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CATALYSIS ON ORGANIC SEMICONDUCTORS OBTAINED FROM POLYACRYLONITRILE BY ITS THERMAL TREATMENT

Until recently, only inorganic substances were used as solid catalysts in industry and in laboratory practice. In contrast to this, enzymatic catalysis, with its very high rates and selectivity of processes, is based on organic microheterogeneous catalysts. In recent years, outstanding catalytic properties have been found in organic ion-exchange resins with respect to a number of acid–base reactions.

The search for organic solid catalysts for reactions of the redox type was begun comparatively long ago. As is known, good catalysts for reactions of this type are metals and inorganic semiconductors (⌒1). Therefore, one could also expect a noticeable catalytic activity with respect to reactions of the oxidation–reduction type from organic semiconductors. However, in the few known studies ($^{2-}$4) of the catalysis of redox reactions in the liquid phase in the presence of such solid organic substances with semiconductor properties as phthalocyanine and its complexes with certain metals, only comparatively weak catalytic effects were observed. Concerning the catalytic activity of organic semiconductors with respect to vapor- and gas-phase redox reactions, only the work of Tamaru and Shimada (⌒5) is known; they established the absence of catalytic activity of violanthrone with respect to the reactions of H_2–I_2 exchange and the formation of HI from H_2 and D_2.

The reason for the absence of strong effects in the cases studied should probably be sought in the very low electrical conductivity and the large band gap of the organic substances used (⌒6). Recently, new polymeric organic materials with semiconductor properties have been obtained which, owing to the presence in their structure of polyatomic chains with delocalized π-electrons, possess a small band gap and considerable electrical conductivity at room temperature ($^{7-}$9, ⌒12). As has already been noted in the literature (⌒10, ⌒11), according to modern views on the mechanism of catalysis, it is natural to expect high catalytic activity in such semiconductor organic materials with respect to reactions of the oxidation–reduction type. Confirmation of this point of view can so far be provided only by data on the catalytic activity of thermally treated polyacrylonitrile and polyaminoquinone with respect to the decomposition of hydrogen peroxide, obtained by A. V. Topchiev, M. A. Geiderikh, and others (⌒7), and by

A. A. Berlin, L. A. Blumenfeld, and N. N. Semenov (⁀11). The qualitative character of these data, as well as the high sensitivity of hydrogen peroxide to the catalytic action of a wide variety of solid bodies, do not make it possible to connect unambiguously the catalytic activity found with the outstanding electronic properties of the indicated polymeric organic substances. In this connection, it seemed essential to investigate the catalytic activity of polymeric semiconductors with a system of conjugated bonds with respect to a number of vapor- and gas-phase redox reactions.

type. The semiconductor materials prepared from polyacrylonitrile were chosen as the object of the present investigation. Data on the methods of preparing semiconductors of this type and on their electrical properties are contained in papers (7, 12).

Table 1

Results of experiments on the decomposition of formic acid over PAN-1 and PAN-2

Experiment No.	Temp., °C	Rate of formation of gaseous products, ml/h	Ratio H_2 : CO	Rate of formic-acid feed, g cat.$^{-1}$ h^{-1}
PAN-1				
3—1	242	153	2.8	0.02
3—2	255	265	2.8	0.02
3—3	272	494	2.8	0.02
PAN-2				
6—1	260	66	3.2	0.3
6—2	287	232	3.2	0.3
6—3	299	402	3.2	0.3
6—4	261	86	3.2	0.3
7—1	264	114	3.6	0.3
7—2	288	302	3.6	0.3
7—3	304	554	3.6	0.3
8—1	290	336	–	0.3

We tested the catalytic activity of two different samples of thermally treated polyacrylonitrile. The first sample (PAN-1) was polyacrylonitrile into which 0.01% $CuCl_2$ had been introduced before thermal treatment. The specific surface area of this sample, measured by the volumetric method with krypton, was 0.06 m^2/g. The other sample (PAN-2) contained no copper, and its specific surface area was 0.4 m^2/g.

