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Figure 1

Figure 1: Figure 1

Abstract

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γ-RADIOLYSIS OF *n*-HEPTANE ADSORBED ON OXIDE CATALYSTS

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The aim of the present work was to investigate the features of the radiolysis of *n*-alkanes in the adsorbed state, using *n*-heptane as an example, the homogeneous radiolysis of which had previously been studied in detail ([1–3]).

Kinetic investigations of this type were first carried out by L. V. Pisarzhevskii as early as 1936 ([4]). In 1959 Allen and co-workers investigated the radiolysis of *n*-heptane in the adsorbed state in the region of surface coverage $\theta < 1$. They found that, with increasing θ, the yield

Fig. 1. Dependence of the increase in gas pressure, referred to 1 g of heptane, on the ratio of electron fractions catalyst : heptane (β)—for catalyst II

Table 1

Data on the catalysts used in the work

Catalyst	Composition, wt. %	Bulk density, g/cm^3	mM of heptane in a monolayer per 1 g of catalyst
I	Al_2O_3 100	0.525	0.650
II	Al_2O_3 90Cr_2O_3 8K_2O 2	0.846	0.526
III	Al_2O_3 87MoO_3 10basic sulfates 3	0.836	0.881
IV	Al_2O_3 79MoO_3 15.5CoO 5.5	0.721	0.678

(H_2+CH_4) increases by a factor of 2–4. It was concluded that a redistribution of the absorbed radiation energy takes place between the solid substance and the adsorbed hydrocarbon. It was assumed that the energy transfer is connected with the migration of free electrons or holes (^{5}).

In our work, γ-radiolysis of n-heptane was carried out on the following catalysts: aluminum oxide (I); aluminochromium catalyst promoted with potassium oxide (II); aluminomolybdenum catalyst (III); and cobalt-aluminomolybdenum catalyst (IV). The necessary data on these catalysts are given in Table 1.

Preparation of the samples was carried out according to the procedure described in (^{6}); the study of the kinetics—in the same way as in (^{7}). The kinetics of radiolysis of n-heptane on catalyst (II) was studied at $\theta \leq 1$, and also under multilayer adsorption. In all other cases the work was carried out at monomolecular surface coverage ($\theta = 1$). Let us note that heptane adsorption occurred at $t \sim 10°$ and was reversible. Owing to this, and also because the heats of adsorption differ little from the heat of condensation of heptane, chemisorption, in its usual sense, does not occur in our case.

Figure 1 presents the dependence of the increase in gas pressure (ΔP), referred to 1 g of heptane, on the ratio of electron fractions catalyst/heptane for catalyst II. The reproducibility of the results was good, and the error in determining ΔP shown in Fig. 1 is small.

Table 2

Values of ΔP_{rel} and Z for various catalysts

Catalyst	$\varepsilon \cdot \frac{k_1}{k_4} \cdot 10^2$	$\Delta P_{\text{rel}} \cdot (W_s/W_s')$	Z
Homogeneous system		1.0	
I	3.5	12.7	0.41
II	3.24	2.0	0.032
III	3.36	1.7	0.026
IV	2.42	3.6	0.073

The break point in Fig. 1 corresponds to monolayer coverage. This curve can evidently be used to determine the specific surface area of catalysts.

Table 2 gives the values of ΔP_{rel} for monomolecular coverage on various catalysts. The value of ΔP for homogeneous radiolysis was taken as unity.

Figure 2 presents a kinetic curve, typical for all the catalysts studied, for the radiolysis of heptane on catalyst (I); the curve is a continuous recording of $\Delta P = f(t)$ with an EPP-09 recorder. The presence of nonlinearity at the beginning of the curve is noteworthy. In experiments in which adsorption was carried out on pre-irradiated catalysts, the yield of gaseous radiolysis products

Fig. 2. Kinetic curve of heptane radiolysis on catalyst I

Figure 2: Fig. 2. Kinetic curve of heptane radiolysis on catalyst I

decreased substantially. Thus, for example, the values of ΔP_{rel} on catalyst (I) are respectively 12.7 and 5.1, and on catalyst (II) respectively 2.0 and 0.27*.

