A New Method of Investigation of Heterogeneous Catalytic Reactions

I. Ammonia Decomposition on Platinum

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In this paper a new method of investigation of heterogeneous catalytic reactions is described. This method is especially useful for studying the mechanism of catalytic reactions. By analysis of dependences $I(T)$ (I is the intensity of some lines in the mass spectrum, T is the temperature of the catalyst), for secondary ions knocked out of the surface of the catalyst by a beam of primary ions and for ions formed by means of ionization of the gas near the catalyst by an electron impact, definite conclusions about the mechanism of catalytic reactions can be drawn. This method was used for studying ammonia decomposition on platinum. The mechanism of poisoning and activation of platinum catalyst was determined. The decomposition of ammonia on platinum consists of two stages. In the first stage the adsorbed molecules of ammonia dissociate to NH and H_2. The second stage is the formation of molecules N_2 and H_2 in the process of association of two NH particles.

INTRODUCTION

There are very many investigations dedicated to studying heterogeneous catalytic reactions, but little is known about the elementary processes which take place on the surface of the catalyst. Such a state of affairs in this important branch of chemical science is explained by the absence of direct methods for studying elementary processes of heterogeneous catalytic reactions. The development of such methods has a great importance for the science of catalysis.

In our previous investigations (*1, 2*) it was established that the composition and the state of a layer of gases adsorbed on a surface of metal influence essentially the composition of negative and positive secondary ions knocked out of the surface of the metal by the impact of primary ions. It was found that some superficial chemical reactions could be investigated by studying the dependence of the intensity of definite lines in the mass spectrum of secondary ion emission on the temperature of the metal. Thus the possibility arises to use the phenomenon of secondary ion emission for studying heterogeneous catalytic reactions. In order to obtain more complete information about the course of catalytic reaction we studied both the mass spectrum of secondary emission and the mass spectrum of the gas phase near the catalyst.

We have chosen as a first object of investigation the catalytic decomposition of ammonia on platinum. Such a choice was stipulated by the following considerations: (1) The reactions of decomposition are among the simplest chemical reactions. (2) At low pressures of ammonia ($\sim 10^{-2}$ mm Hg) this reaction has been investigated by purely chemical methods (*3, 4*). (3) The data obtained for this reaction could prove useful for further investigation of ammonia synthesis by the same method.

APPARATUS

The experimental setup consisted of three main parts: (a) the injector of primary ions; (b) the catalyst chamber; and (c) the mass spectrometer. See Fig. 1.

(a) The Injector of Primary Ions

The beam of Ar^+ ions is produced by an ion gun consisting of the high-frequency ion source (1), the three-electrode lens (2), and the accelerating tube (3). Alignment of a beam axis with an axis of the quadrupole lens (6) is attained by means of a flat ground joint (4) and the electrostatic corrector (5). The quadrupole lens focuses the beam at the entrance of the magnetic analyzer (9). The total current of an ionic beam is measured by a Faraday cylinder (7). The second electrostatic corrector (8) directs the beam along an axis of the magnetic analyzer chamber. A monoenergetic beam of Ar^+ ions with an energy of 20 kev is selected by the magnetic analyzer. The beam of Ar^+ ions, after being collimated by the channel (11) with dimensions $2 \times 4 \times 9$ mm and the slit (12) is sent into the catalyst chamber.

(b) The Catalyst Chamber

The beam of primary ions enters the catalyst chamber through an exit slit (12) with dimensions 2×4 mm. This slit is at the end of the tube (14) which serves as a shielding screen against electrical fields produced by potentials applied to the electrodes of the lens focusing the beam of secondary ions. The primary ions, having passed through the slit (12) impinge on the surface of a catalyst (23). A catalyst is a strip of platinum 0.1 mm thick, 4 mm wide, and 13 mm long stretched between two molybdenum rods soldered in glass. A platinum strip is heated by electric current. Its temperature is measured by the thermocouple welded to the back of a strip.

The special arrangement permits movement of the catalyst in a horizontal direction. By this motion one can choose an optimal position of a catalyst in respect to a primary beam and ion lens focusing secondary ions at the entrance slit of the mass spectrometer.

