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1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE POSSIBILITY OF APPLYING THE PHENOMENON OF SECONDARY ION-ION EMISSION TO THE STUDY OF HETEROGENEOUS CATALYTIC REACTIONS

(Presented by Academician A. N. Frumkin, 7 VII 1962)

In our previous works ([1,2]) it was shown that: 1) adsorption of a gas by a metal surface not only substantially changes the relative intensities of individual lines in the mass spectrum of secondary ion emission, but also leads to the appearance of new lines; 2) the temperature dependence of the intensity of certain mass-spectral lines makes it possible to establish the occurrence of chemical reactions on the metal surface.

Since the stages of a heterogeneous catalytic process are adsorption of the molecules of the reacting gases by the surface of the catalyst and a surface chemical reaction between adsorbed molecules, one may attempt to use the phenomenon of secondary ion-ion emission to study the nature of elementary processes in heterogeneous catalysis. In the present work the method of secondary ion-ion emission was applied to consideration of the catalytic decomposition of ammonia on platinum. At low ammonia pressures (10^{-2} mm Hg) this process was studied by purely chemical methods in work ([3]). The study of ammonia decomposition was carried out on a double mass-spectrometric apparatus described in works ([1,4]). In the present work the chamber of the target (catalyst) was reconstructed in such a way that, in addition to ion bombardment of the catalyst surface, electron bombardment of the gas surrounding the catalyst could be carried out*. Thus, the course of the catalytic reaction could be followed from changes in the mass spectrum of ions formed as a result of ionization of the gas by electrons. From changes in the mass spectrum of secondary ion-ion emission arising as a result of the catalytic process, it was proposed to judge the course of chemical reactions on the catalyst surface.

A platinum ribbon measuring 13×4 mm^2 was used as the catalyst. The ribbon was heated by passing a current through it. The temperature of the ribbon was measured with a platinum-platinum-rhodium thermocouple. The ribbon was bombarded with a beam of Ar^+ ions at a current of 10^{-8} A and an energy of 22 keV. The experiments were carried out at an NH_3 pressure equal to

10^{-4} mm Hg. Observation of the course of the catalytic reaction was performed using the ions H^+, N_2^+, and NH_3^+ in the spectrum of gas ionization by electron impact. The intensity of the beams of these ions remains constant when the temperature of the catalyst is changed, if catalytic decomposition of NH_3 for some reason does not take place (the catalyst is poisoned, or its temperature is insufficient for the catalytic process to occur)**. The intensity of the ion beam NH_4^+ decreases, while the intensity of the beams of H_2^+ and N_2^+ ions increases in the case when catalytic decomposition of NH_3 is taking place.

In the mass spectrum of the secondary ion emission of platinum in an atmosphere of residual gas (pressure $5 \cdot 10^{-6}$ mm Hg), negative ions were observed 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^-) and 223(PtN_2^-); positive ions with masses 1(H^+), 14(N^+), 16(O^+), 17(OH^+), 28($N_2^+ + CO^+$), 32(O_2^+), 44(CO_2^+) and 195(Pt^+). Admission of NH_3 into the catalyst chamber greatly increased the intensity of the PtN^- and PtN_2^- beams in the spectrum of negative ions. In the spectrum of positive ions, ions with mass 2(H_2^+), 15(NH^+) appeared, and the intensity of the mass-spectral lines with masses 16, 17 and 28 increased owing to the sputtering from the catalyst surface of NH_2^+, NH_3^+ and N_2^+ ions.

Preliminary heating of the platinum catalyst in the residual gas at a temperature of 1200° led to a complete loss of its catalytic activity. A similar fact was also observed in work (^{3}), where no explanation was given for it. We assumed that heating of the catalyst leads to its poisoning by free carbon deposited on the catalyst surface as a result of cracking of the hydrocarbons contained in the residual gas. This assumption is confirmed by experiments whose results are characterized by the curves in Fig. 1. The course of the curve for the dependence of the intensity of the C_2^- ion beam on temperature may be explained as follows: the drop in intensity at the beginning of the curve is associated with desorption of hydrocarbon molecules from the catalyst surface; at a temperature of about 600°, complete desorption of these molecules occurs and, in connection with this, the emission of C_2H^- and $C_2H_2^-$ ions disappears. However, at a temperature of 600° the emission of C_2^- ions not only does not disappear, but with further increase in temperature continues to grow, passes through a maximum at a temperature of about 1000°, and disappears only at 1200°. Such a course of the curve $I_{C_2^-}(T)$ can be explained by the fact that, beginning at a temperature of approximately 200°, deposition of free carbon takes place on the Pt surface, from which C_2^- ions are also sputtered. If the assumption made about the nature of the poisoning of the platinum catalyst is correct, then its activity can

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* A more detailed description of the apparatus and experimental procedure will be given elsewhere.

** The presence of N_2^+ ions in the mass spectrum of gas ionization in the case of an inactive catalyst is due to the fact that nitrogen is a component of the residual gas.

Fig. 2

Figure 1: Fig. 2

be restored by heating in an atmosphere of oxygen. Such an experiment was carried out and confirmed our expectations.

Fig. 1. *a*—dependences of the intensity of the beams of secondary ions C_2^-, C_2H^-, and $C_2H_2^-$ on the temperature of the catalyst in an atmosphere of residual gas; *b*—the same, on the temperature of the catalyst in an atmosphere of oxygen; *v*—dependences of the intensity of the beams of CO^+ and CO_2^+ ions, obtained by ionization of the gas phase by electron impact, on the temperature of the catalyst in an atmosphere of oxygen.

