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Electronic Factors in Catalytic Reactions Under the Influence of Ionising Radiation

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A comprehensive analysis of published data on catalytic reactions under the influence of ionising radiations is given. The combination of heterogeneous catalysis and ionising radiation effects is shown to be a new area in which the study of electronic factors leads to an understanding of the role of free and of localised charge carriers in the elementary acts of catalytic reactions. Some problems in the electronic theory of catalysis involving the effect of radiation are formulated, and data on the role of the catalytically active centres produced by prior irradiation of the catalyst are reported. Catalytic reactions taking place under the influence of ionising radiation are discussed, and possible mechanisms (usually involving electronic and free-radical steps) are considered. 138 references.

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I. PROBLEMS IN THE ELECTRONIC THEORY OF CATALYSIS INVOLVING THE EFFECT OF RADIATION ON SOLIDS

The use of ionising radiation in the study of heterogeneous catalysis offers the possibility of controlled modification of the electronic properties of solid catalysts.

It is well established[1-5] that the main effect of ionising radiation on solids is to generate excess charge carriers (electrons and holes). In some cases structural defects are produced.

These effects, often accompanied by colour changes, enhanced electrical conductivity, and paramagnetic properties, are intimately connected with the catalytic activity of the solid. Therefore, the use of ionising radiation in the study of catalysis and catalytic reactions can provide additional information on the role of various defects and impurities, and also on the formation of catalytically active centres and on the effect of the concentration of excess current carriers on the catalytic properties of solids†.

Thus, the purpose of using an agency as powerful as radiation in heterogeneous catalysis is to generate structural defects able to act as catalytically active centres. From the standpoint of the electronic theory of catalysis the main interest lies in the appearance of excess charge carriers in solids exposed to irradiation, i.e. of electrons and holes, which can take part in the elementary acts of chemical reactions on catalyst surfaces.

Over 30 years ago the founder of the electronic theory of catalysis (Pisarzhevskii[6]) carried out the first investigations of the combined effect of radiation and catalysts on chemical reactions. He was able to show that the rate of oxidation of hydrogen on platinum is significantly increased by the action of u.v. radiation. The effect of u.v. and X-rays on hydrogen peroxide decomposition catalysts (platinum, graphite, lead dioxide) was more complicated: depending on the experimental conditions and on the pretreatment of the catalyst, the reaction could be accelerated or inhibited. Pisarzhevskii's explanation of this behaviour relies on the relative number of active centres, which can increase or decrease on different parts of the surface.

† This review is not concerned with photocatalytic and photoadsorption effects, which constitute a self-contained field of study.

We need not dwell on this early period of the study of radiation effects in catalysis: the development of radiation catalysis as a field of study began in the late 1950's, following the advances in nuclear technology and in solid-state physics and physical chemistry. Significant advances in the study of the electronic mechanism of catalytic reactions and of their elementary acts were also made at about this time[7-9].

The modern electronic theory of catalysis, based on the band model of the solid state, is primarily concerned with catalysts having semiconductor properties[9]. However, the conclusions of the electronic theory are equally applicable to dielectrics, because these two classes of solids differ only in the width of the forbidden gap. According to the electronic theory, the entities responsible for the adsorption and catalytic properties of solids are electrons and holes, which can be either free or localised on lattice defects. The equilibrium concentrations of these carriers are determined by the position of the Fermi level at the surface, itself a function of the bulk Fermi level. Various factors, known to influence the position of the Fermi level, can be expected to affect the adsorption and catalytic properties of the semiconductor.

Attempts are now being made to apply the electronic models of the theory of adsorption and catalysis to the effect of radiation on the catalytic and adsorption properties of semiconductors. Vol'kenshtein[10-13] treats radiation as a factor with a profound effect on the electronic structure of solids. Two limiting cases can be envisaged. In the first case the effect of radiation is confined to direct ionisation, i.e. to the generation of non-equilibrium concentrations of charge carriers in the semiconductor, and hence to a perturbation of the electronic equilibrium in the solid. The perturbation decays very rapidly when the source of radiation is removed. "Memory" effects, i.e. permanent changes in the catalytic and adsorption properties, are practically non-existent in semiconductors. A radiation-induced "memory", on the other hand, can persist for a long time in the second limiting case, when the preliminary irradiation (e.g., by neutrons) induces a nuclear reaction in the semiconductor and is therefore equivalent to chemical doping. There is also an intermediate, and very common, case in which irradiation produces structural defects without altering the chemical composition of the semiconductor.

The resulting radiation "disorder" of the lattice shifts the Fermi level and thus displaces the electronic equilibrium. On ceasing the irradiation electronic equilibrium in the semiconductor is gradually re-established. This process is accelerated by heating. Vol'kenshtein discusses also the case of an anomalous radiation-induced "memory", which can persist for relatively long periods after irradiation is discontinued even though no structural defects have been produced. The anomalous memory effect manifests itself as a change in the catalytic and adsorption properties of the catalyst, and is ascribed to trapping of the radiation-induced non-equilibrium current carriers on intrinsic surface defects (i.e. defects originating otherwise than by the action of radiation). Thus, the anomalous radiation-induced memory is closely associated with the concept of *F*, *V*, and other centres, which can be treated as electrons and holes trapped at cation and anion vacancies. The existence of these centres has been established by extensive investigations of the radiation physics of solids[1,4,5]. In the following section we shall discuss experimental evidence that centres of this type can be catalytically active in previously irradiated catalysts (mainly in insulators).

On the basis of the general ideas of the electronic theory, Vol'kenshtein[12,13] has discussed the mechanism by which previous irradiation can affect the kinetics and the equilibrium of adsorption processes, and the rate of catalytic reactions. He has shown, in particular, that for a given set of irradiation conditions the magnitude and the sign of the effect are determined by the temperature and by the initial value of the Fermi level.

Baru and Vol'kenshtein[14,15] have considered, from the standpoint of the electronic theory of chemisorption and catalysis, the mechanism of charge formation and of ionisation in a semiconductor subjected to radioactive self-irradiation (i.e. doped with a radioactive element). They were able to define the conditions under which one or the other of these competing mechanisms is predominant.

Coekelbergs and coworkers[16] gave a theoretical analysis of the effects stemming from a change in the steady-state concentration of charge carriers, and calculated the influence of this change on the kinetics and the equilibrium of heterogeneous catalytic reactions.

Thus, the use of ionising radiation has stimulated further developments in the electronic theory of catalysis. It must be stressed that existing theoretical ideas are as yet largely qualitative, because of the lack of key experimental data on the localised energy levels of various defects and impurities in the solid or arising from adsorbed molecules. There are no data on excess carrier concentrations, surface barrier heights, etc. after irradiation. Special investigations, and refined experimental techniques, are needed to obtain this type of information.

II. NATURE OF THE ACTIVE CENTRES FORMED BY PRIOR IRRADIATION OF THE CATALYST

The physical and chemical processes induced by prior irradiation give rise to "long-lived" active centres on the surface of the catalyst. Catalysts which have been thus modified by radiation can then be used in ordinary heterogeneous catalytic reactions.

The effect of prior irradiation on catalyst activity has been the object of extensive investigations: references to the early work can be found in existing review articles[17-22]. It should be noted that the formation of active centres is only one of the phenomena which can determine the influence of prior irradiation on the catalytic activity of the sample. Thus, there are reports of prior irradiation causing poisoning of the catalyst[23], desorption of catalytic poisons from the surface[24,25], and enhanced gas adsorption[26,27], which also affects the catalytic activity. Prior irradiation can also influence the topochemical stage of catalyst preparation, and thus affect its properties[28]. Hence, it is essential to exclude all these complicating factors when studying the effect of radiation on catalytic activity: in particular, the catalysts must be thoroughly degassed before irradiation to ensure reproducible results.

Since most catalytic reactions take place at elevated temperatures, the stability of the radiation-induced active centres becomes an important consideration. For the same reason, the model reactions chosen to investigate the effect of irradiation on catalytic activity are usually relatively simple, low-temperature reactions, such as hydrogen isotope exchange, hydrogen peroxide decomposition, ethylene hydrogenation, oxidation of carbon monoxide, etc. For convenience, we shall classify the published data by catalyst type (metals, semiconductors, and insulators).