The electron gun (25) is used for an investigation of the behavior of gas phase in the catalyst chamber. This gun produces a narrow electron beam with an energy 600 ev. The electrons emitted by an incandescent tungsten helix (27) are accelerated to the anode, which has a diaphragm (28). The diaphragm (26) collimates a narrow beam which is focused by the magnetic lens (29). By means of an electrostatic corrector (30) the trajectory of an electron beam is corrected in such a way that the electrons of the beam ionize the gas near the surface of the catalyst. The electron gun is screened from the influence of a stray field of the electromagnet of the mass spectrometer by an iron shield. The current of an electron beam is measured by the galvanometer connected with the electrode (13). This electrode is fixed on a fused silica tube which in its turn is fastened to the tube (14). There is a slit with dimensions 4×4 mm at the center of the electrode (13).

Through this slit the primary beam enters the catalyst chamber. Ions which result from the ionization of the gas by the electron beam and ions knocked out of the catalyst surface by the primary ion beam are focused by the electrostatic symmetrical lens (31). At the top and the bottom of the first electrode of this lens there are two orifices to allow the electron and the ion beam to pass through.

The primary beam current is measured by the galvanometer connected with the plate (15). This plate is driven by an electromagnet and when a measurement is performed it is pushed into the gap between the bottom surface of the first electrode of the lens (31) and the electrode (13).

The gas admission into the catalyst chamber is accomplished through the tube, which has at its end the nozzle. An exit section of the nozzle is at 10 mm distance from the surface of the catalyst.

The connection between the catalyst's chamber and the mass spectrometer consists of a glass insulator (16) soldered to two kovar cylinders and a steel bellows (17).

(c) The Mass Spectrometer

The mass analysis of the secondary ions and ions originating owing to ionization of the gas by an electron beam was accomplished by the magnetic mass spectrometer
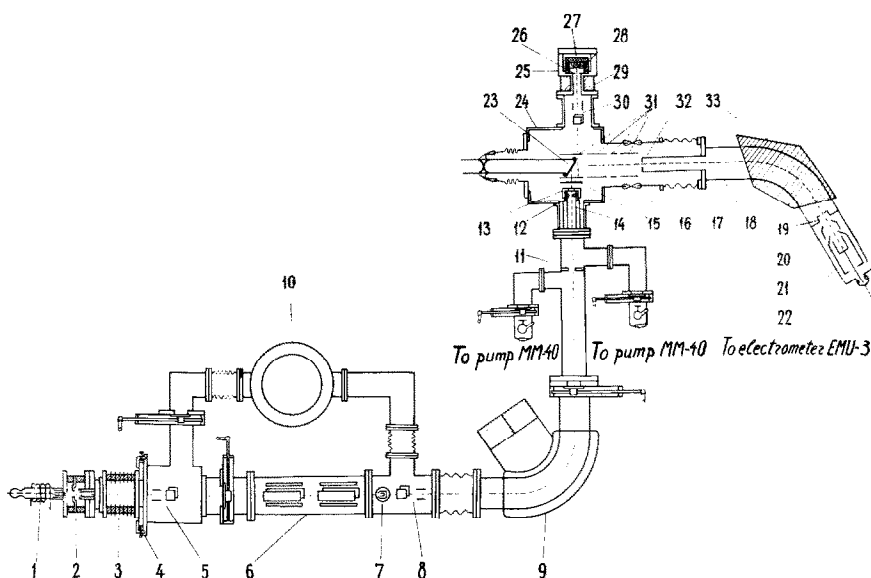
FIG. 1. Diagram of apparatus.

(33) with a beam rotation of 60°. The mean radius of the beam trajectory was 20 cm. The planes of the electromagnet poles made an angle of 80°51' with the entry and exit directions of the ionic beam. This condition secured second order focusing. The chamber (18) of the mass spectrometer was fixed on porcelain insulators. The covers of the chamber were separated from the poles of the electromagnet by an air gap 3 mm high. Thus the chamber and the collector part of the mass spectrometer were insulated from the earth.

The entry (32) and exit (19) slits of the mass spectrometer were situated at the foci of the electromagnet and had dimensions of 1.3 × 13 mm and 3 × 13 mm.

The collector of the mass spectrometer consisted of the Faraday cylinder (21), the grounded shield (22), and the diaphragm (20), which served for suppression of secondary electron emission. In order to avoid an influence of the stray field of the electromagnet of the mass spectrometer the collector was shielded by an iron tube.

