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On the Relative Importance of the Bulk and Surface of a Dielectric in Radiation–Catalytic Processes

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The contribution from bulk and surface to radiation-catalytic conversion of methanol was studied for a set of samples of two dielectrics: silica gel and aluminum oxide. It was found that the extent of methanol conversion for the same amount adsorbed and for the same dose of energy taken up depends neither on the specific surface, nor on its coverage or sizes of the adsorbent globules, but is a function only of the relationship between the amount of adsorbed substance and the number of excess charge carriers formed in the bulk of the solid. The diffusion of charge carriers under the action of ionizing radiation does not interfere with the radiation-catalytic process and adsorbed molecules act only as effective surface traps (holes) for charge carriers. This conclusion is consistent with the concept that practically all excess charge carriers formed in the bulk of the dielectric take part in the radiation chemical process occurring on its surface.

Much research has been carried out lately on the radiation catalysis or heterogeneous radiolysis of various compounds adsorbed on solids. This research comprises both radiation chemistry and heterogeneous catalysis and makes use of methods and concepts related to both.

Investigation of radiation-catalytic processes may be of interest from the standpoint of finding out the effect of electronic factors on the catalytic properties of solids and establishing the contribution of the catalyst to energy transfer.

Radiation-catalytic processes occurring at low temperatures involve transfer of the ionizing radiation energy absorbed by the solid to the reacting molecules at the surface. The fact of energy transfer was established experimentally. It was found that the radiation chemical yields in the radiolysis of molecules adsorbed on certain solids, such as silica gel, aluminum oxide, and zeolites, calculated with respect to the energy taken up by the adsorbed species, are considerably higher than those for homogeneous radiolysis of the same species (*1–8*).

The authors, together with Kazanskii and Pariiskii (*1–3*), have found that the activity of radiation catalysts and, thus, their capacity for transferring the absorbed energy, increases with the width of the forbidden band. A scheme of this process developing via electron and radical steps was considered for radiation-catalytic decomposition of methanol. It will be noted that the conclusion on the contribution from the forbidden zone to radiation-catalytic activity of solids was confirmed later by Rabe, Rabe, and Allen (*9*) for decomposition of azoethane absorbed on various oxides.

Various schemes based on the concepts of excess free and or localized carriers of the electric charge were suggested for the mechanisms of heterogeneous radiolysis of heptane (*4*, *5*), ispropylbenzene (*6*), ammonia (*7*), and carbon dioxide (*8*).

Thus the concept of radiation energy transfer through excess carriers of the electric charges arising in solids seems to be most widespread and sufficiently justifiable.

One of the promising approaches to elucidating the mechanism of energy transfer would be an investigation of the relative importance of bulk and surface for solid dielectrics that are effective in energy transfer.

TECHNIQUE

This would require solid samples of the same chemical composition, but a markedly different volume-to-surface ratio. Hydrothermal treatment is a technique making possible the production of such samples (*10, 11*). The technique of hydrothermal preparation permits obtaining silica gel samples with different sizes of globular particles and of pores at the same chemical composition of the surface. The silica hydrogel was obtained by the standard technique from solutions of liquid glass and sulfuric acid. Salts were washed off the hydrogel and the latter in quartz ampoules was placed into an autoclave and kept there at a fixed temperature under relevant water vapor pressure. The sizes of silica gel globular particles, the surface area, and the porosity were a function of the temperature and of residence time. The maximum temperature was 350°C. Silica gel samples different in globule sizes and in specific surface were prepared from silica hydrogel making use of this technique. The globule diameter D was calculated from the silica gel taking into account the globular structure of silica gel, making use of expression

$$D = 6/S\gamma$$

where $\gamma = 2.2\ \mathrm{g/cm^3}$ is the silica gel specific weight, and S is the specific surface.

The chemical nature of silica gels obtained in this way was the same for all samples. The number of silanol groups at the surface was equal and amounted to 10 μmole/g. In one of the samples the hydroxyl group hydrogen was replaced by calcium ions by means of cation exchange.

The aluminum oxide samples were prepared by standard calcination of aluminum hydroxide at various temperatures and times of calcination. The samples obtained were of a different specific surface and phase content.

The specific surfaces (S) of silica gel and aluminum oxide samples were determined at a temperature of 20°C by the BET technique using purified methanol as adsorbate.