With metallic catalysts, prior irradiation with gamma rays usually produces only a very small increase or decrease in the activity towards low-temperature reactions such as the decomposition of hydrogen peroxide[29,30], the oxidation of hydrogen on platinised alumina–silica[31], and the hydrogenation of nitrobenzene on nickel and platinum catalysts[32].

With high-temperature reactions (e.g. the dehydrogenation of cyclohexene on platinised alumina–silica[29] and the dehydrogenation of cyclohexane on a copper catalyst[33]), prior irradiation had no effect on the activity of the catalyst. More significant changes in activity were observed after bombarding metallic catalysts with inert gas ions[34,35] or neutrons[33].

Prior irradiation of catalysts of the semiconductor or insulator type can also produce either an increase or a decrease in catalytic activity, depending on the particular catalyst, on the irradiation conditions, and on the type of radiation, and also on the chosen reaction.

The radiation-catalytic effects of gamma radiation invariably show a fast decay (annealing) on raising the temperature. Thus, the catalytic activity of silica gel and alumina towards the hydrogen–deuterium isotope exchange reaction induced by gamma irradiation disappears even at 0°C.[36] Changes in catalytic activity produced by neutron irradiation are much more stable[24,36-39].

Small changes in catalytic activity after irradiation have been observed in the oxidation of carbon monoxide on cuprous oxide[40], nickel oxide, and zinc oxide[41], in the dehydrogenation of ethanol on copper oxides[42], in the oxidation of formic acid on a carbon catalyst[43], and in the decomposition of hydrogen peroxide on nickel oxide[44].

Irradiation has a much greater effect on the catalytic activity of insulators, such as alumina, silica gel, magnesium oxide, and alumina–silica. The hydrogen–deuterium exchange reaction is outstanding in its sensitivity to prior irradiation of the catalyst. By using a gamma-irradiated catalyst (e.g. alumina[24,25], titanium dioxide[45], silica gel[36,37,46-53], alumina–silica[54]), the rate of this reaction at 77°K can be increased by several orders of magnitude. A significant increase in reaction rate following irradiation of the catalyst has been observed with magnesium oxide[55], and a somewhat smaller increase with zinc oxide[50].

Irradiation of silica gel[36], magnesium oxide[56,57], and alumina[58] had an appreciable effect on the rate of *ortho–para* hydrogen conversion. Leffler and Ostar[59] found that the rate of this reaction is strongly influenced by prior mixed irradiation (neutrons and gamma rays) of low-activity

catalysts (aluminas with small admixtures of transition-metal salts).

Hentz[60,61] noted a sharp increase in the activity of an alumina–silica catalyst towards the decomposition of isopropylbenzene at room temperature after gamma irradiation.

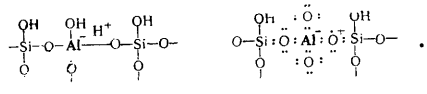
Both increases and decreases in catalyst activity after irradiation have been reported also for reactions of the acid–base type[38,39,60-68]. Particularly interesting in this respect is the work of Mikovsky and Weisz[39], who showed that the catalytic activity of silica gel and alumina–silica samples towards the isomerisation of butene could be increased drastically and stably by prior irradiation in a nuclear reactor using a neutron flux of integrated intensity 10^{20} cm^{-2}, the activity of the silica gel being increased almost 50-fold. Surprisingly, the activity of the catalyst did not fall on heating, suggesting the formation of active centres of the impurity or structural type on irradiation.

Barter and Wagner[67] found that silica gel becomes catalytically active in the isomerisation of cyclopropene and butene after being irradiated with 3 MeV electrons.

The most detailed studies of the hydrogen–deuterium exchange reaction were reported by Kohn and Taylor[24,25,36,37,45-50], and also by Mishchenko and coworkers[51-53]. According to the former, the activity of silica gel increases with content of alumina, probably because the electrons and holes produced by irradiation can be trapped on active centres present in the solid. Kohn and Taylor studied the colour centres and the paramagnetic centres of irradiated silica gel[46-48], and concluded from their results that both the colouration and the appearance of adsorption and catalytic activity after irradiation are associated with the capture of the resulting charge carriers (holes) by impurity atoms (in particular, aluminium). The adsorption centres and the catalytic centres in irradiated silica gel are believed to be of different kind. The authors have not definitely identified the catalytically active centres on the surface of the irradiated catalyst, but they believe that the paramagnetic and the catalytic centres are somehow related.

Kohn and Taylor's conclusion that the specific activity of identically irradiated silica gel samples increases with alumina content has been confirmed[51-53] by independent workers. However, and in contrast to Kohn and Taylor's results, the latter found that the adsorption and catalytic activity in irradiated silica gel change in the same sense as the intensity of the ESR signal on changing the temperature (Fig. 1). This suggests that the surface centres responsible for hydrogen adsorption and for isotope exchange are identical. The formation of these surface centres for adsorption and catalysis is related to the presence of aluminium impurities in the silica gel: the impurity atoms create acidic centres in the surface layer of the silica gel, and the free electrons produced by irradiation are captured by protons with formation of hydrogen atoms.

The charge which appears on an aluminium atom when a proton is expelled under the influence of radiation is compensated by a hole which is stabilised by an oxygen atom adjacent to the aluminium atom:



The correlation between the formation of colour centres during irradiation of alumina–silica catalysts and the appearance of catalytic activity was stressed also by Hentz[69], who studied the decomposition of isopropylbenzene on previously gamma-irradiated alumina–silica catalysts of different composition. He concluded that activation centres created by the irradiation and related to solid-state defects are the source of energy for the decomposition of isopropylbenzene with formation of benzene, unsaturated hydrocarbons, and hydrogen. Aluminium atoms, which can trap a positive hole, play the role of defects in alumina–silica catalysts. Other centres, unrelated to colour centres, but active towards the dealkylation of isopropylbenzene, have been postulated in addition to these activation centres.

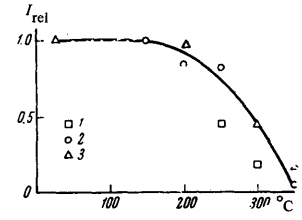


Figure 1. Catalytic activity (*1*), intensity of the sextet in the ESR spectrum (*2*), and adsorption capacity (*3*) of irradiated silica gel, in relative units, as a function of vacuum baking temperature[51].

Lunsford and Leland[55,57] explained the increased catalytic activity of magnesium oxide towards the hydrogen–deuterium exchange and *ortho–para* hydrogen conversion reactions after neutron irradiation, and also the appearance of an ESR signal, in terms of a change in the electronic structure of magnesium oxide. They postulate the formation of electron traps consisting of radiation defects but similar to impurity defects such as tervalent iron cations.

Studies of the action of radiation on alumina–silica butene isomerisation catalysts[65], and of the cracking of isopropylbenzene on alumina–silica after irradiation with protons or gamma rays[70], have revealed parallel changes in catalytic activity and in the strength of the ESR signals from paramagnetic centres.

Sazonov and coworkers[71] showed that prior irradiation of rare-earth oxides (lanthanum, samarium, gadolinium) increases the rate of oxygen isotope exchange by two orders of magnitude. Catalytically active centres are assumed to be formed during irradiation by the trapping of free electrons on anion vacancies. The analogy between the active centres formed by heat treatment in a vacuum and those found in irradiated samples was stressed[72], and it was suggested that the active centres in both cases are metal ions associated with an oxygen vacancy, since the binding energy of an excess electron is different at these sites.

Thus, summarising the results of various investigations, we note that the most widely held view of the nature of the catalytically active centres produced in insulating and in semiconducting oxide catalysts by irradiation is that the centres consist of electric charge carriers localised on various types of surface defects. The active centres created by irradiation can be analogous to the active centres which operate in ordinary catalytic reactions.

The use of ionising radiation offers new methods of creating active centres and of studying their nature and their role in catalytic and chemisorption processes. The

most stable active centres appear, as a rule, in insulators, which are characterised by a wide forbidden gap.

III. FEATURES OF CATALYTIC REACTIONS TAKING PLACE UNDER THE INFLUENCE OF IONISING RADIATION

The width of the forbidden gap of the catalyst, the main factor in determining the stability of radiation-induced catalytic centres, is particularly important in catalytic reactions taking place under the influence of radiation, since in this case the elementary act of a multistage radiation–catalytic reaction can involve the less active centres as well: electrons and holes held in "shallow" traps, and free excess carriers.