The catalyst heated in an O_2 atmosphere (pressure $5 \cdot 10^{-5}$ mm Hg) acquired catalytic activity. The results of this experiment are characterized by the curves in Figs. 1*b* and 1*v*. As is evident from these curves, oxidation of carbon by oxygen takes place, preventing the appearance of a carbon layer on the catalyst surface, as is seen from the curve $I = f(T)$ (emis-

of C_2^- ions ceases at 600°). The carbon oxides CO and CO_2 that are formed desorb into the gas phase, as is seen from the curves of the temperature dependence of the intensity for beams of CO^+ and CO_2^+ ions obtained by ionization of the gas phase. The course of the carbon oxidation processes is traced in the spectrum of secondary ion emission (Fig. 1b), where substantial changes are observed in the emission of CO^+ and CO_2^+ ions; this confirms the general idea that changes in the spectra of secondary ion emission can be used to judge the course of surface chemical reactions.

Figure 2 gives the curves of the dependence of the intensity of beams of $H_2^+, N_2^+, NH_3^+, NH_2^+$, and NH^+ ions on the temperature of the catalyst. The dashed curves refer to ions obtained owing to ionization of the gas by electron impact, and the solid curves to ions knocked out from the surface of the catalyst. As is evident from this figure, ammonia decomposition does not proceed on the poisoned cata-

Fig. 2. Dependences of the intensity of beams of $H_2^+, N_2^+, NH^+, NH_2^+$, and NH_3^+ ions on the temperature of a catalyst in an NH_3 atmosphere; solid curves —secondary ions, dashed curves—ions obtained by ionization of the gas phase by electron impact. 1—poisoned catalyst, 2—activated catalyst, 3, 4—activated catalyst in hydrogen and nitrogen atmospheres, respectively.

lyst. In the case of a catalyst activated by heating in oxygen, decomposition of NH_3 begins at a temperature $T \approx 500°$.

The course of the curves $I(T)$ (I is the intensity of the ion beam for secondary ions) in the case of the active and inactive catalyst is entirely different. From the course of these curves for the active catalyst one can draw a conclusion concerning the elementary processes in the catalytic decomposition of NH_3. Ammonia decomposition proceeds in two stages. In the first stage, at temperatures above 500°, dissociative adsorption of NH_3 molecules takes place. The decomposition of NH_3 molecules proceeds according to the formula

$$NH_3 \rightarrow NH + H_2.$$

The H_2 molecules formed desorb, while the NH particles partly desorb and partly associate according to the formula

$$NH + NH \rightarrow N_2 + H_2$$

(the second stage of the ammonia decomposition process). The H_2 and N_2 molecules formed in the second stage of the process desorb.

A number of facts confirm the above assumption about the character of the elementary processes in the catalytic decomposition of NH_3 on platinum:

1. A decrease in the emission of secondary NH_3^+ and NH_2^+ ions and an increase in the emission of secondary NH^+ ions in the temperature interval 500–1200°.

2. In this same temperature interval, the decrease in the curve $I(T)$ for NH^+ ions from the gas phase is slower than for the corresponding NH_3^+ and NH_2^+ ions. This fact is explained by the circumstance that the decrease in the number of NH^+ ions, associated with a decrease in the number of NH_3 molecules in the gas phase, is partly compensated by desorption of NH particles into the gas phase.

The course of the curve $I(T)$ for secondary H_2^+ ions can be explained as follows. In the temperature region above 500°, the appearance of H_2 molecules on the Pt surface should have led to an increase in the emission of secondary H_2^+ ions; however, with increasing temperature the coverage of the Pt surface by H_2 molecules decreases (see the curve $I(T)$ for H_2^+ ions in the case of Pt in an H_2 atmosphere). These opposing tendencies lead to the emission of H_2^+ ions being constant in the temperature interval 500–1200°. The decrease in the emission of H_2^+ ions in the temperature interval 20–500° can be explained by the decomposition of a chemical compound of Pt with NH_3.

The curve $I(T)$ for secondary N_2^+ ions has the most complex character. It should be noted that N_2^+ ions cannot be knocked out of an NH_3 molecule; therefore, their emission in the temperature interval 20–500° can be explained by the formation of a chemical compound of Pt and NH_3. The N_2^+ ion at temperatures of 20–500° is knocked out of this compound. The formation of such a compound is confirmed by the presence in the mass spectrum of secondary emission of the ions Pt^-, PtN^-, and PtN_2^-. The emission of these ions in the temperature interval 20–500° decreases monotonically, while in this same temperature interval the emission of N_2^+ ions increases. Apparently, this fact can be explained by the decomposition of the chemical compound of Pt with NH_3, occurring as the temperature of the Pt is raised, being accompanied by the formation of N_2 molecules that do not desorb into the gas phase. Above 500°, N_2 molecules appear on the Pt surface, arising from the decomposition of NH_3. The emission of N_2^+ ions at temperatures above 500° is conditioned by these two processes, which can explain the maximum on the curve $I(T)$ for N_2^+ ions. It should be noted that the decomposition of NH_3 begins at the temperature at which the emission of Pt^-, PtN^-, and PtN_2^- ions falls to zero, and the emission of H_2^+ ions falls to a minimum. It is possible that the presence of a surface chemical compound of Pt with NH_3 hinders the decomposition of NH_3 on Pt.

We express our gratitude to V. I. Shvachko, who took part in the measurements.

We consider it our pleasant duty to express our sincere gratitude to Professor A. K. Walter for his constant attention to and interest in the work.

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named after A. M. Gorky

Received
6 VII 1962

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