Decomposition of methanol yielding three main products—formaldehyde, ethylene glycol, and hydrogen—was the reaction investigated.

Investigation was made of the radiation-catalytic activity of both oxides with respect to methanol in the adsorption layer (*3*). Each solid sample was placed in an ampoule sealed to the vacuum apparatus and treated at 450°C up to a vacuum of 10^{-5} mm Hg with subsequent cooling to room temperature. A fixed quantity of methanol vapor corresponding to the coverage required was admitted to the sample. Then the ampoule was sealed off and irradiated by ^{60}Co γ-rays at 20°C. The dose rate was 1.3×10^{16} eV/g sec. The adsorbed dose varied between 1×10^{19} and 9.8×10^{10} eV/g.

RESULTS AND DISCUSSION

Three runs of experiments were made. In the first run the same amount of methanol, 0.15 to 0.17 mmole/g, was adsorbed on aluminum oxide and silica surfaces. Ths was sufficient to form a monolayer on a silica gel sample with the smallest specific surface, namely 20 m^2/g. The coverage of samples having larger specific surfaces amounted to several percent of the monolayer (Table 1).

The coverage of various aluminum oxide surfaces at the same amount of adsorbed methanol varied from 38% to 5% (Table 2). The radiation chemical yields of formaldehyde and ethylene glycol are calculated taking into account only the dose taken up by the methanol adsorbed on silica gel. This refers to both Tables 1 and 2.

It follows from Table 1 that whatever the specific surface area, the globule sizes, and the surface coverage, the amounts of formaldehyde and ethylene glycol formed and thus the degree of methanol conversion and the radiation-chemical yields of corresponding products, were, in fact, almost equal for all samples investigated. It will be of interest to note that a change of the microchemical composition of the SiO_2 surface, namely replacement of the hydroxyl group hydrogen by calcium ions, had no effect on the amount of products formed. The experimental data obtained with methanol adsorbed on various aluminum oxide samples are shown in Table 2.

TABLE 1

RESULTS FOR RADIATION-CATALYTIC DECOMPOSITION OF METHANOL ON SILICA GEL SAMPLES WITH DIFFERENT SPECIFIC SURFACES AND GLOBULE SIZES[a]

Specific surface, S (m²/g)	Globule diameter, D (Å)	Amount of CH_3OH (mmole/g)	Surface coverage, θ (%)	Amount of products formed (mmole/g × 10²)		G $\left(\frac{\text{molecules}}{100\text{ eV}}\right)$		Molar percentage of conversion of methanol	
				CH_2O	$(CH_2OH)_2$	CH_2O	$(CH_2OH)_2$	CH_2O	$(CH_2OH)_2$
20	1400	0.14	100	0.22	0.12	220	120	1.5	0.8
50	550	0.17	51	0.19	0.14	190	140	1.1	0.8
100	270	0.17	25.5	0.14	0.10	140	100	0.8	0.6
150	180	0.17	17	0.14	0.12	140	120	0.8	0.7
190	140	0.17	1.1	0.16	0.12	160	120	0.9	0.7
350	80	0.17	7.2	0.16	0.14	160	140	0.9	0.8
360	75	0.17	7.1	0.21	0.12	210	120	1.2	0.7
390	70	0.17	6,4	0.21	0.16	210	160	1.2	0.9
540	50	0.17	4.7	0.18	0.17	180	170	1.1	1.0
620	40	0.17	4.1	0.18	0.18	180	180	1.1	1.0
640	40	0.17	4	0.16	0.17	160	170	0.9	1.0
800	30	0.17	3.2	0.24	0.18	240	180	1.4	1.0
300[b]		0.17	8.5	0.21	0.15	210	150	1.2	0.9

[a] Temperature 20°C. Dose rate of γ-radiation 1.3×10^{16} eV/g sec. Adsorbed dose 9.8×10^{19} eV/g.

[b] In this sample the hydroxyl group hydrogen was replaced by calcium ions.

It may be seen that also in this case the product yields were the same, independent of the specific surface of various aluminum oxide samples and the surface coverage. The crystal lattice structure also had no effect on the process. The similarity in radiation-catalytic activities of aluminum oxide and silica gel in the heterogeneous radiolysis of methanol seems to be accounted for by close energy values of the forbidden zone for the dielectrics studied.

Thus the features observed for aluminum oxide were the same as for silica gel samples.