The lifetime of radiation-induced defects in a solid is a very sensitive function of temperature for a given set of irradiation conditions. Therefore, catalytic reactions with simultaneous irradiation can be divided into two groups: those taking place at relatively high temperatures, such as are used in ordinary catalysis, and reactions carried out at low temperatures, whose rate would be negligibly small but for the influence of radiation.

1. Catalytic Reactions Under the Influence of Radiation at High Temperatures

In radiation–catalytic reactions at temperatures high enough for the rate to be appreciable even in the absence of radiation, the effect of the radiation is to contribute an additional term to the overall reaction rate. A critical temperature can usually be found, depending on the nature of the reaction, of the catalyst, and of the radiation, above which the radiation ceases to have any effect and the contribution of the radiation term to the overall reaction rate practically vanishes. A similar relationship is found also in studies of the effect of radiation on the electrophysical properties of solids. Unfortunately, no simultaneous studies of the effect of temperature on the electrophysical properties and on the catalytic activity of solids in radiation–catalytic reactions appear to have been made. Data of this type would be very difficult to obtain with the highly disperse solids used as catalysts.

Direct measurements of the radiation component of electrical conductivity, taken under irradiation conditions, have been published. Figs. 2 and 3 give the results of measurements of the electrical conductivity as a function of temperature on quartz[72] and potassium iodide[4], both of which are wide-gap materials. It is evident that the radiation component of the conductivity vanishes at ~140° for both quartz and monocrystalline potassium iodide.

Barry and Roberts[73] found that the rate of the synthesis of methanol from carbon monoxide and hydrogen over zinc oxide (in a flow system at atmospheric pressure) is increased by a factor of 2–3 by gamma radiation at 160–230°, whereas above 230° the radiation has no effect.

The decomposition of methanol on zinc oxide[74] is also markedly accelerated by gamma radiation provided the temperature is below 400°. Above this temperature no radiation effect could be detected.

A peculiar difference in the effect of radiation on the activity of *n*- and *p*-type semiconductors was noted in the same paper[74]. With zinc oxide (an *n*-type semiconductor) the rate of decomposition of methanol was increased by irradiation, but with chromium oxide (a *p*-type semiconductor) the opposite effect was observed under otherwise identical experimental conditions. Evidently, this effect is due to some specific feature of the methanol decomposition mechanism, in conjunction with the electronic structure of the catalysts. As the authors point out, the effect of the radiation decays rapidly when the catalyst is shielded from the source of radiation. There is an interesting "saturation" effect, or some kind of limit to the effect of radiation on the catalytic activity of zinc oxide and chromium oxide samples of different initial activity. The radiation–catalytic activity of the samples of zinc oxide and chromium oxide found to be most active in the ordinary catalytic reaction was independent of the radiation dose. On the other hand, the radiation–catalytic activity of low-activity zinc oxide could be made to approach the activity of the most active zinc oxide sample in the non-irradiated state at high enough doses. This observation is consistent with the hypothesis put forward by Coekelbergs and coworkers[22], according to which radiation can have no effect on a semiconductor already carrying a maximum concentration of current carriers.

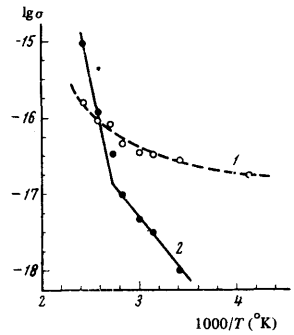


Figure 2. Temperature dependence of the logarithm of the electrical conductivity of crystalline potassium iodide[4]: *1*) not irradiated; *2*) exposed to X-rays.

The radiation–catalytic oxidation of carbon monoxide on alumina[75] under the influence of X-rays has been studied by the dynamic method over the temperature range 23–400°. The effect of irradiation was to increase the reaction rate at temperatures up to 300°.

It has been shown that the activation energy of the reaction is zero in the temperature range 80–300°. At temperatures above 300°, however, the activation energy is 18 kcal mole^{-1}, i.e. is almost indistinguishable from the activation energy of the thermal reaction (Fig. 4).

Spitsyn and coworkers[76–83] have studied catalytic reactions at very high temperatures using radioactive catalysts. These systems are much more complex and specific, because the source of radiation in this case is a radioactive isotope of one of the elements in the crystal lattice of the catalyst. They found that the catalytic activity of sodium and magnesium sulphates and of tricalcium phosphate containing ^{35}S, ^{45}Ca, and ^{32}P towards the dehydration of cyclohexanol and isopropanol increases with the specific radioactivity of the catalyst and with the intensity of β-radiation. The introduction of radio-isotopes into the catalyst led in some cases[76,77] to a fall (100–120 deg) in the optimum temperature for the reaction. According to the authors[14,80,81], these effects can be explained by the charging of the sample.

It must be stressed that the catalytic activity of radioactive catalysts is very dependent on the method of preparation. Spitsyn ascribes[83] to this effect the discrepancy between the results obtained in his laboratory and those of Krohn and Smith[84].

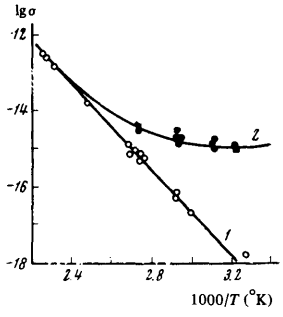


Figure 3. Temperature dependence of the logarithm of the electrical conductivity of quartz[72]: *1*) not irradiated; *2*) exposed to radiation.

In another series of papers[85-88] Spitsyn and coworkers discuss the dehydration of n-decanol and the isomerisation of dec-1-ene over aluminium oxide at 250–450° under the influence of various types of radiation: X-rays, gamma rays, and radiation from a nuclear reactor. The highest increase in reaction rate (a factor of 2–3) was obtained using X-rays. Irradiation with gamma rays and with neutrons lowered the catalytic activity of the alumina: according to the authors, this is explained by the annihilation of active centres on the catalyst surface. The rate of isomerisation was increased by irradiation with sources of all types except gamma rays from ^{60}Co, which caused a decrease in the rate of isomerisation of dec-1-ene. A decrease in the optimum temperature was found also on adding ^{137}Cs as a radioactive impurity. The effect of radiation decreased on raising the temperature of the catalytic reaction, obviously as a result of "annealing" of the radiation defects. The same effect of temperature on the radiation-catalytic activity was found by Maxim and coworkers[89] in their work on the oxidation of carbon monoxide on nickel oxide containing 2.5% of lithium in the presence of radiation. With catalysts of relatively low initial activity and conductivity, and at low reaction temperatures, irradiation had a drastic effect on both the catalytic activity and the electrical conductivity of the system.

Thus, existing data indicate that changes in catalytic activity during radiation-catalytic processes are usually relatively minor, they are most likely to be found at low temperatures, and they vanish completely at high temperatures.

2. Low-temperature Radiation-Catalytic Reactions

This group of reactions includes, mainly, radiation-catalytic reactions in the adsorption layer, which are carried out at low temperatures, where the rate of the normal catalytic reaction is negligible. In this case the radiation effect is all-important, because the ionising radiation is the only source of energy available to low-temperature radiation-catalytic reactions. The "Arrhenius" activation energy for these reaction is usually almost zero.

The most characteristic feature of these reactions is the transfer of the energy absorbed by the solid to molecules adsorbed on its surface. The transfer of energy supplied by the ionising radiation from the solid to the adsorbed molecules is confirmed by a fund of experimental evidence, according to which the radiation-chemical yield of heterogeneous reactions (calculated for the adsorbed species) is well in excess of the corresponding radiation-chemical yield for the homogeneous reaction.

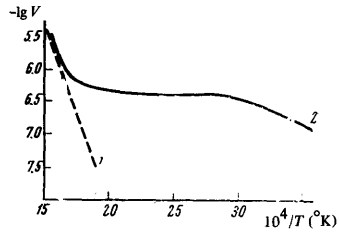


Figure 4. Logarithm of the catalytic activity of Al_2O_3 (V) against reciprocal temperature for the oxidation of carbon monoxide[75]: *1*) dark reaction; *2*) exposed to radiation.

