady states of the operating catalyst.

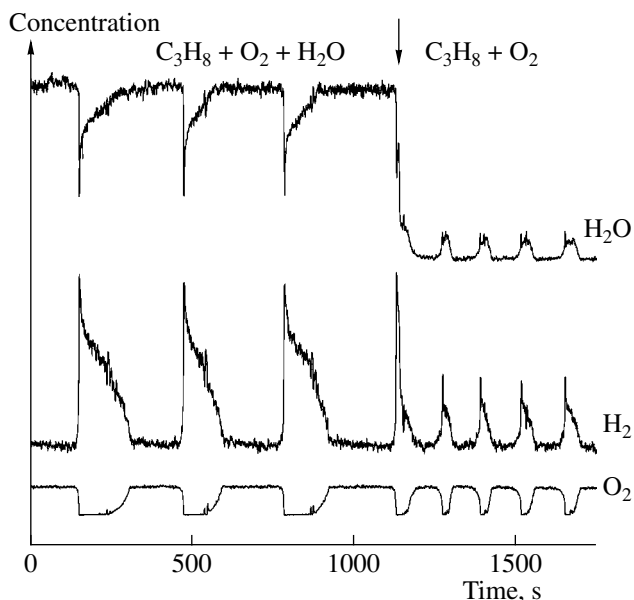


Fig. 6. Changes in the character of oscillations of O_2 , H_2 , and H_2O concentrations at the reactor outlet in the presence and in the absence of water vapor as a constituent of the reactants. $T_{g,p} = 700^{\circ}\text{C}$. The arrow indicates the point in time at which the supply of water vapor was stopped.

The *ex situ* study of the structure and chemical composition of the near-surface layers of nickel catalysts was performed using scanning electron microscopy (SEM) and XPS. Figure 7 shows the micrographs of the fresh nickel wire and the nickel wire activated in the reaction of propane oxidation. It can be clearly seen in these micrographs that the action of a reaction atmosphere considerably changed the surface morphology, resulting in the formation of porous structures with a characteristic size of $\sim 10\ \mu\text{m}$. This phenomenon—catalytic corrosion—has been repeatedly observed earlier. According to published data [18, 19], it may be responsible for the appearance of rate oscillations in catalytic reactions.

A comparative analysis of the chemical composition of the near-surface regions of the fresh and activated nickel foils was performed by XPS. In the latter case, the sample was treated in a reaction mixture with $P_{\text{C}_3\text{H}_8}/P_{\text{O}_2} = 10$ at 700°C for 5.5 h; this sample exhibited high activity in propane oxidation (Fig. 2). Before removal from the reactor, the catalyst was cooled to room temperature immediately in the reaction mixture. A decrease in the temperature always resulted in a transition of the catalyst to a low-activity state. Conse-