The conclusion would naturally follow that an essential part is played by the bulk of the solid absorbing the radiation energy. The surface areas and the corresponding sizes of silica gel globules have no essential effect on this process. As the conversion of adsorbed methanol seems to occur by using the energy imparted from the solid, it would be natural to suggest that the same amount of energy is transferred from the bulk of the solid to the surface independent of the specific surface of a sample. From these results it follows, in turn, that

(1) As the globule sizes have no effect on the process, the diffusion of charge carriers

TABLE 2

RESULTS OBTAINED ON RADIATION-CATALYTIC CONVERSION OF METHANOL ON ALUMINUM OXIDE SAMPLES WITH DIFFERENT SPECIFIC SURFACES[a]

Specific surface, S (m²/g)	Crystalline form	Amount adsorbed (mmole/g)	Surface coverage, θ (%)	Amount of products formed (mmole/g × 10²)		G $\left(\frac{\text{molecules}}{100\text{ eV}}\right)$		Molar percentage of conversion of methanol	
				CH_2O	$(CH_2OH)_2$	CH_2O	$(CH_2OH)_2$	CH_2O	$(CH_2OH)_2$
60	$\alpha + \gamma$	0.17	38	0.22	0.13	220	130	1.3	0.8
90	$\gamma + \alpha$	0.17	28	0.22	0.13	220	130	1.3	0.8
150	γ	0.17	17	0.22	0.12	220	120	1.3	0.7
220	γ	0.17	12	0.16	0.11	160	110	1.0	0.7
300	γ	0.17	8	0.18	0.10	180	100	1.1	0.6
480	γ	0.17	5	0.22	0.14	220	140	1.3	0.8

[a] Temperature 20°C. Dose rate of γ-radiation, 1.3×10^{16} eV/g sec. Adsorbed dose 9.8×10^{19} eV/g.

in silica gel must be faster than an elementary step of the radiation-catalytic process.

(2) As the extent of conversion of methanol adsorbed in equal amounts was independent of the surface coverage, this seems to be evidence for a great affinity of adsorbed alcohol molecules to charge carrier (holes).

These conclusions obtained confirmation in the second and third runs conducted with similar silica gel samples. In the second run the amount of adsorbed methanol was varied while the surface coverage remained the same, amounting to 50% of the monolayer. The minimum amount of methanol adsorbed was, of course, that for the sample with the smallest specific surface.

In the third run the coverage by methanol was varied from 0.7% to 100% of the monolayer over the same silica gel sample with a specific surface of 270 m²/g. The conditions of irradiation were the same as in the first run.

The results obtained in the three runs are shown in Fig. 1. The radiation-chemical yields of formaldehyde and ethylene glycol are plotted against the amount of methanol adsorbed on silica gel.

It may be seen from Fig. 1 that the values of radiation-chemical yields and, thus, of the extent of methanol conversion obtained for silica gel samples with different specific surfaces at a constant coverage, as well as the values corresponding to different coverages of the same sample fall on the same curves. The average value of radiation-chemical yields for the runs given in Table 1 also fall on this curve.

Thus, the extent of adsorbed methanol conversion in a radiation-chemical process seems to be determined only by the relation between the amount of the adsorbed methanol and the number of excess charge carriers formed in the solid bulk and is independent of the specific surface and the sizes of pores and globular particles. When the amount of adsorbed species is the same at different coverage, as in run 1, the amount of products formed, and consequently the extent of conversion and the radiation-chemical yields can be expected to be the same.

