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Abstract

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Radiation-Catalytic Conversion of Methanol

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In our previous studies (^1, ^2) it was established that, under the combined action of ionizing radiation and solids with different electronic properties, oxides of the dielectric type–SiO_2, Al_2O_3, and aluminosilicate–showed the greatest activity with respect to the conversion of cyclohexane in the adsorbed layer. On these same catalysts, the appearance of paramagnetic centers and adsorbed radicals was recorded by the EPR method. By contrast, semiconductors and metals active in ordinary catalytic processes (NiO, ZnO, Ni) not only did not possess radiation-catalytic activity, but even inhibited the radiolysis of cyclohexane. In this case, no appearance of paramagnetic centers or adsorbed radicals was detected. The data obtained made it possible to suggest a possible electron-radical mechanism for the radiation-catalytic process of cyclohexane conversion on solids of the dielectric type.

It is of interest to test the generality of the established regularities using other radiation-catalytic processes as examples. For this purpose, the reaction of radiation decomposition of methanol in the adsorbed layer was chosen.

The regularities of the radiolysis of liquid methanol have been studied fairly well. It was shown (^3, ^4) that radiolysis produces hydrogen, formaldehyde, ethylene glycol, methane, and carbon monoxide. The radiation yield of hydrogen, amounting to 4-5.3 H_2 molecules/100 eV, was approximately equal to the sum of the radiation-chemical yields of formaldehyde and ethylene glycol. A high sensitivity of homogeneous radiolysis to impurities of halide ions (^4) was also established, and assumptions were made concerning the significant role of radical reactions in this process (^5). As the solid catalysts under study, as in the previous investigations (^1, ^2), we selected oxides of the insulator type (SiO_2, Al_2O_3, aluminosilicate), semiconductors with low conductivity (MgO, ZrO_2), semiconductors with appreciable conductivity (ZnO, NiO), and some metals in dispersed form (Pd, Pt). A sample of activated carbon was also tested. The magnitude of the specific surface area of the compounds studied was determined from the adsorption of methanol and cyclohexane at $t = 18^\circ$ by the BET method.

Samples of the solid compounds were first evacuated in glass ampoules at 400° until a vacuum of 10^{-5} mm Hg was reached, followed by cooling to room temperature. Vapors of carefully purified and degassed methanol were admitted

to the samples thus prepared until the surface was filled to 50-55%; then the ampoules were sealed and irradiated with γ-radiation from Co⁀60 for various periods of time at room temperature. The dose rate in most experiments was $4.3 \cdot 10^{16}$ eV/g • sec. The absorbed-energy doses varied from $8.2 \cdot 10^{19}$ to $7 \cdot 10^{21}$ eV/g.

After irradiation, the ampoules were connected to the apparatus by means of a special ground-glass joint. The drawn-out end of the ampoule was broken off in a va—

the cuvette, and the noncondensing products formed passed through a trap cooled with liquid nitrogen into the measuring part of the apparatus. They were then analyzed for hydrogen content by passage through a heated palladium capillary; the gas that did not pass through the capillary was analyzed for carbon monoxide content by absorption with previously conditioned hopcalite. The amount of methane was deter-

Table 1

Summary of data on the radiation-catalytic conversion of methanol in the adsorbed layer at $t = 20°$

Catalyst	S, m^2/g	G, mol/100 eV H_2	mol/100 eV CH_2O	mol/100 eV $(CH_2OH)_2$	mol/100 eV CO	mol/100 eV CH_4
SiO_2	270	67	30	28	1.5	3.1
Al_2O_3	300	65.5	26.6	37.7	0.8	3.0
SiO_2 • Al_2O_3	170	45.5	30.1	21.8	0.45	4.0
ZrO_2	270	14.6	11.8	22	0.36	3.4
ZnO	14	10.1	4.35	4.0	—	—
MgO	100	4.9	2.4	3.3	—	0.6
NiO	50	1.8	—	—	—	—
Pd	29	—	2.5	1.5	—	—
Pt	40	—	1.6	2.5	—	—
Activated carbon	800	0.1	0.5	0.4	0.04	0.2
Homogeneous radiolysis	—	5.1	1.6	3.9	0.1	0.29

mined from the residual gas pressure. The catalyst with the adsorbed reaction products was treated with water, first by washing and then by boiling with a reflux condenser. The formaldehyde formed during the decomposition of methanol was determined quantitatively by means of the color reaction with chromotropic acid according to the MacFadyen method ([6]). The determinations were carried out on an FEK-M photoelectrocolorimeter. Ethylene glycol

Fig. 1. EPR spectra of radicals formed upon irradiation of methyl alcohol in the adsorbed state.

Figure 1: Fig. 1. EPR spectra of radicals formed upon irradiation of methyl alcohol in the adsorbed state.

was oxidized to formaldehyde with periodic acid, with subsequent reduction of the iodates and periodates formed to iodides by an excess of stannous chloride in order to decolorize the solution; the formaldehyde was then determined in the oxidized mixture by the reaction with chromotropic acid.