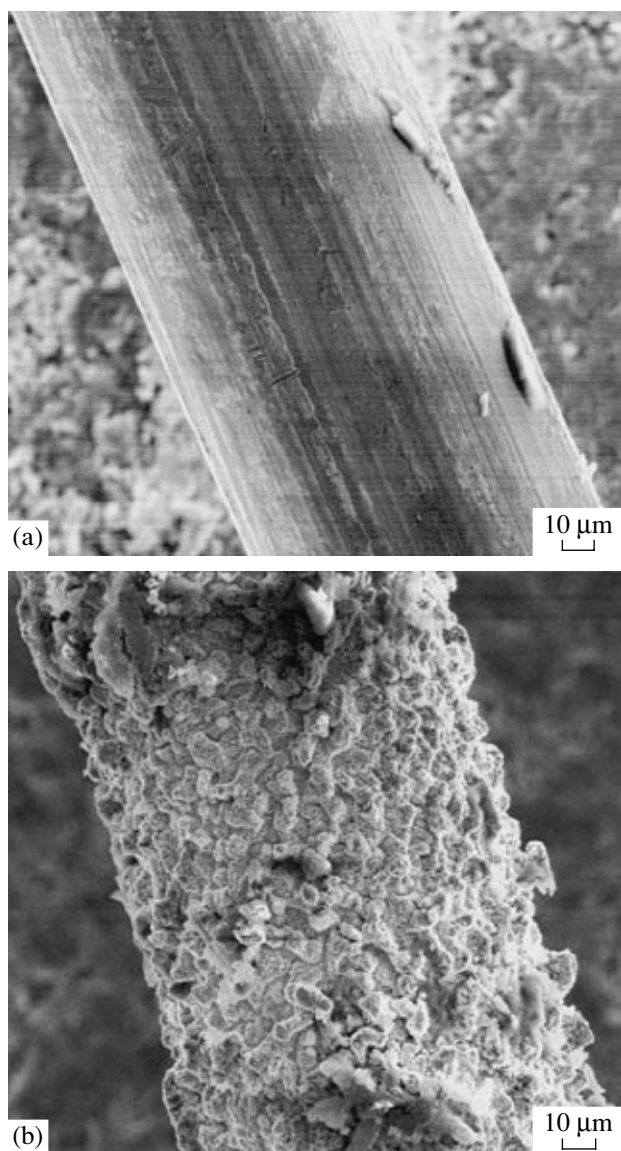


Fig. 7. Electron micrographs of nickel wire (a) before and (b) after reaction.

quently, it is believed that this state of the catalyst was studied by photoelectron spectroscopy.

According to XPS data, nickel, oxygen, and carbon were present in the near-surface region of the activated nickel foil. Within the sensitivity of the technique, other impurity elements were not detected. The C1s spectra (Fig. 8) exhibited an intense peak at 285 eV and a number of weak lines in the region of high binding energies (286.7 and 288.5 eV). The total absence of a characteristic photoemission signal from the region 282–283 eV suggests that nickel carbide was not formed on the catalyst surface in the course of the reaction. The main C1s line ($E_b = 285$ eV) belongs to carbon as a constituent of hydrocarbons [16]. Lines in the region of high binding energies correspond to carbon atoms chemically bound to one or more oxygen atoms. Thus, the line at 288.5 eV

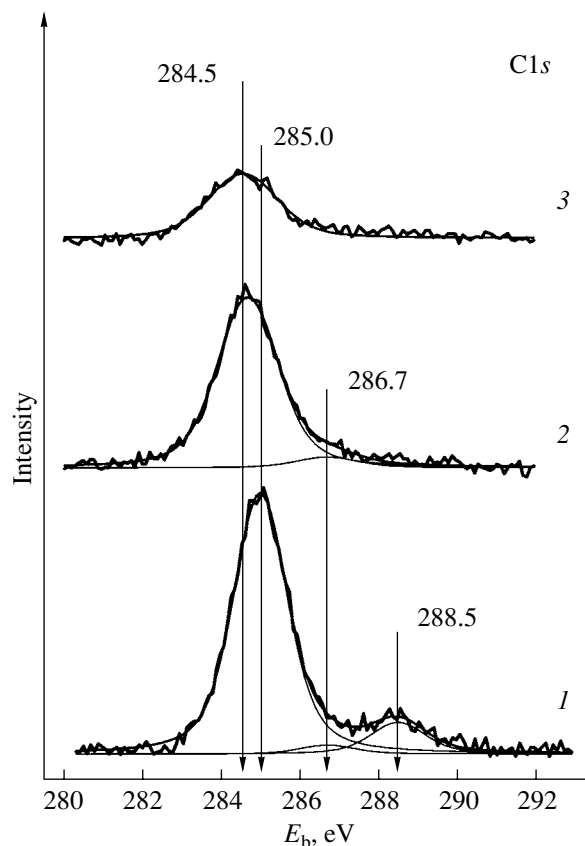


Fig. 8. C 1s XPS spectra obtained in the course of the layer-by-layer surface analysis of activated nickel foil (1) before and after ion etching for (2) 1 and (3) 5 min.

undoubtedly belongs to carbonate groups ($-\text{CO}_3$) [20]. The dramatic decrease in the intensity of the C1s spectrum in the course of ion etching is indicative of the predominant surface localization of carbon fragments, which accumulated on the surface of nickel in the course of the reaction (Fig. 8).

