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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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APPLICATION OF THE PHENOMENON OF SURFACE IONIZATION TO THE STUDY OF CATALYTIC REACTIONS ON A SURFACE

(Presented by Academician B. P. Konstantinov on 21 II 1963)

When molecules are adsorbed on the surface of a metal, various catalytic reactions of their decomposition and of the synthesis of new chemical compounds may occur in the adsorbed layer. By studying the chemical composition of particles thermally desorbed from a surface, for example by means of mass-spectrometric methods, one can obtain information about reactions on the surface. This study is especially simple experimentally in the case when desorption of particles occurs partially in the form of positive or negative ions, i.e., when surface ionization (s.i.) takes place.

Thus, for example, observation of the temperature dependences of the s.i. of alkali-metal atoms and of molecules of alkali-halide salts led to the conclusion that, when adsorbed on a tungsten surface, the salt molecules dissociate completely at all surface temperatures T at which their s.i. occurs (^{1,2}). If this conclusion is correct, then with joint adsorption of molecules of different chemical composition that dissociate on the metal surface, the formation of new molecules and radicals may be expected.

Fig. 1

For the purpose of experimentally verifying the assumption made, we carried out experiments on the joint s.i. on tungsten of barium atoms and molecules of alkali-halide salts (MX)—lithium fluoride and sodium chloride.

Figure 1 shows a diagram of the main unit of the experimental apparatus, analogous to that which had previously been used to determine ionization poten-

Fig. 2

Figure 2: Fig. 2

tials and electron-affinity energies of certain atoms (³). A tungsten filament H, heated to temperature T, was stretched along slit u_1, which was the entrance slit of a magnetic-sector mass spectrometer. Ba atoms and MX molecules arrived at the filament from separate evaporators u_1 and u_2. The molecular beams of Ba and MX could be independently interrupted by means of controlled shutters. The instrument and filament were subjected to the usual conditioning before measurements. The pressure of residual gases in the operating apparatus was $\sim 10^{-6}$ torr.

When Ba and MX molecules were simultaneously deposited on the filament, in addition to the ions Ba^+ and M^+, which are ordinarily formed during independent s.i. of Ba and MX, at certain filament temperatures an intense emission of positive ions of the radical BaX^+ was also observed. Figure 2 presents the temperature dependences of the ionic currents Li^+, Ba^+, and BaF^+ during joint ionization on the filament of Ba atoms and LiF molecules. Similar curves were also obtained for the s.i. of Ba and NaCl. The ion currents BaF^+ and Ba^+ at the maxima of the ionization curves of Ba and BaF were of the same order of magnitude, whereas in the ionization of Ba and NaCl the ion currents BaCl^+ were approximately an order of magnitude smaller than the currents of Ba^+.

The magnitudes of the ion currents of the BaX radicals were proportional to the intensity of each of the molecular beams when the intensity of the other was unchanged. Only at high beam densities is this linearity violated. In this latter case, the curves of the temperature dependence of the MX currents shifted toward higher values of T as the densities of the atomic and molecular beams increased.

The observed dependences of the ion currents on the temperature T of the filament and on the beam density can be explained on the basis of the following assumptions. At temperatures of the tungsten filament $T > 1300^\circ$ K, when emission of Ba^+, M^+, and BaX^+ ions from the filament is observed experimentally (Fig. 2), the following reversible reactions, among other possible reactions, occur on the surface:

$$\mathrm{MX} \rightleftarrows \mathrm{M} + \mathrm{X} \quad \text{and} \quad \mathrm{Ba} + \mathrm{X} \rightleftarrows \mathrm{BaX}.$$

Of all the particles in the adsorbed state, the halogen atoms are held most strongly; their desorption, as is known, begins at $T \sim 1700 \div 1800^\circ$ K. Desorption of alkali-metal atoms and Ba (Fig. 2) begins at $T \simeq 1300^\circ$ K and probably occurs from a tungsten surface covered with adsorbed halogen atoms. In the temperature interval $1300 \div 1800^\circ$ K, the main loss of X atoms on the surface occurs through desorption of BaX radicals.

Fig. 3

Figure 3: Fig. 3

Fig. 2

Adsorption of X atoms on tungsten substantially increases the work function of the filament surface. It is very probable that the ionization potentials of Li, Na, and Ba atoms are smaller in magnitude than the work function of halogenated tungsten, and that their surface-ionization coefficient β is close to unity. This follows from the form of the curves of the temperature dependence of the ion currents (the curves in Figs. 2 and 3).

The magnitude I of the ion current BaX^+ at a surface temperature T is proportional to the surface concentrations n_{Ba} and n_X and to the value β for BaX, i.e.,

$$I \sim n_{\mathrm{Ba}} n_{\mathrm{X}} \beta. \tag{1}$$

It is possible that, in addition to BaX radicals, MX molecules and BaX_2 are also desorbed from the filament surface. However, the ionization potentials of MX molecules and, probably, of BaX_2 are considerably greater than the surface work function [4], and their desorption in our experiments could not be detected.

Fig. 3

We used the detected emission of BaX^+ ions to test the possibility of the reaction of catalytic decomposition on the surface of molecules containing the indicated radical. For this purpose, independent experiments were carried out on the surface ionization of BaF_2 and $BaCl_2$ molecules. If dissociation of the named molecules occurs on the filament surface, then, during their surface ionization, both Ba^+ ions and BaF^+ or $BaCl^+$ ions can be observed.

Figure 3 shows the temperature dependences of the Ba^+ and BaF^+ currents obtained in experiments for the case of surface ionization of BaF_2 molecules; they are analogous to the dependences in Fig. 2. In exactly the same way, the curves of the dependences on T of the Ba^+ currents

and $BaCl^+$ for the case of surface ionization of $BaCl_2$ molecules are similar to the analogous curves measured for the joint ionization on the filament of Ba atoms and NaCl molecules.

Thus, it follows from our experiments that the method of surface ionization can be used to study catalytic reactions on metallic surfaces in those cases where at least some of the particles participating in these reactions have ionization potentials comparable in magnitude with the work function of the surface. On the other hand, if ion emission is observed during thermal desorption, this may serve as an indication that these ions have an electron affinity comparable in magnitude with the work function of the surface.

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