(d) Pumping System and Measurement of Vacuum

The injector part of the installation was evacuated by MM-1000 oil diffusion pump (10). The collimator and the catalyst cham-

ber were evacuated by separate MM-40 oil diffusion pumps. Above all diffusion pumps liquid air traps were inserted in order to freeze out condensable vapors. The residual gas pressure in the injector part of the installation was $2\text{–}3 \times 10^{-6}$ mm Hg, in the catalyst chamber, 10^{-5} mm Hg, and after prolonged pumping $3\text{–}5 \times 10^{-6}$ mm Hg. Mass-spectrometric analysis of the residual gas in the catalyst chamber was made. The gases N_2, O_2, H_2O, H_2, CO, CO_2 were found in the residual gas composition. The presence of some ions (C_2H^+, $C_2H_2^+$) in the mass spectrum of the residual gas was connected with small quantities of hydrocarbon vapors which penetrated into the catalyst chamber from oil diffusion pumps. The ions NH_3^+, NH_2^+, NH^+, N^+, H_2^+, and H^+ appeared in the mass spectrum when ammonia at pressure of 10^{-4} mm Hg was admitted into the catalyst chamber. These ions were connected with an ionization and succeeding fragmentation of the NH_3 molecule.

(e) The System of Gas Admission into the Catalyst Chamber

The gases NH_3, O_2, N_2, and H_2 were admitted into the catalyst chamber when the reaction of ammonia decomposition was studied. With the exception of H_2 all these gases were admitted through the system

which contained seven needle valves. Hydrogen was admitted through a palladium filter. A schematic diagram of the system of gas admission is shown in Fig. 2.
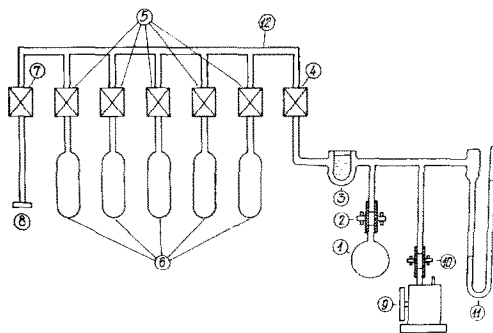

FIG. 2. The system of gas admission.

The gases studied were contained in glass bulbs (6). The bulbs were filled with various gases as follows. With open valves (4) and (5) and closed valve (7) the bulbs were exhausted by the forepump (9). Evacuation of the bulbs to the pressure of about 10^{-5} mm Hg was accomplished by oil diffusion pumps. For this valve (7) was opened and valve (4) was closed, and the bulbs were evacuated through the tube (8) connected with the catalyst chamber. After evacuation of the bulbs the valves (5) and (7) were closed and gas was admitted from bulb (1) through a liquid air trap (3) and valve (4) into tube (12). Then any bulb (6) can be filled by opening of an appropriate valve (5). Such a method of filling was used in the case of N_2 and O_2, which were sufficiently clean (99.7%). The ammonia, which contained about 5% of water vapor and air, was cleaned before admission to the bulb (6). To purify the ammonia from air, trap (3) was filled with liquid air and the system to valve (4) was exhausted by the forepump. Then benzene was added to the liquid air until the temperature of the mixture was $-60°C$. At this temperature the saturation pressures of NH_3 and H_2O were 200 and 0.02 mm Hg respectively and contamination of the ammonia by water vapor was less than 0.01%. Then at the temperature of trap (3) equal to $-60°C$ filling of one of the

bulbs (6) was performed in the same manner as in the case of O_2 and N_2.

(f) The Measurement of Ion and Electron Current

The electron beam current was measured by the microammeter connected with the electrode (13). To this electrode a potential of 100 volts was applied to suppress secondary electron emission. The current of the ionizing electron beam was 600–800 μA amp.

The primary ion beam current was measured with a mirror galvanometer of sensitivity 3×10^{-10} amperes per division. The secondary ion current to the collector of the mass spectrometer was measured with a valve electrometer EMU-3 of a maximum sensitivity 3×10^{-15} amperes per division.

The current density of the primary beam impinging on a surface of the catalyst was 10^{-8} amp/mm². Such small current density of the primary beam was chosen in order that its influence on the state of the catalyst surface should be as small as possible. The choice of Ar^+ ions as bombarding particles was dictated by the same considerations.