We must stress that the radiation-chemical yields of heterogeneous catalytic reactions are very difficult to compute, because of the need to know the distribution of the energy absorbed by the system between the catalyst and the adsorption layer, the mechanism of transfer of the absorbed energy, etc. With radiation-catalytic reactions in the adsorption layer it can be assumed that the energy of the ionising radiation is absorbed by the solid and by the adsorbate in proportion to their electron fractions. In practice, the radiation-chemical yield of a reaction involving the adsorbate can be defined in two ways: the radiation-chemical yield referred to the energy absorbed by the whole system, i.e. solid and adsorbate, and the radiation-chemical yield referred to the energy absorbed by the adsorbate only, G_{ads}‡. The latter does not reflect the true significance of the radiation-chemical yield. However, a comparison of G_{ads} with the corresponding radiation-chemical yield for the homogeneous radiolysis (G_{hom}) leads to some definite conclusions on the role of the solid in the radiation-catalytic reaction and on the ways in which energy absorbed in the bulk of the solid can be transferred to molecules adsorbed on its surface. Radiation-chemical yields per 100 eV of energy absorbed by the whole system are termed G_{tot}, as in a number of other investigations[22]. Large values of this yield (upwards of 100) are evidence that a chain mechanism may be present. The radiation-chemical yield G_{tot} is a measure of the extent to which the radiation energy absorbed by the whole system is utilised.

The chemical nature, and in particular the electronic properties of the solid, play an important role in the energy transfer process. Some solids can accelerate chemical

‡ This quantity is sometimes termed G_{gas} in the foreign literature[22].

processes on their surface, i.e. they are radiation catalysts and they provide an effective medium for the energy transfer; other solid are altogether lacking in these properties. The earliest investigations of the role of the catalyst in the energy transfer process were aimed at the heterogeneous radiolysis of alkanes. Allen and coworkers[90-94] studied the influence of gamma radiation on the low-temperature reactions of pentane adsorbed on silica gel, alumina, magnesium oxide, and various molecular sieves. The relationship between the radiation-chemical yield of hydrogen and the electron fraction of pentane adsorbed on solid surfaces led the authors to propose an energy transfer effect between the solid and molecules adsorbed on its surface. The energy transfer was assumed to be confined to the first adsorbed layer, the rate of the heterogeneous reaction in all other layers being the same as that for the homogeneous reaction.

A large number of products, of different composition, have been detected during the radiation-induced conversion of pentane in the adsorbed state, the most abundant being hydrogen and decane isomers. In contrast to the homogeneous radiolysis of pentane, the yields of unsaturated hydrocarbons were quite low and the yields of isomerisation products were high, suggesting that the selectivity of the reaction had been changed. The radiation-chemical yields were dependent on catalyst composition and (for catalysts of a given composition) on the particle size. Fig. 5 shows the dependence[91] of radiation-chemical yield on the coverage of the adsorbent surface. Radiolysis measurements on NaCoX molecular sieve failed to detect any hydrogen formation on this catalyst.

However, the curves of Fig. 5 relate to the formation of free hydrogen, and may be significantly distorted by radiation-induced hydrogen chemisorption, known to occur to different extents on different solids[95-97].

The authors discuss these results from the standpoint of electronic ideas, the energy transfer process being treated as the motion and recombination of free electrons and holes formed by irradiation.

Topchiev and his coworkers[98-102] studied the heterogeneous radiolysis of heptane adsorbed on aluminium silicate, chromate, molybdate, and other oxide catalysts under the influence of gamma radiation. The reaction was investigated both at room temperature and at liquid nitrogen temperature. The composition of the heterogeneous radiolysis products of heptane differed from the composition of the homogeneous radiolysis products; the heterogeneous catalytic reaction gave fewer unsaturated hydrocarbons and a greater proportion of isomerisation products, again showing that the selectivity of the process had changed. The investigation included a study of the effect of coverage on the reaction rate. The transfer of energy from the solid to the adsorbed molecules, first established by Allen, was confirmed in this work. It was also shown that the rate of radiolysis of hydrocarbon adsorbed in excess of monolayer coverage was the same as the rate of the homogeneous reaction[99]. The rate of the heterogeneous radiolysis of heptane fell steeply at high doses (of the order of 5×10^8 rad); one possible explanation is rapid polymerisation of the resulting unsaturated compounds.

Hentz[103] studied the effect of radiation on the reactions of isopropylbenzene adsorbed on microporous alumina-silica. The following species were detected among the decomposition products: hydrogen, methane, propene, propane, isobutane, benzene, isopropylcyclohexane, etc. The reaction was found to be more specific than the radiation-induced decomposition of liquid or gaseous isopropylbenzene. Thus, the yield of benzene was higher in the presence of the catalyst, the formation of unsaturated hydrocarbons was inhibited, the amount of isomerisation products increased, and isopropylcyclohexane could not be detected in the absence of the catalyst. The radiation-chemical yields of all products decreased at higher doses of absorbed radiation. By studying the dependence of the individual yields on the electron fraction of the particular adsorbate the author concluded that the mechanism of benzene formation is different from that of all the other products. Whereas the yield of methane increased slowly with the electron fraction of isopropylbenzene (in the low-coverage region), and the yield of hydrogen fell, the yield of benzene went through a sharp maximum at 1% coverage of the surface. This behaviour was ascribed to saturation of the centres most active towards dealkylation. In the light of the peculiar relationship between the benzene yield and coverage, and of the high radiation-chemical yields in the presence of the solid, the author concludes that the energy absorbed by the solid is transferred to the adsorbed molecules and is converted into the energy needed to activate the chemical reaction.

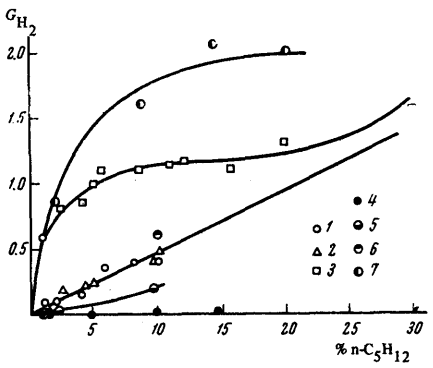


Figure 5. Hydrogen yield as a function of n-pentane adsorbed (wt.%)[91]: *1*) SiO_2 (100 μm); *2*) SiO_2 (62 μm); *3*) SiO_2 (0.02 μm); *4*) Fe_2O_3 (less than 44 μm); *5*) attapulgite (1 μm); *6*) montmorillonite (5 μm); *7*) silica gel.

There have been several recent reports of the effect of radiation on the reactions of inorganic and organic compounds adsorbed on various substrates. The yields are invariably higher than those of the corresponding homogeneous reactions.

The heterogeneous radiolysis of carbon dioxide has been studied by a number of workers. Thus, Coekelbergs and coworkers[104] investigated the radiation-chemical decomposition of carbon dioxide adsorbed on alumina, silica gel, and magnesium oxide under the influence of gamma radiation from ^{60}Co, beta radiation from ^{90}Sr, and X-rays. Energy transfer from the solid to the adsorbed molecules was confirmed in every case. With alumina, the ratio G_{ads}/G_{tot} increased very markedly at lower surface coverages. The radiation-chemical yields remained constant in the temperature range 25-300°, and the nature of the radiation also had little effect.

Other workers[105] studied this reaction on silica gel, alumina, and various semiconductors. The radiation-chemical activity was higher with intrinsic semiconductors than with *n*- or *p*-type semiconductors. Changes in dose rate over the range 0.28–3.18 Mrad h^{-1}, and temperature increase up to 180°, had no effect on the radiation-catalytic process.

Sutherland and coworkers[106] studied the rate of radiolysis of carbon dioxide adsorbed on silica gel as a function of the dose of radiation, of the concentration of adsorbed molecules, of the catalyst preparation conditions, and of the water content in the silica gel. The high radiation-chemical yields of carbon monoxide were ascribed to energy transfer from the sorbate to the sorbent (sic.).

One of the earliest papers from Coekelbergs' laboratory[107] discusses the decomposition of nitrous oxide at 80°, with formation of nitrogen and oxygen, in the presence of silica gel or alumina and under the influence of fission products. The microporous sorbents were found to increase the ratio G_{ads}/G_{hom} by a factor of 3–10. Nitrogen fixation was also investigated (at 25 atm and 80°, in the presence of fission products). The total amount of fixed nitrogen was defined as the sum of the oxides $NO_2 + N_2O_3 + N_2O_5$. The reaction was shown to be strongly influenced by the presence of microporous solids, especially silica gel.