In parallel with the catalytic experiments, experiments were carried out to study EPR spectra. The conditions for preparing the samples were the same. Samples with adsorbed methanol were irradiated in a γ-installation at the temperature of liquid nitrogen. The dose of absorbed energy was $0.6–1.2 \cdot 10^{20}$ eV/g. After irradiation, the EPR spectra were also recorded at the temperature of liquid nitrogen on an EPR-2 spectrometer of the Institute of Chemical Physics.

It was established that in the products of the radiation-catalytic decomposition of methanol, mainly hydrogen, formaldehyde, and ethylene glycol were detected, with a small content of carbon monoxide and methane. Consequently, the products of heterogeneous radiolysis were identical to the products of homogeneous radiolysis.

Table 1 gives a summary of data on the radiation-catalytic action of the solid bodies studied. In calculating the radiation-chemical yield (G), it was assumed that methanol was completely adsorbed on the surface of the catalyst during irradiation and that the energy was absorbed by the adsorbed methanol and the solid body in proportion to their electron fractions.

As follows from the data of Table 1, the greatest radiation catalytic activity, as in the case of heterogeneous radiolysis of cyclohexane, was exhibited by oxide insulators: SiO_2, Al_2O_3, and aluminosilicate. The radiation-chemical yield and the rate of formation of hydrogen, formaldehyde, and ethylene-

glycol on various silica-gel samples exceeded those for the homogeneous radiolysis process by more than a factor of ten.

The amounts of hydrogen, formaldehyde, and ethylene glycol formed on insulating oxides increased linearly with increasing dose of absorbed energy up to $3–4 \cdot 10^{20}$ eV/g. Oxides with semiconductor properties are characterized by a comparatively low radiation-catalytic activity. Thus, the radiation-chemical yield and the rate of formation

Fig. 1. EPR spectra of radicals formed upon irradiation of methyl alcohol in the adsorbed state. a—on SiO_2, recorded at $t = -196°$; 1—corresponds to the radical $CH{\cdot}O$, 2—CH_2OH, 3—CH_3; b—spectrum of CH_2OH radicals on Al_2O_3 at $t = -196°$; v—spectrum of CH_2HH radicals adsorbed on SiO_2 at $t = 20°$.

of hydrogen on ZnO are only 2–3 times greater than those for homogeneous radiolysis. Metals changed the radiation-chemical yield of formaldehyde and ethylene glycol only insignificantly in comparison with the yields of homogeneous radiolysis. The reduced yield of hydrogen may possibly be due to its adsorption on the metal surface.

Activated carbon led to inhibition of the radiation transformation of methanol. The yields of formaldehyde and ethylene glycol were lower than in the case of the homogeneous process. Hydrogen was evidently adsorbed to a considerable extent by the surface of the carbon.

In the EPR spectrum of silica gel with methyl alcohol adsorbed on its surface, a triplet with a splitting of 20 Oe is observed, which may be assigned to the radical CH_2OH ([7]). In addition, in somewhat lower concentrations there are radicals $CH{\cdot}O$ (an asymmetric doublet with a splitting of 69 Oe ([8])) and very weak lines from adsorbed methyl radicals are observed (Fig. 1). EPR spectra of adsorbed CH_2OH radicals were also observed on aluminum oxide (Fig. 1*b*). After irradiation of zinc oxide with adsorbed methyl alcohol, the intensity of the EPR signals was much lower.

In this case, only one triplet with a splitting of 19 Oe is observed in the spectrum. In irradiated samples of nickel oxide, EPR signals were practically absent.

It is interesting to note the great thermal stability of the adsorbed CH_2OH radicals. Signals from these radicals in the case of silica gel and aluminum oxide were observed even at room temperature. Earlier, in work ([9]), we showed that hydrogen atoms and alkyl radicals adsorbed on the surfaces of silica gel and aluminum oxide recombine at a temperature far below room temperature. The considerably higher thermal stability of the adsorbed radicals

CH_2OH is possibly associated with the formation of a hydrogen bond during their adsorption on hydroxyl groups of the adsorbent surface.

Adsorbed free radicals may be intermediate products of heterogeneous radiolysis. This follows from the fact that their concentration is maximal in the case of the most radiation-active catalysts, SiO_2 and Al_2O_3. It is easy to imagine the formation of the main products of the radiation-catalytic decomposition of methanol as a result of reactions between radicals and between radicals and alcohol molecules. Thus, for example, the formation of ethylene glycol may occur as a result of the recombination of two CH_2OH radicals

$$2CH_2OH \rightarrow CH_2OH—CH_2OH.$$

Similarly, the formation of methane can also be explained by the reaction of methyl radicals with alcohol,

$$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH.$$

Naturally, the establishment of a detailed mechanism of heterogeneous radiolysis requires additional investigations.

As follows from the data presented, the formation of adsorbed radicals and the intense course of the radiation-catalytic decomposition of methanol are observed predominantly on oxides of the insulator type. On semiconductor oxides, methanol radiolysis proceeds to a considerably lesser extent. The effect of metals on this process is apparently insignificant.

These results confirm the previously established regularity concerning the relation between the radiation-catalytic activity of solids and their electronic properties.

The substantial increase in the radiation-chemical yields of hydrogen, formaldehyde, and ethylene glycol during the decomposition of methanol on silica gel, alumina, and aluminosilicate is evidently closely connected with the processes of transfer of the energy of ionizing radiation absorbed by these solids to molecules adsorbed on the surface.

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