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Abstract

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ON CATALYSIS ON SEMICONDUCTORS IN THE REGION OF INTRINSIC CONDUCTIVITY

Until now, in works devoted to the electronic mechanism of catalysis on semiconductors, the catalyst has been regarded as an impurity semiconductor, in which the charge carriers participating in catalysis (electrons and electron holes) were formed with the direct participation of impurity levels ([1–4]). In reality, many oxidation-reduction catalytic reactions proceed at temperatures at which the semiconductor catalyst is in the region of intrinsic conductivity. Thus, for example, chromium oxide Cr_2O_3 is used as a technical dehydrogenating contact at 500–600° ([5]), i.e., in the region of intrinsic conductivity ([6]). It is very probable that intrinsic conductivity predominates in Cu_2O, which is used as a catalyst for the oxidation of propylene to acrolein at a temperature of about 300°. Elemental germanium, which according to data of the authors and V. M. Frolov ([7]) is a dehydrogenation catalyst at 200–300°, also operates in the region of intrinsic conductivity. The predominance of intrinsic conductivity is evident in all cases of high-temperature catalysis, in particular in the deep oxidation of hydrocarbons, methane conversion, etc.

With the mechanism of the primary act of interaction of the semiconductor catalyst with the substrate being identical, catalysis in the region of intrinsic conductivity must in many respects differ from catalysis in the region of impurity conductivity, and a number of propositions valid for the latter must lose their significance. For catalysis in the region of intrinsic conductivity the following should be characteristic:

1) a weak dependence of catalytic activity on "structure-sensitive" properties: the amount and nature of the impurity introduced and the prior history of the sample;

2) a connection between the catalytic properties and its substantial, rather than impurity, properties, primarily with the energy levels of the valence electrons of the atom and the sizes of the ions, and through them with the position of the elements forming the catalyst in Mendeleev' s periodic system;

3) the resulting connection of the catalytic properties with the width of the

forbidden band of the semiconductor U, and the entry into the rate equation of the catalytic reaction, as an essential factor, of $\exp(-U/2kT)$;

4) large values of the pre-exponential factor;

5) a smoothing out of the differences between n- and p-semiconductors, making it unlikely that in this region there is any specificity in their catalytic action. Let us note that, according to existing views (^{8}, ^{9}), semiconductors with the minimum value of U and maximum intrinsic conductivity at low temperatures should be semiconductors with covalent bonding, in particular atomic semiconductors: Ge, Si, etc. In binary compounds the width of the forbidden band is the narrower, the smaller the difference in electronegativities of the elements entering into the binary solid ···

body. There is also an empirical relation $U \cdot \varepsilon^2 = \text{const}$ between the width of the forbidden band and the dielectric constant ε, which, as is known (^{10}), also belongs to the substantial characteristics of a semiconductor.

The investigation carried out by the authors, together with E. A. Fokina ($^{11-13}$), on the catalytic decomposition of isopropyl alcohol on binary compounds: ZnO, ZnS, ZnSe, ZnTe—makes it possible to trace the character of the change in catalytic properties with the change in physical characteristics in this group of related compounds. In Table 1, alongside our catalytic data, the electronic characteristics of these compounds taken from the literature ($^{14-16}$) are presented.

Table 1

Changes in properties in the series ZnO—ZnTe

	ZnO	ZnS	ZnSe	ZnTe
Activation energy of dehydrogenation, kcal/mol	25—46	18—41	15—22	—
Activation energy of dehydration, kcal/mol	14—16	23—24	—	—

	ZnO	ZnS	ZnSe	ZnTe
Temperature interval in which the decomposition of the alcohol was studied, °C	120—125	100—170	20—140	20—100
Difference in electronegativities Δx	2.1	1.1	1.0	0.7
Width of forbidden band U, eV	3.2	3.7	2.6	0.6
Dielectric constant ε	8.22	9.7	–	18.6
Distance Me—X, Å	1.968	2.34 (wurtzite) 2.36 (sphalerite)	2.45	2.63

The data obtained show a sharp increase in catalytic activity with respect to the dehydrogenation of isopropyl alcohol on going from ZnO to ZnTe. At the same time the activation energies of dehydrogenation decrease, with their strong dependence on filling, as does the temperature interval in which the reaction was studied. The activation energy of alcohol dehydrogenation on ZnTe could not be measured because of the rapid poisoning of its surface. However, the rate constant of the reaction on ZnTe, calculated per unit surface area at one and the same temperature (20°), was at least 600 times greater than on ZnSe. The degree of dehydration was low for all catalysts, and the percentage of dehydration decreased on going from ZnO to ZnTe.

Considering the changes in other properties in the series ZnO→ZnTe, one can see that, simultaneously with the increase in catalytic activity, the dielectric constant ε increases, while the difference in electronegativities Δx, calculated according to Pauling (^{17}), and the width of the forbidden band U decrease. ZnO is an exception, with $U = 3.2$ eV, smaller than that of ZnS, which may be associated with its crystallization in the wurtzite lattice instead of the zinc-blende lattice in which the other three compounds crystallize*. Catalysis proceeds in the temperature region where at least three of the binary compounds studied—ZnS, ZnSe, and ZnTe—are in the region of intrinsic conductivity**.

Simultaneously with the increase in dehydrogenating activity, the lattice parameter of the compound ZnS increases; however, this change is opposite in direction to the change which A. M. Rubinshtein, S. G. Kulikov, A. A. Dulov, and N. A. Pribytkova ([18]) postulated for the reaction of alcohol dehydrogenation from the multiplet theory.

Thus, for the binary compounds studied, a simple correlation is observed between the width of the forbidden band and the catalytic activity. It would be desirable to carry out such comparisons for other groups of compounds as well.

In conclusion, we note that the dependence of the catalytic activity of semiconductors on the position, in the periodic system of Mendeleev, of the elements that form them cannot be regarded as completely excluded for the region of impurity conductivity either. For elemental semiconductors with homopolar bonding, the depth of the impurity level ΔE_{imp} is determined by the formula [10]:

$$\Delta E_{\text{imp}} = \frac{13.53}{\varepsilon^2} \cdot \frac{m^*}{m} - \alpha \sqrt[3]{N},$$

where m^* is the effective mass of the electron, N is the impurity concentration, and α is a constant; i.e., at small N, the direction of change of the catalytic properties in a series of compounds with different ε should be the same as in the case of intrinsic conductivity. However, for common homopolar semiconductors the values of ΔE_{imp} prove to be very small, and for semiconductors with a partially ionic character of the bond the applicability of this formula is not entirely clear.

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* Strictly speaking, considerations concerning a regular change in semiconductor properties upon replacement of one of the elements in a compound are applicable only to substances with the same lattice structure.

** According to data ([19]), with an increase in the dispersity of ZnO in the region 0–200°, it also approaches intrinsic conductivity.

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