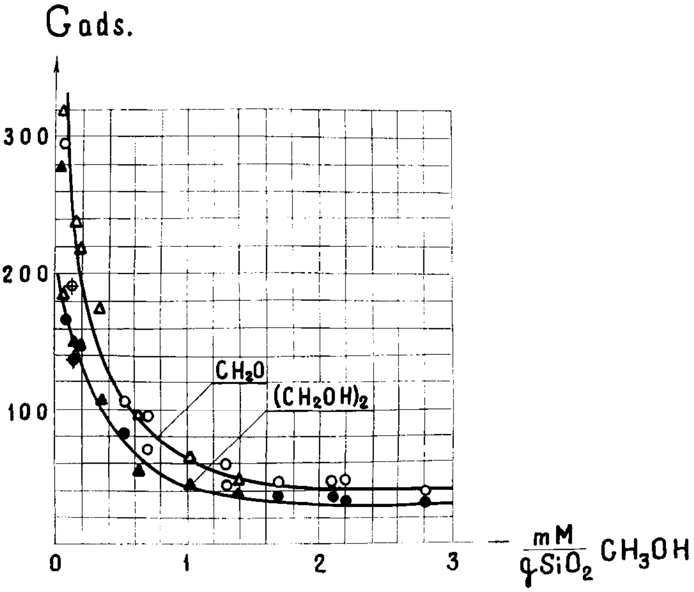

FIG. 1. The radiation-chemical yields as a function of the amount of methanol adsorbed on silica gel: △, ▲ are formaldehyde and ethylene glycol yields, respectively, for a sample with a specific surface of 270 m²/g; ○,● are yields of the same products for silica gel samples having different specific surfaces; crossed circles are averaged values of formaldehyde and ethylene glycol yields given in Table 1. Temperature, 20°C. Dose rate, $1.3 \cdot 10^{16}$ eV/g sec. Absorbed dose, 9.8×10^{19} eV/g.

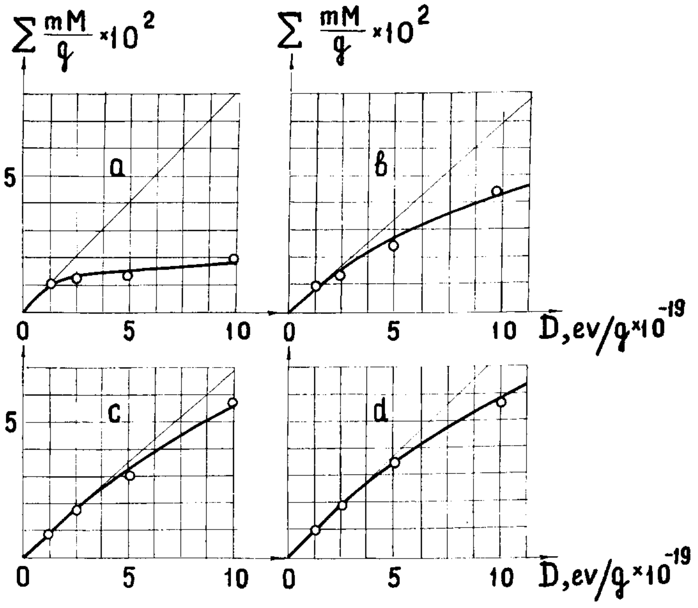

FIG. 2. The overall amount of methanol conversion products as a function of the absorbed dose for different coverage of silica gel with a specific surface of 270 m^2/g: (a) 3.8% of the monolayer; (b) 17.5%; (c) 53%; (d) 100%. Temperature 20°C.

It is evident from this standpoint that at different amounts of adsorbed methanol and the same coverage of a given sample (run 2) or at a different coverage of the same sample (run 3) the amounts of products formed must be equal and, thus, the extent of conversion and the radiation-chemical yields must change inversely to the amount of the species adsorbed.

When the coverage is very low, the radiation-chemical yields and, consequently, the extent of methanol conversion, attain high values. The contribution from secondary processes, i.e., from formaldehyde and ethylene glycol decomposition, increases with the extent of conversion, and for this reason the amount of primary products determined at a standard dose of 10^{20} eV/g seems to be smaller than the real value at low surface coverage. This region had to be investigated at lower doses of the absorbed energy.

We have obtained curves for the amount of products as a function of the absorbed energy at various surface coverages of 3.8%, 17.5%, 53%, and 100% of the monolayer. In order to exclude possible variations connected with different selectivity at low and high coverages, determination was made of the total amount of formaldehyde and ethylene glycol products. The overall amount of methanol decomposition products as a function of the time of irradiation, i.e., of the absorbed dose at different coverages of silica gel, are shown in Fig. 2. It will be seen (Fig. 2, a and b) that even at low energy doses the curves for low coverage showed a limit accounted for by secondary decomposition of the products formed, as stated above. For high coverage (Fig. 2, c and d) the deviation from linear dependence started at higher doses of absorbed energy, and consequently the errors in the amounts of products determined for a standard dose of 10^{20} eV/g were not so great as for low coverage.

The G_{ads} and $G_{overall}$ ethylene glycol values were calculated for the combined production of formaldehyde and ethylene glycol, from the linear regions of the curves (Table 3).