Coekelbergs and coworkers[108] studied the synthesis of ammonia on alumina at atmospheric pressure under the influence of beta rays from ^{90}Sr and gamma rays from ^{60}Co: the former had little effect, but in the presence of gamma radiation the yield of ammonia was proportional to the dose of radiation, independent of hydrogen pressure, but dependent on the pressure of nitrogen. The activation energy in the range 200–600°K was found to be ~0.5 kcal $mole^{-1}$, with a radiation-chemical yield G_{ads} of 100–500 molecules. This high value of G_{ads} is ascribed to the transfer of the energy absorbed by the solid to the adsorbed molecules. Ammonia synthesis occurred on one grade of alumina only: no reaction was observed on the other alumina samples, or on silica gel, magnesium oxide, and zinc oxide.

Thus, the most marked effect of ionising radiation on the reactions of adsorbed molecules is found with solids of the insulator type, which have also been most extensively investigated. Semiconductors have been studied in a few isolated cases in this context, metals hardly at all.

The radiation-catalytic activity of solids with different gap widths (insulators, semiconductors, and metals) was first investigated under otherwise identical experimental conditions by Zhabrova and her coworkers[109,110], who chose cyclohexane in the adsorption layer as their experimental system. Irradiation was by fast electrons and by gamma rays from ^{60}Co. The most active catalysts were found to be insulating oxides (silica gel, alumina-silica, and alumina), whereas metals and low-gap semiconductors (such as zinc oxide, cuprous oxide, nickel oxide, and active carbon) did not develop catalytic activity on irradiation. The radiation-chemical yield of hydrogen was studied as a function of surface coverage of silica gel by cyclohexane (Fig. 6), and it was found that the extent of reaction of cyclohexane with formation of hydrogen increases with decrease of coverage. A possible energy transfer mechanism from the solid to the adsorbed molecules was put forward on the basis of the band theory of the solid state. It must be stressed, however, that in this work the radiation-catalytic activity was determined merely from the amount of hydrogen evolved. Hence, the quantitative data for the radiation-chemical activity of the various solids obtained in this work may be in error by the extent to which hydrogen is adsorbed on these solids.

This deficiency was overcome in a study by the same authors[111-114] of the radiation-catalytic reactions of methanol adsorbed on solids with forbidden gaps of different width. In this work the radiation-catalytic activity was determined for all the main reaction products: hydrogen, formaldehyde, and ethylene glycol. The highest radiation-chemical yields G_{ads} were obtained with insulators (high energy gap materials). Thus, with silica gel the parameter G_{ads} exceeded the corresponding radiation-chemical yield for the homogeneous radiolysis of methanol by over a factor of 10. Significant radiation-catalytic activity was found also in alumina, alumina-silica, and potassium fluoride, whereas semiconducting oxides had lower activity. Metals, active carbon, and graphite showed no radiation-catalytic activity.

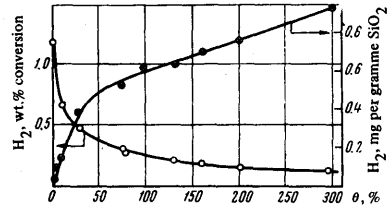


Figure 6. Amount of hydrogen formed and percentage conversion of cyclohexane against coverage of a silica gel surface by cyclohexane[110].

The fact that the radiation-chemical yields of the products of the heterogeneous radiolysis of methanol are much higher on the surface of insulators and some semiconductors than the radiation-chemical yields of the corresponding homogeneous reaction suggests that these solids are able to transfer the energy absorbed from the ionising radiation to molecules adsorbed on their surface. This is evidently not the case for the other group of solids (platinum, palladium, cuprous oxide, nickel oxide, active carbon, and graphite).

Rabe and coworkers[115] studied the radiolysis of azoethane adsorbed on silica gel. Only the gaseous decomposition products were monitored, consisting mainly of nitrogen (with small amounts of hydrogen and methane). The higher yield of nitrogen (as compared with the homogeneous reaction) is explained by assuming that the radiant energy absorbed by the solid is used in the chemical decomposition of the adsorbed azoethane. A more recent communication by the same authors[116] describes the radiolysis of azoethane adsorbed on different solids: silica gel, magnesium oxide, zinc oxide, nickel oxide, titanium dioxide, alkali metal halides, and graphite. The conclusion is that, as in the radiation-catalytic decomposition of cyclohexane and methanol, the strongest tendency to transfer absorbed energy from the solid to molecules adsorbed on the surface is found in insulators. Some semiconductors have a weak effect, others have practically none. The relative radiation-catalytic activity of solids towards the radiolysis of azoethane is illustrated in Fig. 7 as plots of amount of nitrogen formed against surface coverage of the solids by azoethane. With the exception of magnesium oxide, the amount of nitrogen increased monotonically in every case with surface coverage. With magnesium oxide the relationship was more complicated, with maxima at

different coverages for the various products. The radiation-chemical yield of the decomposition products of azoethane decreases with increasing dose of total absorbed radiation.

Sorokin and coworkers[117-119] made a detailed study of the decomposition of ammonia adsorbed on various zeolite surfaces, and found that when the Na form of the zeolite is used the radiant energy absorbed by the solid is transferred to the adsorbed ammonia molecules. The yield of hydrazine—the main radiolysis product of ammonia—expressed in terms of the energy taken up by the adsorbed ammonia was considerably higher than the corresponding yield for the radiolysis of liquid or gaseous ammonia. The radiation-chemical yields of products increased at lower surface coverages of the zeolite by ammonia, and the ratio of hydrazine to hydrogen increased, showing that the selectivity of the process had changed. No energy transfer was observed on irradiating ammonia adsorbed on zeolite in the Ca form.

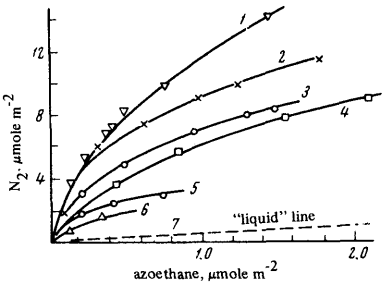


Figure 7. Nitrogen evolved against adsorption of azoethane on various solid surfaces[115]: *1*) SiO_2 (5.9 Mrad); *2*) KI (2 Mrad); *3*) NaF (2 Mrad); *4*) NaCl (2 Mrad); *5*) LiF (2 Mrad); *6*) SiO_2 (1.5 Mrad); *7*) homogeneous radiolysis ("liquid" line).

The influence of the ions present in the zeolite structure on the radiation-catalytic properties of the system has been noted also in the radiolysis of pentane[93] and cyclohexane[120] in the adsorption layer.

The radiolysis of water adsorbed on silica gel has been studied by Krylova and Dolin[121]. The high radiation-chemical yield of hydrogen (calculated on the basis of the energy taken up by the adsorbed water only) is explained by postulating that the adsorbed molecules can acquire additional energy from the solid. The effect of adsorbed water on the ESR spectrum of silica gel irradiated at −196° supports the energy transfer hypothesis. Carbon dioxide was detected among the radiolysis products: according to the authors, this is the result of interaction between traces of residual organic matter on the silica gel surface and oxidising agents formed during the radiolysis of water. More rigorous purification of the silica gel surface from traces of organic compounds lowered the radiation-chemical yield of the radiolysis products of water.

As was pointed out above, there is ample evidence[110,113,116] that, in contrast to ordinary catalysis, the solids most active in radiation-catalytic processes are insulators and wide-gap semiconductors. The dependence of catalyst activity upon the width of the forbidden gap for radiation-catalytic and ordinary catalytic reactions is shown in Figs. 8 and 9. Fig. 8, which refers to the radiation-catalytic decomposition of methanol, shows that semiconductors and insulators behave as active catalysts if their forbidden gap is 4 eV wide or more. We note that the acid-base properties of the solids do not appear to play an important part in radiation-catalytic processes: it can be seen from Fig. 8 that insulators with acidic properties (SiO_2, Al_2O_3) are as effective as basic insulators (MgO, CaO) towards the radiation-catalytic reactions of methanol.

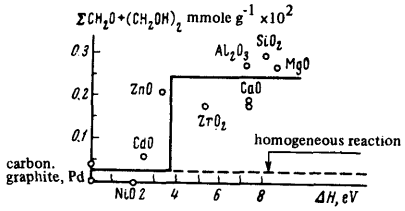


Figure 8. Radiation-catalytic activity of solids as a function of forbidden gap width[122].