Figure 9 demonstrates the Ni 2p spectra of the fresh nickel foil and the nickel foil activated in the reaction of propane oxidation. In an analysis of the spectra, it should be taken into account that the spin-orbital interaction results in the splitting of the Ni 2p level into the two sublevels Ni 2p_{3/2} and Ni 2p_{1/2}. Correspondingly, the Ni 2p spectrum is a doublet with a 2 : 1 ratio between its integrated component intensities. The spectrum of the fresh foil exhibited two narrow lines at 852.8 and 870.0 eV, whose positions correspond to nickel in a metal state (Fig. 9, spectrum 5). In this case, weakly pronounced lines correspond to peaks due to plasmon losses [16]. The spectrum of the activated foil was more complicated in shape and corresponded to nickel in the oxidation state Ni²⁺ (Fig. 9, spectrum 1). Indeed, in addition to the broad Ni 2p_{3/2} and Ni 2p_{1/2} lines at 854.5 and 872.5 eV, respectively, the spectrum exhibited shake-up satellite lines at binding energies 6 eV higher than the main lines [16, 21–26]. Moreover,

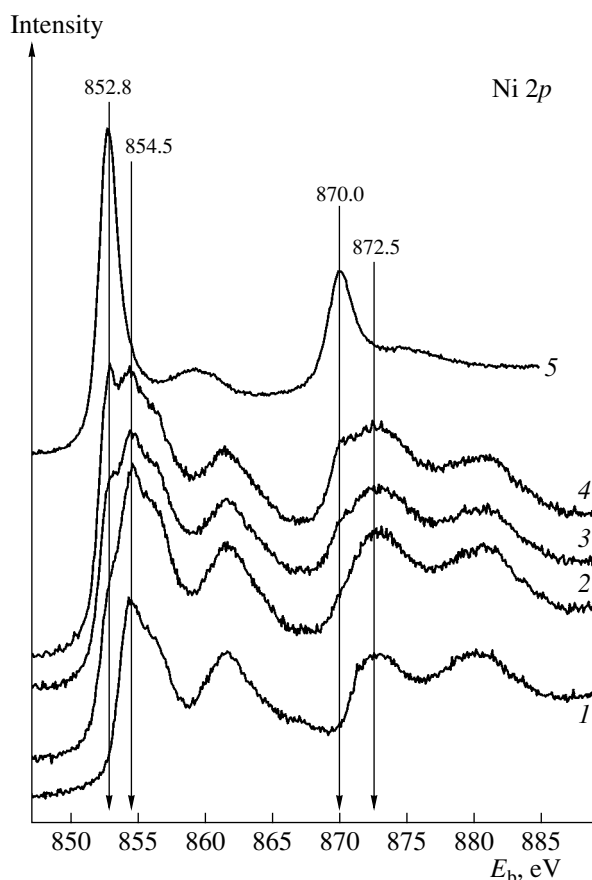


Fig. 9. Ni 2*p* XPS spectra obtained in the course of the layer-by-layer surface analysis of activated nickel foil (1) before and after ion etching for (2) 1, (3) 5, and (4) 20 min; (5) the spectrum of the initial foil after ion etching for 5 min.

the shape of the main Ni 2*p*_{3/2} line and a pronounced shoulder at 856 eV unambiguously indicate that a layer of NiO was formed on the catalyst surface in the course of activation. Other nickel compounds (Ni(OH)₂, Ni₂O₃, etc.) exhibited greater binding energies and a symmetric shape of the Ni 2*p*_{3/2} line [21–27].

In the course of the ion etching of the activated catalyst surface, lines at 852.8 and 870.0 eV appeared in the Ni 2*p* spectra. Undoubtedly, these lines belong to nickel in a metal state (Fig. 9). According to published data, the spin–orbital splitting (binding energy difference between the Ni 2*p*_{3/2} and Ni 2*p*_{1/2} levels) for nickel in a metal state is 17.2 eV, whereas the corresponding value for nickel as a constituent of NiO is 17.8 eV [22, 25]. Taking into account the rate of ion etching (1–2 nm/min) and the depth of XPS analysis (2–3 nm), we can draw the following conclusions: First, nickel foil activation in the course of propane oxidation resulted in the formation of an oxide layer with a considerable thickness (no less than 100 nm). Second, metal nickel clusters were present in the oxide matrix. The formation of this specific structure of an active layer of the catalyst can be explained as a consequence of catalytic corrosion.

Indeed, under the action of a reaction atmosphere, the oxidation and reduction of nickel simultaneously occurred on the catalyst to result in the mass transfer of nickel atoms and in a change in the morphology of the surface (Fig. 7). In this case, the ion etching of a very rough metal surface coated with an oxide film produces the pattern observed in the XPS spectra: the simultaneous presence of both oxidized and reduced nickel species.