It follows from the table that the radiation-chemical yields $G_{overall}$ determined from the initial parts of kinetic curves were almost the same for any coverage. The G_{ads} values, and thus the extent of methanol conversion, were inversely proportional to

TABLE 3

Radiation-Chemical Yields Obtained from the Curves in Fig. 2

Sample	Specific surface, S (m^2/g)	Extent of coverage, θ (%)	$G_{overall}$[a] (molecules/ 100 eV)	G_{ads} (molecules/ 100 eV)
SiO_2	270	3.8	4.8	1970
		17.5	4.2	370
		53	4.2	120
		100	4.4	70

[a] The radiation-chemical yields $G_{overall}$ were calculated with respect to energy taken up by adsorbed methanol and by the solid.

the surface coverage. This dependence, and also the constancy of $G_{overall}$ at different surface coverages provide a confirmation for our suggestion that in a radiation-chemical process the same amount of energy is transferred from the bulk of the solid to its surface.

Let us recall the tentative mechanism of radiation-catalytic decomposition of methanol:

$$\text{Solid} \rightsquigarrow \text{solid}, \ominus, \oplus$$

$$\underset{\text{phys. ads.}}{CH_3OH} + \oplus \rightarrow \underset{\text{chem. ads.}}{CH_3OH^+}$$

$$\underset{\text{chem. ads.}}{CH_3OH^+} + \ominus \rightarrow \dot{C}H_2OH + H$$

$$\dot{C}H_2OH + \dot{C}H_2OH \rightarrow (CH_2OH)_2$$

$$\dot{C}H_2OH \rightarrow CH_2O + H$$

$$H + H \rightarrow H_2$$

Taking into account the importance of bulk and surface in energy transfer, namely, the fact that the diffusion of charge carriers from the bulk to the surface does not hinder the given process and that all free charge carriers are captured by molecules adsorbed at the surface, it will be natural to suggest that all excess charge carriers formed in the bulk of the solid must take part in the given process. From the standpoint of the above suggestion the radiation-chemical yield of the sum of the main products, formaldehyde and ethylene glycol, calculated with respect to 100 eV of energy taken up by the dielectric ($G_{overall}$), should be close to that of charge carriers formed in the bulk of the solid. The overall yield of methanol conversion products determined from the initial part of curves for the amount of methanol adsorbed on silica gel as a function of the dose was 4.4 molecules/100 eV (the average of values given in Table 3). The $G_{overall}$ value for methanol adsorbed on aluminum oxide was determined from the curve providing overall decomposition as a function of dose (Fig. 3). It appeared to be 3.3 molecules/100 eV.

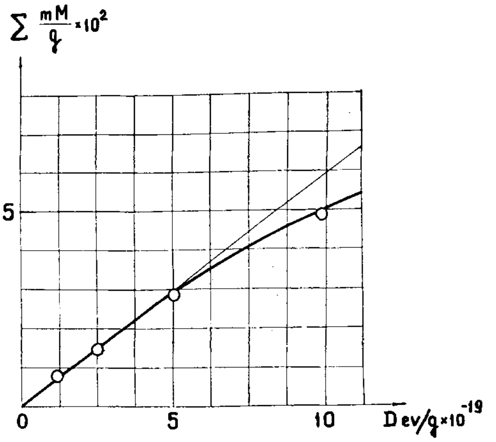

Fig. 3. The overall amount of methanol conversion products as a function of the absorbed energy dose for a monolayer coverage of the aluminum oxide surface. Temperature 20°C.

The mean energy for the formation of a charge carrier pairs in certain dielectrics determined by physical methods was reported to be 20 eV (*13*). No exact data are available on the energy of formation of charge carriers in silica gel and aluminum oxide. It may be conceived that it also amounts to 20 eV for the dielectrics investigated. This seems to be close to the true value.

A correlation of radiation yields of excess charge carriers was made. The charge carriers were estimated approximately from published data and from the radiation chemical yields of oxygen-containing products of methanol conversion $G_{overall}$. It was found that the number of molecules formed at an absorbed dose of 10^{20} eV/g is close to that of recombinations of excess charge carriers needed for the formation of the respective number of molecules. Good agreement between the two values is another proof in favor of the conclusion made, namely, that all excess charge carriers formed in dielectrics, such as silica gel and aluminum oxide, under the action of radiation, contribute to the radiation-catalytic conversion of adsorbed methanol.

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