When the emission of secondary negative ions was studied the distribution of potentials was as follows: to the catalyst a potential of -80 volts was applied; the first, second, and fourth electrodes of the lens (31) had potentials of -80 volts, $+2000$ volts, and $+2000$ volts. The potential of the third electrode could be regulated in the limits from 0 to -400 volts. To the collector diaphragm (20) the potential -100 volts was applied. The Faraday cylinder (21) and screen (22) were grounded.

By studying the emission of secondary positive ions the signs of potentials on the catalyst and the lens electrodes were changed. In this case to the collector diaphragm the potential -2000 volts was applied and the Faraday cylinder and screen were grounded.

The current of a primary beam on the surface of the catalyst could only be measured in that case when an emission of secondary negative ions was studied. By an investigation of secondary positive ions the primary beam current was measured by means of the electrode (15).

THE MASS SPECTRUM OF SECONDARY ION EMISSION

There were many negative and positive ions in the mass spectrum of secondary ion emission for the catalyst in the atmosphere of residual gas (a pressure 5×10^{-6} mm Hg). The negative ions with masses 1 (H^-), 12 (C^-), 13 (CH^-), 16 (O^-), 17 (OH^-), 24 (C_2^-), 25 (C_2H^-), 26 ($C_2H_2^-$), 195 (Pt^-), 209 (PtN^-), 223 (PtN_2^-) and positive ions with masses 1 (H^+), 14 (N^+), 16 (O^+), 17 (OH^+), 28 ($N_2^+ + CO^+$), 44 (CO_2^+) and 195 (Pt^+) were observed. The intensity of all these mass lines to the exclusion of the mass line of C_2^- ion are decreased monotonously with increasing temperature of the catalyst. In the region of 200–500°C the intensity of these mass lines was so small that it was impossible to detect it with the greatest sensitivity of the valve electrometer. An admission of ammonia into the catalyst chamber changed essentially the intensity of some lines in the mass spectrum of a secondary emission. The intensity of PtN^- and PtN_2^- lines greatly increased. This circumstance can be connected with the formation of some chemical compound of platinum and ammonia. The intensity of the line for mass 16 in the mass spectrum of negative ions had somewhat increased. This fact can be explained by the knocking out of NH_2^- ions from the surface of the catalyst. There was also observed some increase of intensity of the Pt^- line. The intensity of other lines of the negative ion mass spectrum was unchanged.

In the mass spectrum of positive ions the ions with mass 2 (H_2^+) and 15 (NH^+) appeared. The intensity of lines with masses 16, 17, and 28 was increased on account of knocking out the NH_2^+, NH_3^+, and N_2^+ ions from the surface of the catalyst. It has to be noted that the emission of NH^+, NH_2^+, and NH_3^+ ions did not cease until the temperature of the catalyst reached 1200°C. This circumstance shows that a strong bond of the ammonia molecule with the hot platinum surface exists.

The experiment was carried out when the catalyst was moved from the path of Ar^+ ions. In this case the beam of Ar^+ ions did not impinge on the surface of the catalyst, but went through the gas. Under this condition all the lines of the mass spectrum disappeared. This experiment proves that all observed ions were knocked out of the surface of the catalyst.

THE MECHANISM OF POISONING AND ACTIVATION OF PLATINUM CATALYST

An investigation of ammonia decomposition on platinum was carried out at an ammonia pressure of 10^{-4} mm Hg. At such low pressure this reaction was not previously investigated; therefore it was necessary to find the conditions at which the reaction took place. In a dynamical system, that is by perpetual admission and pumping of ammonia, the equilibrium pressure of ammonia in the catalyst chamber is settled. In that case when decomposition of ammonia takes place the equilibrium pressure of ammonia decreases and the partial pressures of nitrogen and hydrogen increase. Since the intensity of lines NH_3^+, N_2^+, and H_2^+ in the mass spectrum of ionization of gas phase by an electron beam is proportional to the partial pressure of NH_3, N_2, and H_2, it is possible to watch the course of reaction of ammonia decomposition while observing the dependence of the intensity of the NH_3^+, N_2^+, and H_2^+ lines on the temperature of the platinum catalyst. The beginning of the reaction of ammonia decomposition is manifested by a decrease of the intensity of the NH_3^+ line and by increasing intensities of the N_2^+ and H_2^+ lines. When ammonia decomposition does not proceed, the intensity of these lines does not depend on the temperature of platinum catalyst. In Fig. 7 the curves $I(T)$ [I is the intensity of a line in the mass spectrum, T is the temperature of the catalyst] for NH_3^+, N_2^+, and H_2^+ lines are given. As can be seen from Fig. 7 for an active catalyst (dotted lines) the reaction begins at the temperature 500°C and its rate increases with increasing temperature. After the heating in residual gas at 1200°C for 2 hr the catalyst loses its activity completely. This fact was observed by the authors of ref. (4), but was not explained by them.