DISCUSSION

The reasons for the appearance and the mechanism of self-oscillations essentially depend on the particular nature of the catalyst and on chemical reactions that occur on the catalyst surface [1–7]. The following possible reasons for this phenomenon were described in the literature: “buffer” steps in the interaction of intermediates, autocatalytic transformations of surface intermediates, changes in the activation energy in the course of reaction because of changes in rate-limiting steps, a thermokinetic mechanism for nonisothermal reactions, a heterogeneous–homogeneous reaction mechanism, possible changes in the phase state of the catalyst surface, etc. In all of the above cases, nonlinearities appear in the kinetics of elementary steps of the catalytic process, which are responsible for the appearance of self-oscillations.

It is evident that the mechanism of self-oscillations cannot be adequately described without mathematical simulation of the kinetics of catalytic reactions. However, this simulation should be preceded by discrimination of the most probable schemes of intermediate chemical reactions. An attempt of this discrimination based on the experimental data is given below.

Previously, we hypothesized a heterogeneous–homogeneous mechanism of the catalytic oxidation of propane on nickel [13]. Indeed, this mechanism frequently occurs in high-temperature oxidation reactions. For example, it is believed that the oxidation of cyclohexane on zeolites [28], as well as the oxidation of carbon monoxide on palladium [29] and vanadium catalysts [30], occurs by the heterogeneous–homogeneous mechanism. An analysis of the kinetic models of these processes demonstrated that, indeed, either several stable steady states or a single unstable steady state can exist in a heterogeneous–homogeneous system and, consequently, oscillations can occur [28]. In this context, it could be attempted to explain the observed oscillations of the rate of propane oxidation on nickel in terms of the heterogeneous–homogeneous mechanism. However, subsequent experiments on the direct detection of free radicals in the self-oscillation mode of propane oxidation demonstrated that homogeneous reactions play an insignificant role in the overall reaction of propane oxidation [14]. The reaction examined mainly occurs by a heterogeneous mechanism, and the role of a gas phase is reduced to the synchronization of processes on the catalyst surface.

Nonisothermal chemical processes are often considered as the reason for the appearance of self-oscillations in exothermal heterogeneous reactions on supported metal catalysts [4]. In this case, it is usually believed that the heat released in the course of reaction on the active component of a catalyst results in local surface overheating and the formation of mobile hot spots with a high temperature gradient at their boundaries because of the low efficiency of heat dissipation through the carrier [31–37]. For example, in an IR-thermographic study of self-oscillations in the rate of CO oxidation on a rhodium catalyst, the migration of a high-activity zone over the catalyst surface and a periodic change in the area of this zone were detected [35].

Propane oxidation is also a strongly exothermal reaction. Therefore, the observed oscillations of the rate of propane oxidation on nickel were accompanied by a considerable (up to 100°C [13]) change in the catalyst temperature. Because self-oscillations in our early experiments were observed in propane oxidation on nickel wire, it was hypothesized that the oscillations were related to the formation of a hot spot at an end of the wire followed by the migration of this spot to the other end of the wire, and that this process determined the period of oscillation [13]. For example, the migration of hot spots of this kind was found in the oxidation of ammonia on platinum wire [31, 32]. However, the results of this work demonstrate that the character of oscillations of the rate of propane oxidation on nickel only slightly depends on both the shape and the geometric size of the catalyst (see Fig. 3). In this case, the period and shape of self-oscillations exhibit a simple and regular, that is, nonchaotic, form. Consequently, self-oscillations in the test process were not related to the formation of surface waves or other spatial structures with characteristic sizes that are comparable to the linear dimensions of the catalyst in use.

The mechanism based on catalytic corrosion occupies a special place in the series of nonisothermal models for self-oscillation reactions [18]. It is well known that a surface reconstruction of metal catalysts with the formation of a rough structure can occur under exposure to a reaction atmosphere (Fig. 7). According to Jensen and Ray [18], a catalytic process occurs on the surface of these formations and is accompanied by local temperature fluctuations. The mathematical model developed by Jensen and Ray [18] adequately describes the dynamics of complex oscillations in the reactions of butane and cyclohexane oxidation. However, it is our opinion that this model is suitable for describing only chaotic oscillations. This model is hardly applicable to the description of periodic oscillations with a long period, which occur in the case of propane oxidation on nickel (Fig. 2). Therefore, additional experiments should be performed in order to draw a conclusion on the role of temperature changes in the mechanism of self-oscillations in the catalytic propane oxidation on nickel. However, experimental data on the response of the system to the removal of a gas phase

(Fig. 4) demonstrate that changes in the chemical composition of the surface should be primarily taken into consideration.

