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STUDY OF THE REACTION OF CATALYTIC OXIDATION OF AMMONIA ON PLATINUM BY THE METHOD OF SECONDARY ION EMISSION

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The reaction of the catalytic oxidation of ammonia on platinum has been studied in a very large number of works; nevertheless, the mechanism of this reaction is not clear. At present, the generally accepted view is that the oxidation reaction of ammonia is a multistage process. Various intermediate compounds participate in the different stages of this process ([1–3]). Numerous attempts to detect in the gas phase the intermediate compounds formed in the ammonia oxidation reaction have not been successful. The detection in work ([4]) of nitrous acid among the products of this reaction is, according to the data of work ([5]), erroneous.

In the present work, with the aid of a new method developed by us for the study of heterogeneous catalytic reactions, described in our previous works ([6,7]), which were devoted to the study of the catalytic decomposition of ammonia on platinum, an attempt has been made to clarify certain features of the reaction of the catalytic oxidation of ammonia on platinum. The apparatus and the essence of the method of investigation are not set forth here, since they were described in works ([6,7]).

The ammonia oxidation reaction was studied at a pressure of the reaction mixture $\sim 10^{-4}$ mm Hg in two cases: a) at a ratio of the partial pressures of NH_3 and O_2 equal to $1:3$ (excess oxygen), and b) at a ratio of these pressures $2:1$ (oxygen deficiency).

Figure 1 gives the curves $I(t)$ (I is the intensity of a certain line in the mass spectrum, t is the temperature of the catalyst) for secondary ions knocked out from the surface of the catalyst by a beam of primary Ar^+ ions, and for ions obtained by ionization by an electron beam of the gas surrounding the catalyst. The course of the curves $I(t)$ for ions obtained by ionization of the gas phase, with masses 18 (H_2O^+), 28 ($N_2^+ + CO^+$), and 30 (NO^+), shows that, beginning

at approximately 200°, the oxidation reaction of ammonia proceeds with formation of H_2O, N_2, and NO. The course of the reaction is also traced from the curves $I(t)$ for secondary ions with masses 18, 28, and 30. This circumstance, as well as the fact that the pressure of the reaction mixture is sufficiently low, makes it possible to assert that the ammonia oxidation reaction under our conditions has a purely heterogeneous character. This assertion is in agreement with the data of work ([5]), carried out at a pressure of the reaction mixture two orders of magnitude greater than in our work. It should also be noted that, in the temperature interval in which the ammonia oxidation reaction takes place, the curves $I(t)$ for secondary ions and gas-phase ions with masses 18, 28, and 30 have the same course. This fact permits the conclusion that bombardment of platinum by primary ions does not lead to any substantial change in its catalytic properties.

In order to introduce some clarity into the question of the mechanism of ammonia oxidation on Pt and the possible role of intermediate compounds in the formation of the final reaction products, a careful study was made of the mass spectra of secondary ions and gas-phase ions with the aim of detecting intermediate compounds of the type HNO, NH_2OH, HNO_2, HNO_4, on the basis of which the mechanism of ammonia oxidation was interpreted by Bodenstein and Andrussow ([1],[2]). As a result of these investigations it was found that, in the temperature interval from 20 to 1200°, in the mass spectra of secondary ions and gas-phase ions the lines with masses 31 (HNO^+), 33 (NH_2OH^+), 47 (HNO_2^+), 79 (HNO_4^+) are absent. From this fact it follows that intermediate compounds of the type HNO or NH_2OH during the oxidation of ammonia on platinum in any appreciable quantities ···

substances are not formed. In the oxidation of ammonia, no other nitrogen oxides apart from NO were also observed.

The experiments we carried out also do not confirm the imide hypothesis of Zavadsky ([3]). In ([6]) it was shown that the first stage of the decomposition reaction of ammonia on platinum is the formation of NH owing to the dissociation of NH_3 into NH and H_2. The formation of NH in this reaction was manifested both in the mass spectrum of secondary ion emission and in the mass spectrum of the gas phase. In order to test Zavadsky' s hypothesis about the formation of NH in the ammonia oxidation reaction, a study was made of the influence of adding oxygen to ammonia on the intensity of the line with mass 15 (NH^+) in the spectrum of secondary ions. It turned out that at an oxygen pressure of $\sim 7 \cdot 10^{-5}$ mm Hg the emission of the ion NH^+ disappears*. This fact completely contradicts Zavadsky' s notion of imide formation in the ammonia oxidation reaction. Thus, the experiments performed do not confirm the various hypotheses concerning the mechanism of the ammonia oxidation reaction that are based on the assumption of the formation of intermediate compounds in this reaction. It remains to suppose that in the ammonia oxidation reaction, at least the principal final products of the reaction are formed as the result of the direct combination of ammonia with oxygen. This reaction may proceed both with

Fig. 1. Curves $I(t)$ for secondary ions and gas-phase ions. Dashed curves–gas-phase ions; solid curves–secondary ions. a–$P_{\mathrm{NH3}} : P_{\mathrm{O2}} = 1 : 3$; b–$P_{\mathrm{NH3}} : P_{\mathrm{O2}} = 2 : 1$.