Fig. 2. Kinetic curve of heptane radiolysis on catalyst I

In connection with the experimental data presented above, we shall make the following observations.

The presence of a linear dependence of the radiolysis yield (ΔP) on the ratio of electron fractions catalyst/heptane in the range of values of this ratio from a monomolecular layer to the homogeneous system corresponds to the fact that transfer of energy from the catalyst occurs only in the monolayer and does not take place for any subsequent layer, in which the rate of radiolysis is equal to the rate of the homogeneous process. The fact that in the region $\theta < 1$ the yield increases with filling shows that the probability of energy transfer from the solid to the substance adsorbed on its surface is linearly related to the degree of filling.

The effect of catalytic action depends substantially on the nature of the catalyst. It is of interest to compare the data of the present work with the results of our earlier study of the EPR spectra of these systems ([6]). It turns out that the most active catalyst is the one whose irradiation together with the adsorbed hydrocarbon does not change the form of the EPR spectrum in comparison with the spectrum of the irradiated catalyst. The greater the changes in the EPR spectrum (I < IV < II < III), the less active the catalyst is in the experiment under consideration (see Table 2). Measurements of the electrical conductivity of the catalyst also established a parallelism between changes in electrical conductivity and in the intensity of the EPR signal.

The presence of nonlinearity in the initial section (Fig. 2) and the substantial decrease in the rate of radiolysis on surfaces irradiated beforehand may be connected with the formation in the solid of certain acceptors (of excitation or charge). From the already mentioned experimental data on EPR spectra, it is known that saturation of the intrinsic signal of the cata—

···of the catalyst occurs at doses of less than 6 Mr; from the data of Kitaigorodskii ([8]), which can be interpreted in an analogous way, it follows that the dose for saturation of defects in a molecular crystal of *n*-dichlorobenzene is no more than 0.5 Mr.

It should be noted that the rate of radiolysis on preliminarily irradiated (I)

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* All the data given here and above on pressure increase were obtained in experiments lasting 1 hour, i.e., already beyond the nonlinear region. Preliminary irradiation of catalyst (I) was carried out for 0.5 hour, and of catalyst (II) for 1 hour.

remains higher than the rate of homogeneous radiolysis, whereas on (II) it becomes lower than the rate of homogeneous radiolysis. Catalyst (I) in ordinary thermocatalytic reactions increases its activity after irradiation ([9]), while some oxides (for example, ZnO) decrease it ([10,11]). Apparently, for the radiation sensitivity of a catalyst as well, impurities play an essential role; in one form or another they can capture excitation. Under γ-irradiation of the catalyst its elemental composition does not change. Therefore it is possible to draw the highly plausible conclusion that the probability of energy transfer from the catalyst to the adsorbed substance depends on the amount of impurities. Since the increase in the radiolysis yield of heptane is due to the additional absorption by it of energy over and above that absorbed directly (as if homogeneously), this energy can come only from the solid, in which the absorption of radiation energy under the conditions of our experiments is two to three orders of magnitude greater. It is therefore necessary to assume that the wave functions of the electrons of the adsorbed molecules and of the adsorbent lattice overlap to some extent, and that the bonding forces holding the molecules are at least partly due to exchange interaction.

We also observed a strong dependence of the saturation dose and of the form of the initial part of the kinetic curve on the catalyst training regime. The dependence of the radiation sensitivity of a catalyst on the training regime was observed earlier in work ([9]). Depending on the nature of the impurities, they can both increase and decrease the radiation sensitivity of catalysts.

To estimate the probability of energy transfer from the catalyst to the adsorbed substance, let us use the following formal-kinetic scheme. We shall take into account the processes: 1. $X_{\text{ads}} \rightsquigarrow X^*$ (direct absorption of radiation by the adsorbed substance); 2. $X^* \to X$ (any deactivation processes except a chemical reaction); 3. $X^* \to$ products (chemical reaction); 4. catalyst $\rightsquigarrow$ catalyst* (absorption of radiation by the catalyst); 5. catalyst$^* \to$ catalyst (any processes of loss of absorbed energy except transfer to the adsorbed substance); 6. catalyst$^* + X_{\text{ads}} \to$ catalyst $+ X^*_{\text{ads}}$ (energy transfer to the adsorbed substance).

