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SEMICONDUCTOR PROBES SEPARATELY REGISTERING FREE RADICALS AND MOLECULES

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Many chemical and photochemical processes under ordinary conditions proceed either with the appearance, as intermediate particles, of free atoms and radicals, whose subsequent interaction leads to the formation of stable molecules, or directly with the formation of final molecular products. Investigation of the detailed mechanism of complex processes requires the carrying out of very laborious experiments connected, on the one hand, with identification of intermediate active particles by adding to the reacting system various foreign chemical substances that absorb the active particles at the moment of their formation, and, on the other hand, with subsequent analysis of these products*.

Quite apart from the inaccuracy and laboriousness of such experiments, the chemical method of investigating active particles distorts the original system and does not make it possible to observe it for any prolonged period. Observation of such processes in a stationary state over a long time and control of the concentration of intermediate active particles without distorting the course of the processes themselves would make it possible to judge not only their mechanism, but also to control them automatically. As was shown by us in (1)**, control of this kind is feasible with the aid of semiconductor probes.

In the present work a new step is taken in the development of this method. The electrical conductivity of thin semiconductor films of ZnO and TiO_2 changes considerably more under the influence of chemisorption of free atoms and radicals than it does in the chemisorption of molecules (1).

However, such active molecules as oxygen, ozone, halogens, and hydrogen very strongly change the electrical conductivity of semiconductors, and therefore the appearance of these molecules in the reacting medium, even in insignificant amounts, as in the case of radicals, will cause a change in the electrical conductivity of the probe. It follows from what has been said that, from the electrical signal obtained from a probe located in the reacting system, one cannot unambiguously assert the appearance of one or another particle. The question naturally arises of creating such probes that would respond only to free radicals and atoms, or only to active molecules. For this purpose it is necessary to use

Fig. 1 and Fig. 2: schematic curves of the change in electrical conductivity of zinc oxide under adsorption effects.

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one of the properties of free atoms and radicals common to all of them—namely, their comparatively short lifetimes under ordinary thermodynamic conditions. This property of active particles is due, as is known, to their great reactivity both toward one another and toward molecules. In the presence of a solid body (a wall), in the layer adjacent to its surface (the thickness of such a layer depends on the conditions under which the process proceeds), the destruction of radicals is associated predominantly with their heterogeneous recombination at the phase boundary. If the solid body is a porous adsorbent, then in its pores (provided that their diameter is smaller than the mean free path of the particles) heterogeneous recombination always dominates over volume recombination. The passage of particles along such pore-capillaries under the stated conditions will proceed in accordance with Knudsen’ s law. The time for particles to pass through a capillary is proportional to the square of its length (2). If these particles are radicals, then, in the case of sufficiently long capillaries, they, perishing along the way, will never reach the deep layers of the adsorbent. Consequently, in porous adsorbents the free atoms and radicals appearing outside its volume will perish in a very thin layer of such an adsorbent adjoining its visible surface. The thickness of the layer will depend on the activity of the adsorbent with respect to the particles under consideration, its structure, and external conditions (pressure, temperature).

What has been said means that the change in the electrical conductivity of a semiconductor porous adsorbent caused by the chemisorption of free atoms and radicals appearing outside the adsorbent will tend to zero as its thickness increases, whereas in the chemisorption of active

Fig. 1. Change in the electrical conductivity of zinc oxide under the influence of adsorption of O_2 molecules ($P = 0.002$ mm Hg): on a film (1), on a column (2); H_2 molecules ($P = 0.02$ mm Hg): on a film (3), on a column (4). t of the experiment 300°. a—admission of gas; b—evacuation of gas.

Fig. 2. Change in the electrical conductivity of zinc oxide under the influence of adsorption of CH_3 radicals (photolysis of acetone, $P = 0.5$ mm Hg): on a film (1), on a column (2); H atoms (discharge in H_2 and photolysis of H_2 sensitized by mercury vapor): on a film (3), on a column (4). t of the experiment 300°. a —appearance of atoms and radicals in the vessel; b—disappearance.

* The ESR method is applicable only at high radical concentrations—not less than 10^{12}-10^{14} radicals per cm^3.