The appearance of self-oscillations due to periodic transitions of a system between two main states with different surface compositions has been repeatedly discussed in the literature. For example, a “phase transition” mechanism was proposed [2, 5] to describe the self-oscillation of the rate of CO oxidation on the Pt(100) face. This mechanism is based on a relationship between the self-oscillation of the rate and the reversible phase transition (surface reconstruction) $\text{hex} \longleftrightarrow 1 \times 1$. To explain the self-oscillations of the rate of the above reaction on the Pt(110) surface, similar mechanisms were proposed, which are also based on surface morphology changes in the course of the reaction: the $(2 \times 1) \longleftrightarrow (1 \times 1)$ reconstruction and surface microfaceting [38–40]. The nature of morphological changes in the surface of metal microcrystallites under exposure to a reaction atmosphere has been considered theoretically in detail by Zhdanow and coworkers [7, 41–43]. In this case, the reconstruction of a metal surface induced by the chemisorption of reactants is a rate-limiting step in rate self-oscillations. It is believed that the synchronization of self-oscillations that appear in different regions of the active surface is due to the surface diffusion of adsorbed species.

However, the “reconstructive” mechanisms of the appearance of self-oscillations in a pure form can occur only under high-vacuum conditions at moderate temperatures, when the action of a reaction atmosphere on the catalyst does not cause considerable changes in the chemical composition of an active component. Indeed, even at pressures of about 1 Torr, the possibility of metal \rightarrow oxide and metal \rightarrow carbide transitions, as well as slow processes of the diffusion of fragments of the initial reactants into the bulk of the catalyst, should be taken into account. This can result in changes in the heats of adsorption of the reactants and reaction intermediates depending on substance concentrations in the near-surface layer. Indeed, redox reaction mechanisms have been successfully used in the past few years for describing self-oscillations observed in various heterogeneous oxidation reactions [6, 44–52]. For example, a self-oscillation model based on the transition of oxygen atoms from a chemisorbed state to a state dissolved in the near-surface region has been used on order to describe CO oxidation on Pt(110) and Pd(110) [44–46]. In this case, maximum and minimum rates of the oxidation reaction in a self-oscillation cycle were related to the presence of highly reactive chemisorbed oxygen on the metal surface and the absorption of oxygen in the bulk of the active component, respectively.

The experimental data obtained in this work allowed us to assume that the redox mechanism of oscillations occurred in the oxidation of propane on nickel. Probably, during the half-period of oscillations when the rate of oxidation was maximal, surface nickel existed in a

metal state, as evidenced by the occurrence of the water-gas shift reaction (Fig. 6). In this case, the intense oxidation of propane with the participation of chemisorbed oxygen occurred on the metal surface with the formation of both partial oxidation products (CO, H₂) and complete oxidation products (CO₂, H₂O) (Fig. 2). Chemisorbed oxygen, on the one hand, participated in propane oxidation and, on the other hand, diffused into the bulk of the metal to form a surface phase of NiO. The presence of this nickel oxide was detected by XPS in the postreaction analysis of the surface layers of activated nickel foil (Fig. 9). In turn, the oxidized state of the nickel surface decreased the rate of formation of chemisorbed oxygen. Correspondingly, this decreased the rate of propane oxidation: the catalyst changed to an inactive state. As this took place, the products of complete propane oxidation were accumulated on the catalyst surface (Fig. 8).

Although the above qualitative model of surface processes accompanying the appearance of self-oscillations in the test system principally explains the experimental data, the real reason for the appearance of oscillations calls for further investigation. In particular, the reason for the stepwise "trigger" transition of a catalyst surface from a high-activity state to a low-activity state remains unclear. The mechanism of synchronization between various regions of the catalyst surface is unclear; this synchronization can occur both through a gas phase (for example, by heat and mass transfer) and by oxygen diffusion in the near-surface layers of the catalyst. Evidently, additional studies with the use of methods for monitoring changes in the chemical composition of surfaces immediately in the course of reaction are required for detailing the mechanism of propane oxidation on nickel.