We assumed that the loss of activity was connected with the poisoning of the plati-

num catalyst by free carbon formed on the surface of platinum as a result of thermal cracking of hydrocarbon vapors entering the composition of residual gas. In order to confirm this supposition some experiments were carried out.
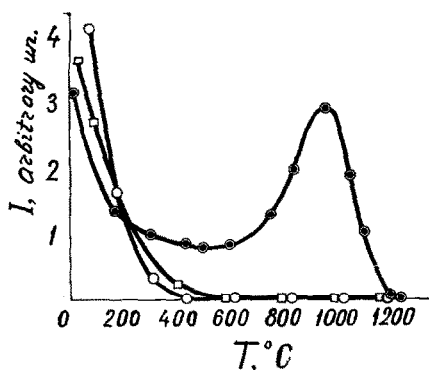

FIG. 3. The curves $I(T)$ for C_2^-, C_2H^-, and $C_2H_2^-$ secondary ions; the catalyst in the atmosphere of residual gas: $\odot$, C_2^-; $\square$, C_2H^-; $\bigcirc$, $C_2H_2^-$.

In Fig. 3 the curves $I(T)$ for secondary C_2^-, C_2H^-, and $C_2H_2^-$ ions are given. The curves were obtained after 2 hr heating of the catalyst in the residual gas atmosphere. As can be seen from these figures, with increasing temperature of the catalyst a monotonous decrease of the intensity of the C_2H^- and $C_2H_2^-$ lines is observed. At the temperatures 400° and 600°C the emission of these ions is so small that it cannot be measured by a valve electrometer. The dependence of the emission of C_2^- ions on the catalyst temperature is quite different. The shape of the curve $I(T)$ for C_2^- ions can be explained if it is taken into consideration that these ions can be knocked out both from hydrocarbon molecules and from a free carbon. The initial decrease on the curve $I(T)$ for C_2^- ions is due to the desorption of hydrocarbon molecules from the surface of the catalyst. The free carbon begins to form at about 200°C; therefore in the temperature range 200–600°C the shape of the curve $I(T)$ is determined by the knocking out of the C_2^- ions both from hydrocarbon molecules and a free carbon. At temperatures higher than 600°C, as judged from the curves $I(T)$ for C_2H^- and $C_2H_2^-$ ions, the complete desorption of hydrocarbon molecules from

the surface of the catalyst takes place; the knocking out of C_2^- ions results only from the free carbon.

The experiments done when oxygen was admitted to the catalyst chamber confirmed the supposition about the formation of free carbon on the catalyst surface. Oxygen in the catalyst chamber must oxidize the carbon on the surface of the catalyst and carbon oxides must desorb from this surface. The presence of oxygen in the catalyst chamber must also influence the shape of the curve $I(T)$ for C_2^- ions. In fact the shape of this curve for the catalyst in the oxygen atmosphere [Fig. 4(a)] differs essentially
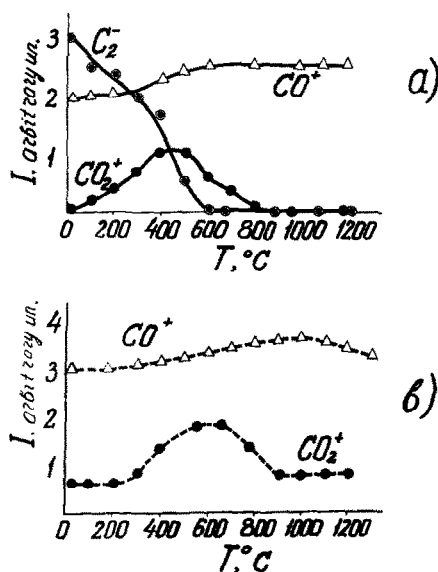

FIG. 4. (a) The curves $I(T)$ for C_2^-, CO^+, and CO_2^+ secondary ions, the catalyst in the atmosphere of oxygen. (b) The curves $I(T)$ for CO^+ and CO_2^+ ions obtained by ionization of the gas by an electron impact; the catalyst in the atmosphere of oxygen.

from that for the catalyst in the atmosphere of residual gas (Fig. 3). From Fig. 4(a) one can see that in the presence of oxygen the intensity of the C_2^--ion line monotonously decreases with increasing temperature of the catalyst and at about 600°C cannot be measured by the valve electrometer. Beginning from the temperature of about 200°C the desorption of CO and Co_2 into the gas phase is observed, as may be seen from Fig.

