
V. N. Ageev, E. Ya. Zandberg, N. I. Ionov, and A. Ya. Tontegode. *Adsorption-desorption processes on solid surfaces*. Atoms on the surface of a solid have specific properties that differ from their properties in the bulk of the solid and in free space. These special properties determine many physicochemical and even mechanical properties of solids and depend on the chemical composition, concentration, and geometric arrangement of the adsorbed particles. The concentration and chemical composition of adsorbed particles are related to the rates of adsorption-desorption processes.

This report concerns the kinetics of adsorption and desorption in a gas-solid system. The report presents part of the results obtained in a series of investigations

of adsorption-desorption processes and interaction of adsorbed particles with different chemical properties on the surface of transition metals and especially metals in the platinum group, which are widely used in industrial heterogeneous catalysis. This work was performed at the Laboratory of Physical Electronics at the A. F. Ioffe Physicotechnical Institute using thermodesorption spectrometry and surface ionization. These methods successfully supplement one another, since the first method yields information on processes occurring on the surface at relatively low temperatures and the second at relatively high temperatures.

The method of thermodesorption spectrometry¹ (heat flashes) is based on recording the change in the gas

pressure or flow of neutral particles with a sharp change in the temperature of the surface. The sensitivity of the method to the degree of coverage of the surface by adsorbed particles reaches $\sim 10^{-5}$ of the single-layer covering with an adsorbent surface area of 1 cm^2 . By measuring the pressure of intensity of the particle flux accompanying the flash as a function of time and surface temperature, it is possible to obtain information on the coefficient of attachment of particles on the surface and the nature of their adsorption (dissociative, nondissociative, or island formations), the binding energy of particles bound on the surface and with each other, as well as on the catalytic and corrosion processes occurring on the surface of the solid. When interpreting experimental data on the kinetics of adsorption and desorption, it is necessary to keep in mind lateral interactions between particles in the adsorbed layer and weakly coupled pre-states for the given adsorption system.

The method of surface ionization² is based on recording the charged-particle flux accompanying thermal-equilibrium ionization on the surface and permits studying processes with very low coverage and high temperatures, which are inaccessible to other methods.

In the works described here, atomically pure metals with known crystallographic orientation of the surface at residual gas pressures of 10^{-10} – 10^{-11} torr were used; the composition of the gaseous atmosphere and fluxes of desorbing particles were recorded using mass-spectrometric techniques.

The mechanism of oxidation of hydrogen,³ carbon monoxide,⁴ and carbon⁵ was investigated. It was shown that the oxidation reactions, independent of the degree of valence saturation of reacting molecules, follow the Langmuir-Hinshelwood adsorption mechanism, and their kinetics are determined by the nature of the lateral interactions between the adsorbed particles.⁶

Two states of carbon were discovered on the surface with sharply differing activity with respect to interaction with oxygen. In the more active state, the carbon atoms are randomly distributed on the surface, while in the other state, carbon forms two-dimensional islands with a graphite structure on the surface. The graphite islands are more passive than carbon monoxide gas in oxidation reactions due to saturation of the valences of carbon atoms in them. They oxidize only through the peripheral atoms and require higher temperatures.

Graphite islands form due to a first-order condensation-type phase transition in two-dimensional carbon monoxide gas on the metal surface. It was shown that the metal, covered by two-dimensional carbon monoxide gas, retains high catalytic activity in dissociation reactions, while carbon in the graphite structure poisons such reactions, decreasing their rate by a factor $\sim 10^6$.⁷ Individual metal atoms, deposited on an ordered graphite layer, can cause complete dissociation of molecules entering from the gas phase.⁸

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