The results of this study suggest that the observed relaxation oscillations of the rate of propane oxidation on nickel were accompanied by the periodic oxidation/reduction of the catalyst surface (Ni \longleftrightarrow NiO). In this case, the high-activity phase was characterized by the presence of nickel metal clusters on the catalyst surface, whereas the low-activity phase was characterized by the presence of surface nickel(II) oxide.

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REFERENCES

1. Yablonskii, G.S., Bykov, V.I., and Elokhin, V.I., *Kinetika model'nykh reaktsii geterogennogo kataliza* (Kinetics of Model Reactions in Heterogeneous Catalysis), Novosibirsk: Nauka, 1984.
2. Ertl, G., *Adv. Catal.*, 1990, vol. 37, p. 213.
3. Schüth, F., Henry, B.E., and Schmidt, L.D., *Adv. Catal.*, 1993, vol. 39, p. 51.
4. Slin'ko, M.M. and Jaeger, N.I., *Stud. Surf. Sci. Catal.*, 1994, vol. 86, p. 1.
5. Imbihl, R. and Ertl, G., *Chem. Rev.*, 1995, vol. 95, p. 697.
6. Werner, H., Herein, D., Schulz, G., Wild, U., and Schlögl, R., *Catal. Lett.*, 1997, vol. 49, p. 109.
7. Zhdanov, V.P. and Kasemo, B., *Surf. Sci. Rep.*, 2000, vol. 39, p. 25.
8. Zhabotinskii, A.M., *Kontsentratsionnye avtokolebaniya* (Concentration Autooscillations), Moscow: Nauka, 1974.
9. Hugo, P. and Jakubith, M., *Chem. Ing. Tech.*, 1972, vol. 44, p. 383.
10. Beusch, H., Fieguth, P., and Wicke, E., *Chem. Ing. Tech.*, 1972, vol. 44, p. 445.
11. Belyaev, V.D., Slin'ko, M.M., Timoshenko, V.I., and Slin'ko, M.G., *Kinet. Katal.*, 1973, vol. 14, no. 3, p. 810.
12. *Int. Conf. on Unsteady State Processes in Catalysis*, Matros, Yu.Sh., Ed., Utrecht: VSP, 1990, vol. 3.
13. Gladky, A.Yu., Ermolaev, V.K., and Parmon, V.N., *Catal. Lett.*, 2001, vol. 77, p. 103.
14. Gladky A.Yu., Ermolaev V.K., and Parmon V.N., *React. Kinet. Catal. Lett.* (in press).
15. Gladky, A.Yu., Ermolaev, V.K., and Parmon, V.N., *React. Kinet. Catal. Lett.*, 1999, vol. 67, p. 183.
16. *Handbook of X-ray Photoelectron Spectroscopy*, Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F., and Muilenberg, G.E., Eds., Eden Prairie: Perkin-Elmer, 1978.
17. Ford, P.C., Rinker, R.G., Laine, R.M., Ungermann, C., Landis, V., and Moya, S.A., *Adv. Chem. Ser.*, 1979, vol. 173, p. 81.
18. Jensen, K.F. and Ray, W.H., *Chem. Eng. Sci.*, 1980, vol. 35, p. 2439.
19. Anderson, D.R., *J. Catal.*, 1988, vol. 113, p. 475.
20. Khassin, A.A., Yurieva, T.M., Kaichev, V.V., Bukhtiyarov, V.I., Budneva, A.A., Paukshtis, E.A., and Parmon, V.N., *J. Mol. Catal. A*, 2001, vol. 175, p. 189.
21. Kim, K.S. and Davis, K.S., *J. Electron Spectrosc. Relat. Phenom.*, 1972/1973, vol. 1, p. 251.
22. McIntyre, N.S. and Cook, M.G., *Anal. Chem.*, 1975, vol. 47, p. 2208.
23. McIntyre, N.S., Rummery, T.E., Cook, M.G., and Owen, D., *J. Electrochem. Soc.*, 1976, vol. 123, p. 1164.
24. Shalvoy, R.B., Reucroft, P.J., and Davis, B.H., *J. Catal.*, 1979, vol. 56, p. 336.
25. Li, C.P., Proctor, A., and Hercules, D.M., *Appl. Spectrosc.*, 1984, vol. 38, p. 880.
26. Lorentz, P., Finster, J., Wendt, G., Salyn, J.V., Zumadilov, E.K., and Nefedov, V.I., *J. Electron Spectrosc. Relat. Phenom.*, 1979, vol. 16, p. 267.
27. Carley, A.F., Jackson, S.D., Roberts, M.W., and O'Shea, J., *Surf. Sci.*, 2000, vols. 454-456, p. 141.
28. Berman, A.D. and Elenek, A.V., *Dokl. Akad. Nauk SSSR*, 1979, vol. 248, p. 643.