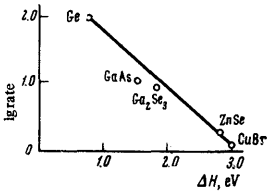


Figure 9. Activity of semiconductor catalysts as a function of forbidden gap width[123].

In contrast to radiation catalysis, the activity of the catalyst in ordinary oxidation-reduction catalysis decreases as the width of the forbidden gap increases[123].

Coekelbergs and coworkers[16] have shown theoretically that large qualitative and quantitative changes in catalytic activity can be obtained even at low radiation intensities in the case of insulators. On the other hand, only minor changes in activity are possible (even at high radiation intensities) in the case of "good" semiconductors. This behaviour is sometimes found also with radiation-catalytic chain reactions. Thus, the radiation-chemical yield for the polymerisation of ethylene (in terms of the energy absorbed by the whole system) is 20–50 times higher on silica gel, alumina, or zeolites than in the homogeneous reaction. The lowest catalytic activity was that of the semiconductor zinc oxide, whereas active carbon actually inhibited the reaction.

The rate of the radiation-catalytic polymerisation of acrylonitrile and methyl methacrylate at −78° increased by an order of magnitude in the presence of magnesium oxide and some *p*-type semiconductors[125], whereas *n*-type semiconductors were less effective. The polymers obtained by this reaction had a high molecular weight, a high density, and a stereoregular structure.

A group of workers[126,127] has studied the radiation-induced graft polymerisation of methyl methacrylate and styrene on powdered magnesium oxide and Aerosil (SiO_2). The rate of the reaction was found to depend on the monomer concentration in the adsorption layer. The high radiation-chemical yield of the reaction is ascribed by the authors to transfer of the energy absorbed by the catalyst to the surface.

The radiation-catalytic synthesis of higher carboxylic acids from ethylene and carbon dioxide has been achieved in the presence of an insulator (alumina)[128,129]. The consumption of ethylene, related to the total energy absorbed, was $G_{(-C_2H_4)} = 10^3$. The carboxylic acids contained approximately 100 molecules, i.e. the yield of radiation-induced polymerisation centres was about 10. The catalyst appears to act not only by increasing the initiation efficiency but also by partly suppressing the chain-breaking step. In the absence of radiation the reaction did not take place, even on adding free-radical initiators.

The radiolysis of heptane in the adsorption layer on alumina above 150° is also stated to be a chain reaction[101].

Kohn has made a detailed study of the radiation-catalytic oxidation of approximately 70 different hydrocarbons on silica gel and alumina[130]. The radiation-chemical consumption of oxygen was often very high, with $G_{(-O_2)} \simeq 100$, suggesting the possibility of chain reactions. The yield of reaction products was independent of temperature, and increased on lowering the oxygen pressure. According to the author, existing views on the mechanism of chain growth on the surface for "dark" heterogeneous reactions cannot explain the growth of chains during the radiation-catalytic oxidation of hydrocarbons. Radiation-catalytic chain reactions are characterised by a very high radiation-chemical yield (on the basis of total absorbed energy). One possible explanation is more effective chain initiation at the surface of an irradiated solid, coupled with a lower mobility of the growing molecules in the adsorption layer of a solid surface. The latter effect can inhibit the rate of chain breaking. Also, the "orientation" of the molecules on the surface of a solid can influence the mechanism of chain growth, and sometimes leads to the formation of stereoregular polymers[125] as in the case of thermal heterogeneous polymerisation.

3. Possible Mechanism and Electronic Steps in the Radiation-induced Transformation of Adsorbed Molecules

As was stated above, in radiation-catalytic processes the radiant energy absorbed by a wide-gap solid can be transferred to chemisorbed molecules, the result being a radiation-chemical yield G_{ads} of reaction products much greater than the corresponding yield for homogeneous radiolysis.

Early workers used the statistical approach to explain the main features of energy transfer[98,102]. According to others[131], the radiation-catalytic activity of solids is determined by their specific heat, the more active catalysts having relatively low specific heats. These ideas have not been confirmed experimentally. Various reaction schemes involving surface hydrogen atoms are considered in a series of investigations of the radiation-catalytic activity of silica gel. One such scheme was proposed by Sutherland and Allen[94] in order to account for the selectivity of the heterogeneous radiolysis of pentane on the surface of silica gel and on NaHX molecular sieve:

$$SH \rightsquigarrow S + H \quad (1)$$

$$H + C_5H_{12} \longrightarrow C_5H_{11} + H_2 \quad (2)$$

$$C_5H_{11} + C_5H_{11} \longrightarrow C_{10}H_{22} \quad (3)$$

where SH is a surface compound with Si-OH groups.

In the liquid-phase radiolysis the yield of decane is 1/2, consisting almost entirely of isomeric decanes. If silica gel is used the yield of decane becomes 2/3, of which 1/6 is n-decane and the remaining 5/6 are a mixture of isomers. With NaHX at low coverages, a higher ratio of decane isomers to normal decane is obtained.

According to Sutherland and coworkers[106], during the heterogeneous radiolysis of carbon dioxide on silica gel energy is absorbed also by surface Si-OH groups, which then interact with adsorbed molecules. It must be noted, however, that schemes involving OH groups of the silica gel are usually supported only by indirect evidence. Strelko and Suprunenko[132] observed the formation of $\cdot C_6H_6D$ and $\cdot C_6H_7$ radicals during isotope exchange between the hydrogen atoms of benzene adsorbed on silica gel and partially deuteriated OH groups, under the influence of ionising radiation.

Unambiguous proof of the participation of silica gel surface groups in radiation-catalytic reactions of organic compounds obviously requires a study of hydrogen exchange between the surface groups and the reacting molecules during the radiolysis.

On the other hand, studies of the radiation-catalytic reactions of methanol on silica gel have shown unequivocally that surface hydrogen atoms are not involved in the reaction, since the radiation-catalytic activity of silica gel is not affected when the hydrogen ions of OH groups are replaced by calcium ions[136].

Electronic models are widely used to explain the features of energy-transfer phenomena in radiation-catalytic reactions.

Caffrey and Allen[91], in their work on the heterogeneous radiolysis of pentane on silica gel and on molecular sieves, discussed a possible mechanism for the transfer of absorbed energy from the solid to adsorbed molecules, involving the recombination of electrons with positive charges localised on adsorbed molecules. The authors postulated the formation of a pentyl radical.

ESR studies of the radiation-catalytic reactions of cyclohexane[110] revealed the formation of adsorbed $\cdot C_6H_{11}$ radicals and the appearance of paramagnetic centres on the surface of the insulating oxides and fairly-wide-gap semiconductors which catalyse this reaction. No adsorbed $\cdot C_6H_{11}$ radicals or paramagnetic centres were observed with semiconductors lacking radiation-catalytic activity towards the reaction. The cyclohexane was assumed to be adsorbed on an excess charge carrier (hole) with formation of a positively charged molecule of cyclohexane. Recombination of an electron from the conduction band can take place on this charged molecule, and the recombination energy, determined by the width of the forbidden gap, is localised on the adsorbed molecule and enables it to decompose. There is a high probability that the decomposition is accompanied by the formation of free radicals, but the composition of the radiation-catalytic decomposition products of cyclohexane is so complicated that it was not possible to compare the amounts of products and radicals formed and to establish the role of the latter in the overall process.

The mechanism of the radiation-catalytic transformation of methanol has been studied in greater detail[111-113]. Irradiation of methanol adsorbed on insulators and on semiconductors showing radiation-catalytic activity leads to the formation of adsorbed $\cdot CH_2OH$ radicals and much smaller

amounts of·CHO and·CH_3. A typical ESR spectrum of irradiated methanol adsorbed on silica gel is shown in Fig. 10. In order to characterise the role of adsorbed radicals, the amounts of radicals and of radiation–catalytic decomposition products of methanol were compared in a special series of experiments. The results (Fig. 11) show the variation of the numbers of resulting ethylene glycol molecules (upper curve) and·CH_2OH radicals (lower curve) with the dose of radiation absorbed. It can be seen that the two curves deviate in the region of high absorption, evidently due to radical recombination at high concentration, whereas in the low-absorption region the curves are close together. This suggests that·CH_2OH radicals are intermediate products in the formation of ethylene glycol. Analogous investigations of the role of·CHO radicals[122] showed that these are not intermediates, but they probably arise by the decomposition of formaldehyde under the influence of radiation.