4(b), where the curves $I(T)$ for ions CO^+
and CO_2^+ obtained by ionization of the gas
by electron impact are plotted. The reaction
of carbon oxidation can be stated by means
of the curves $I(T)$ for the CO^+ and CO_2^+
secondary ions [Fig. 4(a)].

It is possible to render the catalyst active
by heating it in an oxygen atmosphere, for
it is known (5–7) that incandescent platinum
absorbs a great quantity of oxygen. The
oxygen absorbed on platinum catalyst will
diffuse by the heating to its surface and,
oxidizing the carbon, will protect the catalyst
from poisoning. As our experiments have
shown, a short heating in oxygen does not
render the catalyst active. This means that
hydrocarbon cracking and formation of free
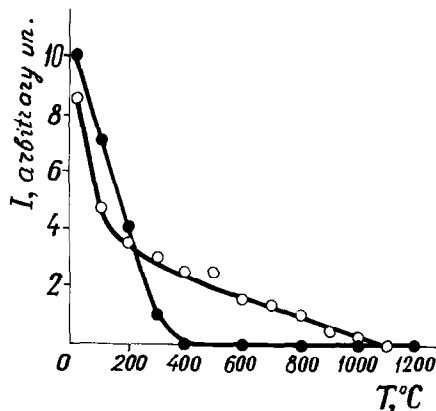carbon on the catalyst surface also take place

FIG. 5. The curves $I(T)$ for O_2^- secondary ions;
the catalyst was previously heated in the oxygen
atmosphere at 1200°C: ●, the heating of short
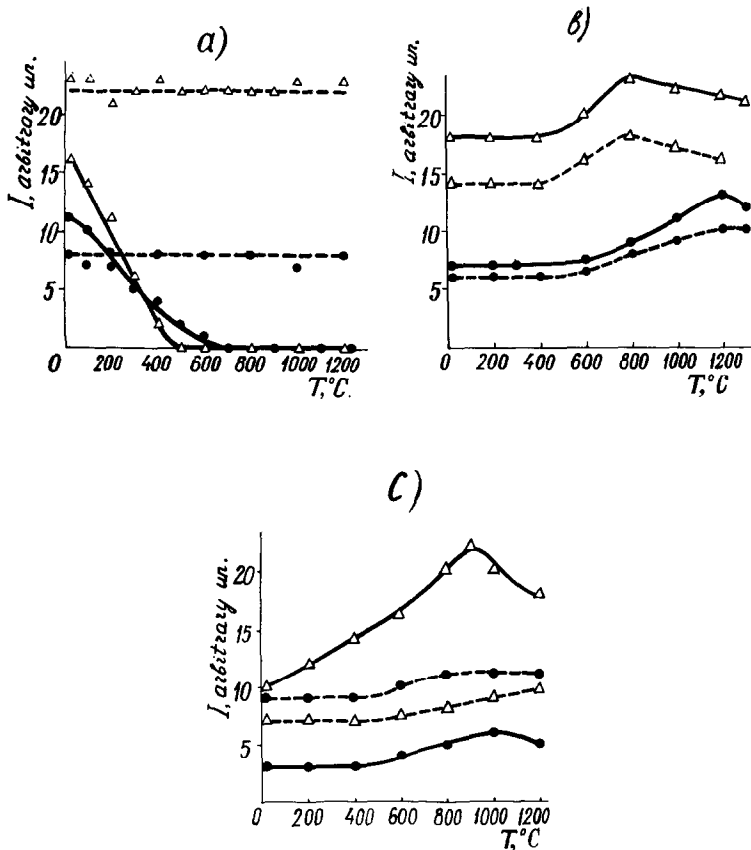duration; ○, the heating during 2 hr.

FIG. 6. The curves $I(T)$ for CO^+ and CO_2^+ ions, solid curves, secondary ions; dotted curves, ions
obtained by ionization of the gas by an electron impact: △, CO^+ ions; ●, CO_2^+ ions. (a) The
poisoned catalyst in the atmosphere of residual gas. (b) The active catalyst in the atmosphere
of residual gas. (c) The active catalyst in the atmosphere of ammonia.