Figure 1: Fig. 1. Curves $I(t)$ for secondary ions and gas-phase ions. Dashed curves–gas-phase ions; solid curves–secondary ions. a–$P_{\mathrm{NH3}} : P_{\mathrm{O2}} = 1 : 3$; b–$P_{\mathrm{NH3}} : P_{\mathrm{O2}} = 2 : 1$.

molecular and with atomic oxygen; therefore it is important to determine in what state oxygen is present on the platinum surface–molecular or atomic. For this purpose, experiments were carried out with a platinum catalyst in an oxygen atmosphere ($P_{\mathrm{O2}} = 1.5 \cdot 10^{-4}$ mm Hg). The dependences of the intensities of the mass lines 32 (O_2^+) and 16 (O^+) in the spectrum of secondary ions on the temperature of the catalyst were investigated. The results of these experiments are illustrated by the curves in Fig. 2. The existence of secondary emission of O_2^+ ions over the entire temperature range studied shows that, at least, part of the oxygen on platinum is in the molecular state. O^+ ions can be knocked out both from molecular and from atomic oxygen; therefore no definite conclusions can be drawn from the mere fact of the existence of secondary emission of O^+ ions. Such conclusions can be drawn from a comparison of the $I(t)$ curves for the secondary ions O_2^+ and O^+. The currents of the secondary ions O_2^+ and O^+ at a given catalyst temperature are deter-

Fig. 1. Curves $I(t)$ for secondary ions and gas-phase ions. Dashed curves –gas-phase ions; solid curves–secondary ions. a–$P_{\mathrm{NH3}} : P_{\mathrm{O2}} = 1 : 3$; b–$P_{\mathrm{NH3}} : P_{\mathrm{O2}} = 2 : 1$.

* The disappearance of the emission of NH^+ ions upon addition of oxygen to ammonia indicates that the decomposition reaction of ammonia ceases to proceed when oxygen is introduced into the adsorbed layer. An analogous phenomenon was observed during the decomposition of ammonia on tungsten ([8]).

are determined by the formulas:

$$I_{\mathrm{O2^+}} = k_1 N_{\mathrm{O2}}, \tag{1}$$

$$I_{\mathrm{O^+}} = k_2 N_{\mathrm{O2}} + k_3 N_{\mathrm{O}}, \tag{2}$$

where k_1 and k_2, k_3 are the relative coefficients of ejection of O_2^+ ions from O_2 and of O^+ from O_2 and O, respectively, and N_{O2} and N_{O} are the numbers of oxygen molecules and atoms per 1 cm^2 of catalyst surface. From formulas (1) and (2) it follows that

$$\frac{I_{\mathrm{O^+}}}{I_{\mathrm{O2^+}}} = a + b\frac{N_{\mathrm{O}}}{N_{\mathrm{O2}}}. \tag{3}$$

If the oxygen on the platinum surface were not dissociated at all, i.e., $N = 0$, then, as follows from formula (3), the ratio $I_{O^+}/I_{O2^+} = \text{const}$ over the entire temperature interval. As is seen from Fig. 2, this ratio changes with temperature. It follows from this that $N_O \neq 0$, i.e., part of the oxygen on the platinum surface is dissociated.