The catalytic activity of the indicated samples with respect to the decomposition of alcohols, formic acid, and hydrazine hydrate was tested in an apparatus essentially similar to the apparatus of Schwab and Theophilides (13). Experiments on ethylene hydrogenation were carried out in a circulating apparatus at a pressure somewhat below atmospheric. Before testing catalytic activity, PAN-1 and PAN-2 were subjected to 1–3 h conditioning at temperatures up to 450°. Significant catalytic activity in PAN-1 and PAN-2 was found only with respect to the reaction of decomposition of formic acid.* The corresponding data are given in Table 1.

On PAN-1, a noticeable rate of decomposition of formic acid is observed already at 240°. PAN-2 is distinguished by somewhat lower catalytic activity. At similar values of the total surface area of PAN-1 and PAN-2 in parallel experiments (0.186 and 0.135 m^2, respectively), the catalytic activity of PAN-2 reaches the same values as that of PAN-1 at temperatures 20–25° higher. The indicated relationship of the activities of PAN-1 and PAN-2 in the temperature interval 242–299° is fairly well conveyed by the values of the rates of decomposition of formic acid, referred to unit surface area of the catalyst, given in Table 2.

Table 2

Rates of decomposition of formic acid over PAN-1 and PAN-2, referred to unit surface area of the catalyst

PAN-1 Temp., °C	PAN-1 Rate of acid decomposition, $mmol/sec \cdot m^2 \cdot 10^2$	PAN-2 Temp., °C	PAN-2 Rate of acid decomposition, $mmol/sec \cdot m^2 \cdot 10^2$
242	0.58	261	0.44
255	1.0	287	1.2
272	1.9	299	2.1

It is significant that on both PAN-1 and PAN-2, as also on many inorganic semiconductors, the principal direction of decomposition is dehydrogenation of formic acid. In the initial period of their operation, the PAN samples increased their catalytic activity from experiment to experiment. For PAN-2 the stationary state of the surface was attained only after four experiments had been carried out.

Since the change in the rate of decomposition of formic acid with increasing the temperature was determined by us in a single continuous experiment with a stepwise increase in temperature, a constant rate of acid feed into the reactor, and comparatively small degrees of conversion (from 1 to 10%), then the activation energy of the reaction studied can be determined from the dependence

* An 85% aqueous solution of formic acid (chemically pure) was used in the work.

Fig. 1. Dependence of the rate of decomposition of formic acid over PAN-1 and PAN-2 on temperature: a—experiment 3, b—experiment 7, c—experiment 6. v—mmol/hour · m^2

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of the logarithm of the rate of acid decomposition on the reciprocal absolute temperature. Figure 1 presents the corresponding plots, constructed from the data of experiments 3, 6, and 7. The activation energies calculated from these plots are, for PAN-1 and PAN-2, respectively, 21 and 25 kcal. It should be noted that the observed increase in the activity of PAN-1 and PAN-2 from experiment to experiment has little effect on the activation energies. Thus, in experiments 6 and 7 with PAN-2, the activation energy of the process remained practically unchanged.

Fig. 1. Dependence of the rate of decomposition of formic acid over PAN-1 and PAN-2 on temperature:
a—experiment 3, *b*—experiment 7, *c*—experiment 6.
v—mmol/hour · m^2

From the results obtained it follows that, in the temperature interval studied, PAN-1 and PAN-2 exhibit catalytic activity of the same order of magnitude as the catalytic activity of a number of metallic and inorganic semiconductor catalysts for this reaction ([14]).

The considerable catalytic effect observed in the case of PAN-2 permits the conclusion that, also in the case of PAN-1, the presence of copper in it is not of decisive importance in the manifestation of catalytic activity by this PAN sample*. PAN-1 and PAN-2 also exert a catalytic action on the decomposition reaction of hydrazine hydrate in the direction of the formation of ammonia and nitrogen. However, noticeable catalytic decomposition of hydrazine hydrate takes place at comparatively high temperatures (250°), at which the reaction on the glass surface of the reactor and homogeneous decomposition play a substantial role.

The significant catalytic activity of the PAN samples studied with respect to the decomposition reaction of formic acid is apparently connected with the chemical structure of the polymer. There are grounds for assuming that the nitrogen atoms in the chain of conjugated double bonds of the polymer may be adsorption centers for acid molecules. It may also be considered that, through directed modification of the chemical and electrophysical properties of polymers with a system of conjugated double bonds, highly selective organic catalysts for oxidation-reduction reactions may be obtained.

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