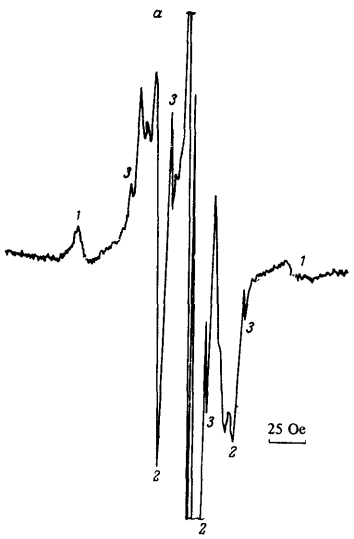


Figure 10. ESR spectrum[113] of methanol adsorbed on silica gel and irradiated at −196° (dose: 10 Mrad): *1*)·CHO radical; *2*)·CH_2OH radical; *3*)·CH_3 radical.

The correlation between the radiation–catalytic activity of solids in the heterogeneous radiolysis of methanol and their electronic properties (forbidden gap width), and also the correlation with the appearance of adsorbed radicals, justify the assumption that the heterogeneous radiolysis of methanol involves both electronic and radical steps, and that the energy transfer process is associated with the motion and recombination of excess charge carriers generated in the solid by the radiation. From the experimental results, the following scheme was put forward for the radiation–catalytic conversion of methanol adsorbed on solid surfaces:

$$\Gamma \text{ solid} \rightsquigarrow \Gamma \text{ solid} \oplus \ominus$$
$$CH_3OH \oplus \longrightarrow \underset{\text{chem.ads.}}{CH_3OH^+} \quad (CH_3OH \text{ phys.ads.})$$
$$CH_3OH^+ + \ominus \longrightarrow \dot{C}H_2OH + \dot{H} \quad (CH_3OH^+ \text{ chem.ads})$$
$$\dot{C}H_2OH + \dot{C}H_2OH \longrightarrow (CH_2OH)_2$$
$$\dot{C}H_2OH \longrightarrow CH_2O + \dot{H}$$
$$\dot{H} + \dot{H} \longrightarrow H_2 .$$

Under the influence of radiation, excess non-equilibrium charge carriers (electrons and holes) are formed in the solid. Methanol molecules adsorbed on the surface interact with these carriers, and since alcohols have electron-donating properties we may assume that the methanol molecules interact with holes. As in the case of cyclohexane, an adsorbed positively charged methanol molecule acts as a recombination centre for an excess electron from the conduction band. Recombination of a pair of charges liberates an amount of energy equal to the width of the forbidden gap minus the height of the energy level of the chemisorbed molecule. If this energy is high enough (≥ 4 eV), an atom of hydrogen is eliminated from the methanol molecule with formation of a·CH_2OH radical. Recombination of the·CH_2OH radicals produces ethylene glycol molecules, and dissociation of these radicals produces formaldehyde molecules. A hydrogen molecule is formed by the recombination of two hydrogen atoms.

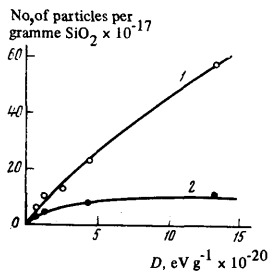
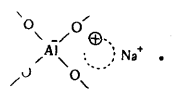
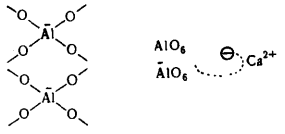


Figure 11. Number of·CH_2OH radicals and of ethylene glycol molecules (expressed as CH_2OH particles) as a function of dose absorbed; surface coverage of silica gel 30% at −196°:[113] *1*) $(CH_2OH)_2$; *2*)·CH_2OH.

A similar energy transfer scheme involving the recombination of excess current carriers, but with the participation of intermediate charged centres, has been proposed from a study of the heterogeneous radiolysis of ammonia on zeolites[117]. By using the ESR method it was shown that hydrazine is formed through the recombination of $\dot{N}H_2$ radicals. As the number of $\dot{N}H_2$ radicals on the surface increases, the number of paramagnetic centres falls (Fig. 12). In order to explain the mechanism of heterogeneous radiolysis, the ESR spectra of ammonia adsorbed on sodium and calcium zeolites were investigated[119], and it was concluded that the paramagnetic entities obtained by gamma irradiation of these two types of zeolite are different. In the Na form the radiation-induced catalytic centres are, according to the authors, of the *V*-centre type, and are similar to the centres formed by irradiation of silica gel containing alumina:



Irradiation of the Ca-form, on the other hand, is said to produce paramagnetic F-centres consisting of excess electrons localised on Ca–O bonds. According to the authors, these centres have the structure



In both forms of zeolite, the energy absorbed in the bulk of the solid must be re-evolved during recombination of the electrons and holes. In the presence of adsorbed ammonia molecules, which have a high affinity for positive charge because of the unshared electron pair on the nitrogen atom, a donor–acceptor bond is formed between the molecule and the surface. In the case of the Na-form, the holes formed by irradiation reinforce the bond between the ammonia molecule and the surface. On the other hand, with the Ca-form the electrons localised at the surface weaken the bond between the ammonia molecule and the surface, and energy transfer by electron–hole recombination has a low probability. As required by this model, the zeolite in the Ca-form was found to be inactive towards the heterogeneous radiolysis of ammonia.

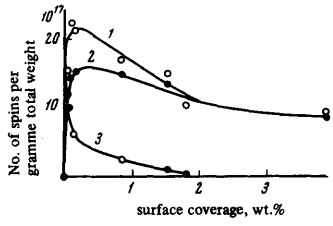


Figure 12. Effect of surface coverage on the concentration of radicals[119]: *1*) total concentration; *2*)·NH_2 radicals; *3*) paramagnetic centres in the zeolite.

Similar recombination mechanisms for the energy transfer process are proposed in other investigations of the radiation–catalytic reactions of organic molecules, recently published[103,117,134]. In most of the schemes put forward a molecule of the organic compound, adsorbed on the surface, acts as the recombination centre for excess current carriers. Intermediate paramagnetic F- and V-centres, formed in the solid during irradiation by capture of an electron or a hole at various defects, are not usually postulated. Yet, these centres must play an important part in processes involving prior irradiation of the catalyst. They stabilise the free current carriers, and thus give rise to "long-lived" excitation in the solid (the "memory" effect). On the other hand, it was shown in a number of investigations that the presence of impurities or other structural defects in the catalyst is relatively unimportant when irradiation is applied during the reaction. For example, the radiation–catalytic activities of silica gel and of alumina–silica containing 10% of alumina were found to be the same in the radiolysis of methanol[111] and of isopropylbenzene[134]. A sample of spectroscopically pure silica gel, containing less than 10^{-4}% of aluminium, had the same radiation–catalytic activity as a sample of silica gel of SMKh grade, containing a significant amount of alumina[122]. Thus, most workers (with the exception of Sorokin[117]) assume that energy transfer in dielectrics involves free charge carriers, and that localised charge carriers (if they are formed) play a minor part. It would appear that direct trapping of excess carriers by adsorbed molecules is the basic process in the radiation–catalytic reactions of adsorbed molecules.

4. Role of the Bulk and Surface of Solids in the Energy Transfer Process

As stated above, the most commonly held view of the energy transfer process involves the recombination of excess non-equilibrium charge carriers formed in the bulk of the solid under the influence of radiation. However, the extent to which these excess carriers from the bulk are used in the radiation–chemical reaction at the surface is still uncertain.

Under these conditions, the radiation-induced chemical reactions of adsorbed molecules offer some insight into the physical processes taking place in the bulk of the solid exposed to ionising radiation. This approach was used by Zhabrova and coworkers[122,135,136], who studied the radiolysis of methanol in the presence of two of the most active radiation catalysts—silica gel and alumina—with different surface-to-volume ratios. The silica gel samples, prepared by the hydrothermal method[137,138], had identical chemical compositions but different specific surface areas and globule diameters D. In the first series of experiments the amount of methanol adsorbed on the samples was the same (0.17 mmole g^{-1}). This amount was sufficient to give monolayer coverage on the sample with the smallest specific surface (20 m^2 g^{-1}), but on the large-area samples the coverage was only a few per cent.