On the basis of the above, one may conclude that oxygen on the platinum surface is present in both molecular and atomic states. As a result, ammonia on the platinum surface can be oxidized by both molecular and atomic oxygen. Apparently, it may be asserted that oxidation of ammonia by atomic oxygen takes place. This assertion is confirmed by the following facts. Comparison of the $I(t)$ curves for the secondary ions NO^+, H_2O^+, and O^- indicates that oxidation of ammonia is carried out by the particle from which the O^- ion is ejected. On the other hand, we established that the value of I_{O2^+} increases with increasing oxygen pressure, whereas the value of I_O decreases. This means that the O^- ion is not ejected from the same particle from which O_2^+ is ejected, i.e., it is not ejected from molecular oxygen. Only one possibility remains, namely the ejection of O^- from atomic oxygen.* As for the oxidation of ammonia by molecular oxygen, the experimental material available on this question does not allow an unambiguous conclusion to be drawn. The course of the $I(t)$ curve for secondary O_2^+ ions differs substantially from the course of the corresponding curve for secondary O^- ions. However, it cannot yet be concluded from this that molecular oxygen plays no role in the oxidation of ammonia, since the course of the $I(t)$ curve for O_2^+ ions in the temperature region above 600° is affected by the process of oxidation of hydrocarbons adsorbed on platinum from the residual gas. The existence of this process was established by us experimentally from the $I(t)$ curves for CO^+ and CO_2^+ ions from the gas phase. Since no intermediate compounds were found by us during the oxidation of NH_3 on Pt, the one-stage oxidation of NH_3 must proceed according to the reactions:

$$NH_3 + O_2 \rightarrow NO + H_2O + H, \tag{4}$$

$$NH_3 + O \rightarrow NO + H_2 + H. \tag{5}$$

Fig. 2. *a*–$I(t)$ curves for secondary ions O_2^+ and O^+; *b*–$I_{O^+}/I_{O2^+} = f(t)$, $P_{O2} = 2 \cdot 10^{-4}$ mm Hg.

* Ejection of O^- from platinum oxides is excluded, since no mass lines corresponding to platinum oxides were observed in the mass spectrum of secondary ions.

The atomic and molecular hydrogen formed in reactions (4) and (5) is also oxidized and converted into H_2O. The course of the curves $I(t)$ for the ions H^+ and $H_2{}^+$ in Fig. 1 confirms this assumption. Thus, as a result of the direct oxidation of ammonia, only NO and H_2O molecules should be formed.

The formation of N_2 during the catalytic oxidation of ammonia may occur as a result of the following secondary processes:

$$NO + NO \rightarrow N_2 + O_2, \tag{6}$$

$$NO + NH_2 \rightarrow N_2 + H_2O + H. \tag{7}$$

To determine which of reactions (6) and (7) is responsible for the formation of N_2 in the oxidation reaction of NH_3, these reactions were investigated*. In accordance with literature data ([9], [10]), it was established that catalytic decomposition of NO on Pt takes place according to formula (6). However, reaction (6) cannot be regarded as responsible for the formation of N_2 in the ammonia oxidation reaction, because: 1) the curve $I(T)$ for gas-phase N_2^+ ions in the case of reaction (6) has an entirely different form compared with the corresponding curve in the case of ammonia oxidation; 2) the addition of NH_3 to NO inhibits reaction (6). On the other hand, the $I(T)$ curves in the case of reaction (7), both for secondary N_2^+ ions and for gas-phase N_2^+ ions, are completely analogous to the corresponding curves in the case of ammonia oxidation. The addition of O_2 to the mixture $NO + NH_3$ practically does not inhibit reaction (7). These facts allow one to conclude that the formation of N_2 in the ammonia oxidation reaction proceeds by means of reaction (7).

Thus, the results of the experiments described above give grounds for asserting that the molecules NO, H_2O, and N_2 in the process of ammonia oxidation are formed by reactions (4), (5), and (7).

The curves $I(P)$ (P is the pressure of O_2 for secondary ions NH_3^+ and O_2^+), obtained in an experiment in which NH_3 was first admitted into the catalyst chamber to a pressure of $1 \cdot 10^{-4}$ mm Hg, and then oxygen was admitted, show that O_2 penetrates into the adsorbed film of NH_3, but does not completely displace it. An analogous result is obtained in an experiment in which oxygen was first admitted into the catalyst chamber, and then ammonia. On the basis of the results of these experiments, contrary to the opinion of the authors of work ([5]), one may conclude that the ammonia oxidation reaction proceeds by the Hinshelwood-Langmuir mechanism (both reacting particles are adsorbed on the catalyst surface), and not by the Rideal mechanism (the catalyst is covered with an adsorbed film of only one of the reactants; molecules of the other reactant enter the reaction coming from the gas phase). The fact that the ammonia oxidation reaction on platinum proceeds by the Hinshelwood-Langmuir mechanism is also supported by the occurrence of the emission of secondary ions NO^+ and H_2O^+, and by the analogous course of the $I(T)$ curves for secondary and gas-phase ions NO^+ and H_2O^+.

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* A detailed account of the results of the study of reactions (6) and (7) is contained in our article submitted to the journal *Kinetics and Catalysis*.

Note: Figure translations are in progress. See original paper for figures.