29. Ostapyuk, V.A., Boldyreva, N.A., and Korneichuk, G.P., *React. Kinet. Catal. Lett.*, 1981, vol. 16, p. 151.
30. Chashechnikova, I.G. and Golodets, G.I., *React. Kinet. Catal. Lett.*, 1981, vol. 17, p. 291.
31. Barelko, V.V. and Merzhanov, A.G., *Problemy kinetiki i kataliza* (Problems of Kinetics and Catalysis), Krylov, O.V. and Shibanova, M.D., Eds., Moscow: Nauka, 1978, vol. 17.
32. Barelko, V.V., *Problemy kinetiki i kataliza* (Problems of Kinetics and Catalysis), Krylov, O.V. and Shibanova, M.D., Eds., Moscow: Nauka, 1981, vol. 18.
33. Kellow, J.C. and Wolf, E.E., *Chem. Eng. Sci.*, 1990, vol. 45, p. 2597.
34. Kellow, J.C. and Wolf, E.E., *AIChE J.*, 1991, vol. 37, p. 1844.
35. Chen, C.C., Wolf, E.E., and Chang, H.C., *J. Phys. Chem.*, 1993, vol. 97, p. 1055.
36. Lane, S.L. and Luss, D., *Phys. Rev. Lett.*, 1993, vol. 70, p. 830.
37. Graham, M.G., Lane, S.L., and Luss, D., *J. Chem. Phys.*, 1993, vol. 97, p. 7564.
38. Krischer, K., Eiswirth, M., and Ertl, G., *Surf. Sci.*, 1991, vols. 251/252, p. 900.
39. Krischer, K., Eiswirth, M., and Ertl, G., *J. Chem. Phys.*, 1992, vol. 96, p. 9161.
40. Ladas, S., Imbil, R., and Ertl, G., *Surf. Sci.*, 1988, vol. 198, p. 42.
41. Person, H., Thormahlen, P., Zhdanov, V.P., and Kasemo, B., *Catal. Today*, 1999, vol. 53, p. 273.
42. Zhdanov, V.P., *Catal. Lett.*, 2000, vol. 69, p. 21.
43. Zhdanov, V.P. and Kasemo, B., *J. Catal.*, 2003, vol. 214, p. 121.
44. Vishnevskii, A.L. and Savchenko, V.I., *React. Kinet. Catal. Lett.*, 1989, vol. 38, p. 167.
45. Vishnevskii, A.L., Elokhin, V.I., and Kutsoskaya, M.L., *React. Kinet. Catal. Lett.*, 1993, vol. 51, p. 211.
46. Basset, M.R. and Imbihl, R., *J. Chem. Phys.*, 1990, vol. 93, p. 811.
47. Sales, B.C., Turner, J.E., and Maple, M.B., *Surf. Sci.*, 1982, vol. 114, p. 381.
48. Yeates, R.C., Turner, J.E., Gellman, A.J., and Samorjai, G.A., *Surf. Sci.*, 1985, vol. 149, p. 175.
49. Hartmann, N., Imbihl, R., and Vogel, W., *Catal. Lett.*, 1994, vol. 28, p. 373.
50. McCabe, R.W., Wong, C., and Woo, H.S., *J. Catal.*, 1988, vol. 114, p. 354.
51. Oertzen, A.V., Mikhailov, A., Rotermund, H.H., and Ertl, G., *Surf. Sci.*, 1996, vol. 350, p. 259.
52. Rotermund, H.H., Lauterbach, J., and Hass, G., *Appl. Phys. A*, 1993, vol. 57, p. 507.