The rates of these processes are respectively:

$$W_1 = k_1' I\theta; \qquad W_2 = k_2[X^*]; \qquad W_3 = k_3[X^*]; \qquad W_4 = k_4' I;$$

$$W_5 = k_5[D] \quad \text{and} \quad W_6 = k_6[D]\theta,$$

where $[D]$ is the concentration of elementary excitations in the solid.

$$[D] = \frac{k_4' I}{k_5 + k_6\theta} \quad \text{and} \quad W_6 = k_6\theta\frac{k_4' I}{k_5 + k_6\theta},$$

$$[X^*] = \frac{k_1' I\theta + k_6\theta \dfrac{k_4' I}{k_5 + k_6\theta}}{k_2 + k_3},$$

whence

$$W_3 = \frac{k_3 I\theta}{k_2 + k_3}\left(k_1' + \frac{k_4' k_6}{k_5 + k_6\theta}\right).$$

Neglecting the difference in the binding energies of molecules located in the bulk and on the surface (see below), we write for the rate of homogeneous···

of radiolysis the expression

$$W_3' = \frac{k_1' k_3 I}{k_2 + k_3}.$$

For $\theta = 1$ we have

$$W_3/W_3' = 1 + \frac{1}{\varepsilon \dfrac{k_1}{k_4}\left(\dfrac{k_5}{k_6} + 1\right)},$$

where ε is the ratio of the amounts of radiation energy absorbed in 1 cm^3 of heptane and of catalyst.

In the last equation W_3/W_3' is determined experimentally. The value of ε was determined (at known intensity) by calculation, taking into account the densities and effective atomic numbers (according to ^{12}) of heptane and catalyst. $k_1/k_4 \cong 1$, since in both cases we are interested only in excitations whose energy is not less than the bond-breaking energy. Then it becomes possible to estimate the value of k_5/k_6 and, correspondingly, the probability of useful redistribution of energy

$$Z = \frac{k_6}{k_5 + k_6}.$$

The calculated values of Z are given in Table 2.

The accuracy of the estimate of Z depends on the accuracy of determining W_3/W_3', which experimentally is ±5%.

It should be noted that the obtained values of Z are somewhat overestimated because of the small difference in the bond energies of molecules located in the bulk and on the surface. However, the heats of sorption of paraffins on these catalysts constitute only a small fraction of the bond energy; we were unable to note any correlation between the values of the heats of adsorption and the radiation activity. Therefore it may be assumed that our estimate of Z is quite acceptable.

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CITED LITERATURE

1. H. A. Dewhurst, J. Phys. Chem., **61**, 1466 (1958).
2. A. M. Brodskii, Yu. A. Kolbanovskii et al., DAN, **122**, 1035 (1958).
3. V. G. Berezkin, I. M. Kustanovich et al., DAN, **131**, 593 (1960).
4. L. V. Pisarzhevskii, *Selected Works in the Field of Catalysis*, Kiev, 1955, p. 133.
5. G. W. Sutherland, A. C. Allen, Radiolysis in the adsorbed State, Conf. Appl. of large radiat. Sources in Industry, Warsaw, 1959.
6. Yu. A. Kolbanovskii, I. M. Kustanovich et al., DAN, **129**, 145 (1959).
7. A. M. Brodsky et al., Intern. J. Appl. Rad., No. 5, 57 (1959).
8. A. I. Kitaygorodskii, E. I. Fedin, DAN, **130**, 1005 (1960).
9. E. H. Taylor, H. W. Kohn, J. Phys. Chem. **63**, 500 (1959).
10. E. H. Taylor, H. W. Kohn, J. Am. Chem. Soc., **79**, 252 (1957).
11. E. H. Taylor, J. A., Wethington, J. Am. Chem. Soc., **76**, 971 (1954).
12. M. Day, G. Stein, *Collection: Radiation Chemistry*, IL, 1953, p. 235.

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