The arbitrary scale for Figs. 6(a), (b), and (c) is the same with exclusion of curve $I(T)$ for CO^+
gaseous ions in Fig. 6(c). The ordinates of this curve were multiplied by the factor 0.2.

in the ammonia atmosphere. Only the heating of the catalyst in oxygen atmosphere for 2 hr renders it active. After this processing of the catalyst the curve $I(T)$ for the catalyst in the ammonia atmosphere had the same shape as in Fig. 4(a). The curves $I(T)$ for O_2^- secondary ions (Fig. 5) illustrate well the absorption of oxygen by incandescent platinum. As can be seen from Fig. 5, in the case of a short heating of platinum in oxygen atmosphere the emission of O_2^- ions exists only until the temperature reaches about 400°C. By long heating this emission is maintained until the temperature is about 1200°C. This means that up to this temperature a marked quantity of oxygen on the catalyst surface is maintained.

Examination of the curves $I(T)$ [Fig. 6(a), (b), and (c)] for the CO^+ and CO_2^+ secondary ions and the ions obtained by ionization of the gas by electron impact shows that on the surface of an active catalyst there goes per-

petually the process of carbon oxidation with desorption of carbon oxides into the gas phase. This process goes in the same way both in the ammonia and the residual gas. On the surface of poisoned catalyst the process of carbon oxidation does not take place.

ELEMENTARY PROCESSES BY THE DECOMPOSITION OF AMMONIA ON PLATINUM

In Fig. 7 the curves $I(T)$ for NH_3^+, NH_2^+, NH^+, N_2^+, and H_2^+ ions are given. For some secondary ions (H_2^+, N_2^+, NH^+) the shape of the curve $I(T)$ greatly depends on the state of the catalyst; that is, for an active catalyst this curve has a quite different shape in comparison to that for a poisoned catalyst. By analysis of dependences $I(T)$ for an active catalyst one can draw conclusions about elementary processes for catalytic decomposition of ammonia. The catalytic
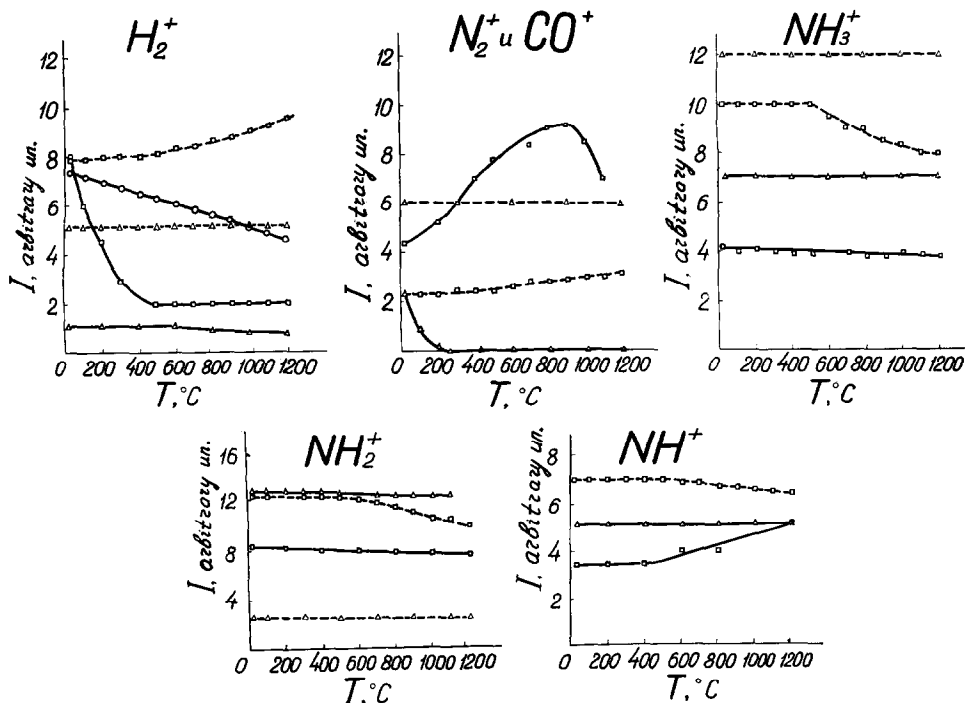