** The work will be published in the *Journal of Physical Chemistry*.

molecules, as experiment shows (oxygen, hydrogen, etc.), the magnitude of the relative change in the electrical conductivity ($\Delta\sigma/\sigma_0$) of the semiconductor sample does not depend on its thickness. Only at sufficiently small thicknesses of semiconductor films is this magnitude practically constant also in the chemisorption of free atoms and radicals.

In our experiments ($t = 20$—300°, $= 0.1 \div 1.0$ mm Hg), in the case of ZnO films their critical thickness was approximately 10—20 μ (depending on the conditions of preparation of the film). The critical thickness of semiconductor porous films with respect to particular radicals can be determined experimentally from the degree to which the independence of the values ($\Delta\sigma/\sigma_0$) from its thickness is disturbed. When the thickness of ZnO films is increased, for example from 10 μ to 1 mm, the time required for the particles to traverse the indicated thicknesses increases by 10^4 times, i.e., from 10^{-4} to 1 sec.

Experiment shows that a column 1 mm thick, made of zinc oxide (sintered at 1000° without preliminary compression), is not sensitive (with respect to electrical conductivity) to the appearance, outside its volume, of free atoms and radicals (H atoms, see Fig. 2, 4; CH_3 radicals, see Fig. 2, 2). When molecules appear (hydrogen, oxygen), its electrical conductivity changes (O_2 molecules, see Fig. 1, 2; H_2 molecules, see Fig. 2, 4). A ZnO film changes its conductivity both in the presence of atoms and radicals (see Fig. 2, 1 and 3) and of molecules (see Fig. 1, 1 and 3)*.

It should be noted that the activity of free atoms and radicals with respect to changes in the values ($\Delta\sigma/\sigma_0$) of zinc oxide is considerably greater. Thus, in Figs. 1-3, signals of similar magnitude are shown, caused by chemisorption on ZnO of radicals and molecules. However, the concentration of molecules in these experiments exceeded the bulk stationary concentration of radicals by 7-8 orders of magnitude.

Combining a film and a column made of zinc oxide in one probe and using an electrical compensation circuit, we obtained a device (a miniature quartz frame, on the bar of which a thin film is deposited and next to it a small column of zinc oxide is placed) that responds only to the appearance in the reaction sphere of free atoms and radicals (but not molecules!) (see Fig. 3). Separately, the elements of this device respond only to molecules (the column) and to molecules and radicals together (the film). The dimensions of such a device (a combined probe) can be made very small: thus, for example, the column can be replaced by a ball of diameter 0.5-1.0 mm, while the film may be a spot about 1.0 mm in diameter deposited between electrodes on quartz.

Fig. 3. Change in the electrical conductivity of a combined probe under the experimental conditions (see Figs. 1 and 2) under the influence of adsorption

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* The signals shown in the figures were recorded on an EP-08 self-recording instrument with a scale of 10 mV without preliminary amplification. The voltage applied to the probe was about 1 V.

of H_2 molecules (4) and O_2 molecules (2); CH_3 radicals (1); H atoms (3). Experimental temperature 300°. *a* –appearance of particles in the vessel; – disappearance

The semiconductor probes described by us may find application in a wide variety of studies (photolysis, radiolysis, cracking, homogeneous and heterogeneous chemical reactions involving active particles).

Combined probes may also find application for studying the mechanism of processes in which radicals and active molecules (for example, oxygen or hydrogen) are formed simultaneously. With respect to H atoms and H_2 molecules, studies of the photolysis processes of saturated hydrocarbons, proceeding with detachment of both atoms and hydrogen molecules, are of interest.

The simultaneous appearance of O_2 molecules and OH radicals occurs, for example, in the very interesting reaction of potassium ozonide with water vapor or organic acids (^{3}):

$$KO_3 + RCOOH \rightarrow RCOOK + OH + O_2.$$

Separate registration of free radicals and molecules with the aid of semiconductor probes can also be carried out with the aid of two thin semiconductor films placed in different parts of the reaction vessel, separated from one another by a porous partition (foam glass, foam quartz, porous plastic, etc.), which constitutes a barrier only for radicals. This principle may be applied to semiconductors that do not possess a porous structure. With the aid of porous partitions it is possible to study the specificity of the influence of radicals (as distinct from molecules) also on other electrical and optical properties of semiconductors (work function, luminescence, photoelectric and other phenomena).

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