ON THE QUESTION OF THE DIRECTION OF THE CONTACT OXIDATION REACTION ON SEMICONDUCTOR CATALYSTS

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Abstract

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ON THE QUESTION OF THE DIRECTION OF THE CONTACT OXIDATION REACTION ON SEMICONDUCTOR CATALYSTS

(THE EXAMPLE OF BENZENE OXIDATION)

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In recent years, the work of a number of authors ([1–4]) has shown that the process of vapor-phase oxidation of hydrocarbons by molecular oxygen on semiconductor catalysts proceeds not as a series of consecutive transformations, but as a system of parallel-consecutive reactions.

Until now there have in fact been no attempts to explain theoretically the causes of the different direction of oxidative processes on different semiconductor catalysts. It seems expedient to us to try to explain the phenomena under consideration from the standpoint of the electronic theory of catalysis being developed by one of us ([5–7]). Convenient objects for analyzing the mechanism of the process are the simplest aromatic hydrocarbons (benzene, naphthalene), since for them sharply defined directions are observed in heterogeneously catalytic and homogeneous reactions.

In the vapor-phase contact oxidation of benzene and naphthalene by molecular oxygen on oxides of vanadium, tungsten, molybdenum, and uranium, furan derivatives stable under oxidation conditions are formed in considerable amounts —maleic and, respectively, phthalic anhydrides.

In the oxidation of the same benzene or naphthalene over copper oxide (cupric oxide), it is comparatively easy to oxidize completely the entire hydrocarbon entering the reaction. The oxides of manganese and nickel act similarly.

The difference covers a wide temperature interval, beginning with relatively low temperatures (about 200°) up to 400-600° (the region of impurity conductivity).

Since it is known that V_2O_5, WO_3, MoO_3, UO_3 are, as a rule, electron semiconductors, while CuO, Cu_2O, NiO, and, apparently, MnO_2 are hole semiconductors, it seems probable to relate the catalytic action of the two indicated groups of oxides to their electron or hole nature. The present note is an attempt in this direction.

In the heterogeneous-catalytic oxidation of benzene on copper oxide (copper

gauze), the reaction proceeds to a certain extent analogously to the process of homogeneous oxidation, which follows a chain mechanism with the initial formation of phenyl radicals and rupture of the C–H bond ([8,9]). In this case phenol is found in the reaction products, and a considerable fraction of the benzene is oxidized to carbon oxides. The formation of phenolic products in the oxidation of benzene over copper oxide was noted by E. I. Orlov ([10]). According to the observations of Ya. S. Levin, I. G. Kronich, and one of us, in the oxidation by oxygen on a copper surface of a mixture of benzene with water vapor at a temperature of 660°, 0.3 mol.% phenol, 1.2 mol.% condensed substances containing diphenyl, and 6.4 mol.% carbon oxides are formed.

In the catalytic oxidation of benzene on vanadium catalysts, the main product is maleic anhydride (1,4-dihydrofurandione); 1,4-benzoquinone is formed in much smaller amounts. The difference in direc-

directions of the reaction on the two types of catalysts under consideration is also confirmed by other examples. Naphthalene, when oxidized on vanadium catalysts, is converted with high yields into phthalic anhydride (2,3-phenylene-1,4-dihydrofuranedione), without forming either products of transformations of the naphthyl radical (dinaphthyls) or naphthols. According to Grigor' ev and Borzenko' s data ([11]), resorcinol on copper and copper–chromium catalysts gives tetraoxydiphenyl–the product of recombination of the dioxyphenyl radical –whereas this is not observed over vanadium catalysts.

In accordance with the observations set forth, we consider it possible to put forward certain suppositions concerning the possible mechanism of benzene oxidation on electronic and hole semiconductors, representatives of which may be, respectively, vanadium pentoxide and copper oxide (cuprous oxide).

In doing so, we proceed from the assumption that, upon adsorption of benzene, one of the bonds within the benzene molecule is broken and the valence thus set free is saturated by a free valence of the catalyst. Here there are two and only two possibilities: upon adsorption of the benzene molecule, either a C–H bond or a C–C bond may be broken.

As the adsorbent we shall consider a crystal of the type $M_{mR}r$ (where M is the symbol of a metal, R the symbol of a metalloid), which we shall imagine as built up of ions M^{+p} and R^{-q}, where $pm = rq$. It may be assumed that the majority of semiconductors used as catalysts (oxides, sulfides) have lattices of this type.