FIG. 7. The curves $I(T)$ for H_2^+, N_2^+, NH^+, NH_2^+, and NH_3^+ ions; the catalyst in the atmosphere of ammonia; solid curves, secondary ions; dotted curves, ions obtained by ionization of the gas by an electron impact; $\triangle$, the poisoned catalyst; $\square$, the active catalyst; $\bigcirc$, the active catalyst in the atmosphere of hydrogen.

decomposition of ammonia proceeds in two stages. In the first stage at temperatures higher than 500°C, part of the NH_3 molecules dissociate by adsorption on the surface of platinum. The NH_3 molecule dissociates by adsorption to H_2 and NH. The H_2 molecules formed by dissociative adsorption of NH_3 molecules desorb from the surface of the catalyst. The NH molecules partly desorb from the surface of the catalyst and partly associate on the surface of platinum according to the reaction $NH + NH \rightarrow N_2 + H_2$ (the second stage of ammonia decomposition). The N_2 and H_2 molecules formed in this second stage of ammonia decomposition also desorb from the surface of the catalyst.

The following facts confirm the supposition about elementary processes by catalytic decomposition of ammonia on platinum:

1. There is a decrease of NH_3^+ and NH_2^+ secondary ion emission and an increase of NH^+ ion emission in the temperature range 500–1200°C.

2. In the same temperature range the decrease on the curve $I(T)$ for NH^+ ions from the gas phase is slower than for NH_3^+ and NH_2^+ ions. This fact can be accounted for if it is taken into consideration that the decrease of intensity of the NH^+ line due to the decrease of the partial pressure of NH_3 in the gas phase is partly compensated by desorption of NH molecules from the surface of the catalyst.

Proceeding from the scheme of elementary processes of ammonia decomposition one can account for the shape of the curve $I(T)$ for H_2^+ secondary ions. The formation of H_2 molecules in the temperature region higher than 500°C would bring an increase of emission of H_2^+ secondary ions. But with an increase of temperature the surface covering of platinum by H_2 molecules is decreased [see the curve $I(T)$ for H_2^+ secondary ions in the case of platinum in hydrogen atmosphere]. Owing to these opposite tendencies the emission of H_2^+ ions in the temperature range 500–1200°C is constant (in this case the constancy of emission is incidental). The decrease of H_2^+ emission in the temperature range 20–500°C can be explained by the decay of some chemical compound of Pt

and NH_3. The monotonous decrease of intensity of PtN^- and PtN_2^- lines in this range of temperatures confirms this supposition.

It is more difficult to explain the shape of the curve $I(T)$ for N_2^+ secondary ions. An interpretation of this curve is hampered by the fact that in emission of ions with mass 28, besides N_2^+ ions, the CO^+ ions also take part. Nevertheless one can draw some conclusions from the curve $I(T)$ for ions with mass 28. It is necessary to pay attention to the increase of the emission of these ions in the temperature range 20–500°C. It is not possible to connect this increase with the emission of CO^+ ions [see the curve $I(T)$ for CO^+ secondary ions in Fig. 6(b)]. The increase of N_2^+ ion emission, which cannot be knocked out from NH_3 molecules, can be accounted for by the decay of a chemical compound of Pt and NH_3. This decay is accompanied by formation of N_2 molecules which are not desorbed from the surface of the catalyst. Further increase of the emission of ions with mass 28 is explained by the formation of N_2 molecules as a result of ammonia decomposition and the oxidation of carbon on the surface of the catalyst [see curve $I(T)$ for CO^+ ions in Fig. 6(b)]. It is possible to get more definite conclusions about the true shape of the curve $I(T)$ for N_2^+ ions by using ammonia which contains a nitrogen isotope with mass 15.

In conclusion, it has to be noted that ammonia decomposition on platinum begins at the same temperature as the emission of PtN^- and PtN_2^- ions decreases to zero and the emission of H_2^+ ions decreases to a minimum value. It is possible that at temperatures less than 500°C the adsorption of NH_3 molecules onto the surface of platinum is accompanied by the formation of a chemical compound between ammonia and platinum and only at temperatures higher than 500°C do the elementary processes of ammonia decomposition begin to proceed.

The results of the experiments permit it to be stated that the new method of investigation of catalytic reactions described in this paper gives the possibility of obtaining new information about catalytic processes which it was not possible to get by other methods used earlier for studying catalysis.

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