Let us first consider adsorption accompanied by rupture of the C–H bond. In this case adsorption leads to dissociation of the benzene molecule into two ions, as shown in Scheme I. We note that Scheme b may be replaced by the equivalent Scheme b'. In the symbols of the electronic theory of catalysis, the mechanism shown in Scheme I may be represented as shown in Scheme II. We have here, as a result of the very act of adsorption, the birth of two unlike valences on the surface of the catalyst ([7]), i.e., the formation of an electron-hole pair; in this case the electron performs the function of a positive valence, and the hole the function of a negative valence. These valences hold the radicals C_6H_5 and H,

which thus reside on the surface in the form of valence-saturated and therefore electrically charged entities.

The adsorption mechanism accompanied by rupture of the C–H bond, shown in Scheme II (or, what is the same, in Scheme I), may occur both on an electronic and on a hole semiconductor. The difference between an electronic and a hole semiconductor appears at the next stage. This stage is the interaction of the surface compounds that have formed with the wandering free valences of the catalyst. This is shown in Scheme III, in which *a* refers to the case of an electronic semiconductor, and *b* to the case of a hole semiconductor. Thus (and this is essential), the surface electrically neutral radical shown in Scheme III *b* in the dashed frame is formed on hole semiconductors and can practically not be formed on semiconductors of the electronic type.

Let us now consider the adsorption of a benzene molecule accompanied not by rupture of the C–H bond, but by rupture of the C–C bond. The mechanism of such adsorption in the symbols of electronic theory is shown in scheme IV. Here too, as in the preceding case, the act of adsorption leads to the appearance of positive and negative valences on the catalyst surface, the negative valence (hole) remaining free, while the positive valence (electron) binds to the benzene molecule, holds it on the surface, and thereby converts it into a surface electrically charged radical (ion-radical), as shown in scheme IV. Indeed, the C–C bond in the benzene molecule is effected by two paired electrons. This bond can be broken by an electron of the lattice (a positive valence of the catalyst), which replaces the electron of one of the C atoms and thus pairs with the electron of the other C atom. As a result, instead of a bond between two C atoms, we obtain a bond of one of the C atoms with the lattice; the benzene molecule thereby acquires a free valence. Such a mechanism of adsorption with rupture of a C–C bond also occurs both on electron and on hole semiconductors. However, on a hole semiconductor the ion-radical formed is unstable. As a result of interaction with a free negative valence of the catalyst (i.e., with a free hole), such an ion-radical is again desorbed in the form of an electrically neutral benzene molecule, as shown in scheme V*a*. In the case of an electron semiconductor, however, such a surface ion-radical proves stable. Interaction with a free valence of the catalyst leads in this case (see V*b*) not to desorption of the ion-radical, but to annihilation of two unlike free valences of the catalyst.

Thus, the surface ion-radical shown in scheme V*b* within the dotted frame is formed practically only on electron, and not on hole, semiconductors. Radicals of two different types, shown within dotted frames in schemes III*b* and V*b*, carry the reaction in two different directions and, thus, the direction of the reaction is determined by the electronic nature of the catalyst.

The phenyl radicals formed on the surface of a hole semiconductor (scheme III*b*) can enter into all reactions into which they enter in homogeneous reactions ([8]). In this case, along with products of complete oxidation, phenols, diphenyl, and other condensation products observed in actuality are formed.

The sequence of transformations of the ion-radical formed on electron semiconductors (scheme V*b*) is less clear, since up to now no intermediate products have been isolated in the reaction chain leading

to the formation of maleic anhydride. As indicated by one of us (8), in the first stage the formation of dihydrohydroxybenzene containing a furan ring, shown in Scheme VI, appears very probable.

Scheme VI.

Further oxidation of this compound to maleic anhydride should proceed quite smoothly (12, 13).

The hypothetical mechanism considered by us here is, of course, highly schematic. It merely indicates paths toward understanding the action of electron and hole semiconductor catalysts in the oxidation reaction of benzene.

The notion that on electron-type semiconductor catalysts oxidation proceeds through addition of an oxygen atom at a double bond, whereas on hole-type catalysts it proceeds through cleavage of the C—H bond, can explain certain facts from the practice of catalytic oxidation of hydrocarbons. For example, the ease, observed by Brenton on V_2O_5 (14), of oxidizing butadiene to maleic anhydride as compared with butane becomes understandable from Scheme VII, which is impossible for butane. Also understandable are

Scheme VII.

the oxidation of propylene to acrolein over a selenium-poisoned copper catalyst (15), the formation of benzaldehyde in the oxidation of toluene on copper (10), and the poor yield of phthalic anhydride in the oxidation of *o*-xylene on vanadium catalysts (8).

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