Table 1. Influence of specific surface area and globule diameter of silica gel on the radiation–catalytic decomposition of methanol. Temperature 20°C, dose rate of gamma radiation 1.3×10^{16} eV g^{-1} s^{-1}, dose 10^{20} eV g^{-1}.

Specific surface area S, m^2 g^{-1}	Globule diameter D, Å	Surface coverage θ, %	Amount of products formed, mmole g^{-1} $\times 10^2$		G_{ads}, mmole per 100 eV		Extent of conversion, mole %	
			CH_2O	$(CH_2OH)_2$	CH_2O	$(CH_2OH)_2$	CH_2O	$(CH_2OH)_2$
20	1400	100	0.22	0.12	220	120	1.5	0.8
50	550	51	0.19	0.14	190	140	1.1	0.8
100	270	25.5	0.14	0.10	140	100	0.8	0.6
150	180	17	0.14	0.12	140	120	0.8	0.7
190	140	11	0.16	0.12	160	120	0.9	0.7
350	80	7.2	0.16	0.14	160	140	0.9	0.8
360	75	7.1	0.21	0.12	210	120	1.2	0.7
390	70	6.4	0.21	0.16	210	160	1.2	0.9
540	50	4.7	0.18	0.17	180	170	1.7	1.0
620	40	4.1	0.18	0.18	180	180	1.1	1.0
640	40	4	0.16	0.17	160	170	0.9	1.0
800	30	3.2	0.24	0.18	240	180	1.4	1.0

The results, summarised in Table 1, show that the radiation–chemical yields of products are almost constant for all the samples. Since the methanol undergoes radiation–catalytic reactions only by virtue of the energy transferred from the solid, it is obvious that for a given dose the same amount of energy has been transferred from the bulk to the surface of all the samples examined. The fact

that the energy transferred is independent of the globule diameter of the silica gel and of the surface coverage is evidence that the diffusion of carriers from the bulk to the surface is not rate-limiting, and that the adsorbed alcohol molecules have a fairly large affinity for charge carriers (holes). An analogous series of experiments with alumina samples gave similar results.

In another series of experiments, the adsorption of methanol on the surface of the various samples was varied so as to give a constant surface coverage of 50% of a monolayer. The effect of changing the adsorption of methanol on the surface of one of the samples was also studied. The variation of the radiation-chemical yields of formaldehyde and ethylene glycol with surface concentration of methanol on the silica gel is shown in Fig. 13.

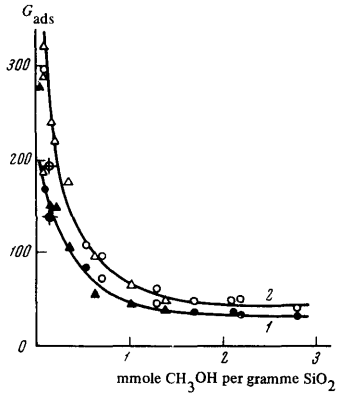


Figure 13. Radiation-chemical yields of oxygen-containing products against adsorption of methanol on the surface of silica gel[136]: *1*) $(CH_2OH)_2$; *2*) CH_2O.

As the Figure shows, the radiation-chemical yields (and therefore also the extents of conversion of the methanol, which are proportional to the yields) for silica gels of different surface areas but constant coverage, and the values for different coverages of the same specimen, all lie on the same curve. The mean of the radiation-chemical yields obtained in the series of experiments of Table 1 also lies on the same curve. For a given dose of absorbed radiation, the highest radiation-chemical yields G_{ads} were obtained on samples with the lowest amount of adsorbed methanol. As the adsorption of methanol was increased, the radiation-chemical yields of both products fell. Thus, this work has shown that the extent of conversion of adsorbed methanol in a radiation-catalytic reaction is determined only by the relationship between the amount of methanol and the number of excess current carriers formed in the bulk of the solid (SiO_2 or Al_2O_3), whereas the specific surface area, the pore size and globule diameter, and the extent of coverage of the surface have no effect on the reaction.

Since all the free charge carriers are effectively captured on adsorbed molecules, irrespectively of the surface coverage, these results justify the conclusion that all or practically all the excess carriers formed in the bulk of the solid are used in the radiation-catalytic process. The values of G_{tot} and G_{ads} (from the sum of the oxygen-containing products), determined from the initial slopes of the kinetic curves, are set out in Table 2. It can be seen that the mean value of G_{tot} for silica gel is 4.4. According to electrophysical measurements[2], the average energy of formation of a pair of charge carriers for a number of insulators is 20 eV. Since this value can be equated to the width of the forbidden gap for insulators, we conclude that the yield of pairs of carriers per 100 eV of energy absorbed in a dielectric of the SiO_2 type should lie between 4 and 5. This agrees satisfactorily with the experimental value of 4.4, thus providing a further argument in favour of the hypothesis that practically all the excess carriers formed in the bulk of a dielectric take part in the radiation-chemical process at the surface.

Table 2. G_{ads} and G_{tot} for the radiation-catalytic conversion of methanol on silica gel at different surface coverages[135].

Coverage, %	G_{ads}, molecules per 100 eV	G_{tot}, molecules per 100 eV
3.8	1970	4.8
17.5	370	4.2
53	120	4.2
100	70	4.4

Further indirect evidence for this conclusion comes from other investigations. Thus, Rojo and Hentz[134] found that the yield of benzene (measured from the initial slope of the kinetic curve) is 4 in the decomposition of isopropylbenzene on silica gel previously irradiated at −196°. In the radiation-catalytic dealkylation of adsorbed isopropylbenzene at room temperature the yield G_{tot} was 2. However, this quantity was determined at a relatively high dose (not from the initial portion of the kinetic curve at low doses), and might therefore be too low. According to the authors, the capture efficiency of current carriers by adsorbed molecules is close to 100%.

Rabe and coworkers[115] obtained curves of the yield of radiolysis products against surface coverage of various solids by azoethane (Fig. 7). In every case (except magnesium oxide) the yield of radiolysis products of azoethane increased with surface coverage up to monolayer coverages, whilst the reaction rate decreased. The authors suggest that the excited species generated in the solid by the radiation have a fairly large radius of action, and that the adsorbed molecules must compete for the energy transferred from the solid.

Thus, the conclusion that the excess current carriers generated in the bulk of the solid are fully utilised in radiation-chemical processes at the surface appears to be generally applicable to all solids of the dielectric type.

It is evident from a survey of published data that the use of ionising radiation in heterogeneous catalysis has opened a new field for the study of electronic factors, which allows the role of free and of localised carriers in the elementary acts of catalytic reactions to be identified, and can suggest ways of controlling these processes.

The use of ionising radiation provides a test of various propositions of the electronic theory of catalysis, and it allows us to formulate new theoretical problems and to extend the range of experimental approaches to the study of elementary acts in catalysis and chemisorption.

The ability of adsorbed molecules to act as "traps" for electrons and holes in competition with other traps (impurities and structural defects on solid surfaces) has been demonstrated by the use of ionising radiation.

It has been amply demonstrated that the creation of charge carriers in insulators and semiconductors often leads to the formation of various kinds of charged and free-radical species on the surface, which play an important part in catalytic and chemisorption processes.

The mechanism of radiation–catalytic reactions is often closely dependent on the transfer of energy absorbed by the solid to molecules adsorbed on the surface. The energy transfer problem is also very relevant in ordinary catalytic reactions, but the elementary mechanism of transfer, involving the motion of electric charges, can differ in the two cases. The width of the forbidden gap is an important consideration in catalysts for ordinary oxidation–reduction reactions. This factor is of major importance also in radiation–catalytic reactions. However, in contrast to ordinary catalysis, the most active catalysts in radiation catalysis are solids with a wide forbidden gap.

It has been shown in a number of systems that the increase of radiation–catalytic activity with gap width stems from the recombination mechanism for the interaction of a charged adsorbate–hole complex and an electron arriving from the conduction band. Hence a comparison of the forbidden gap with the energy required to break various bonds in the reacting molecule is particularly relevant. This comparison suggests some principles for the selection of radiation–active catalysts.

The study of the nature of catalytically active centres, their structure, the role of free carriers, and the extent to which these take part in the elementary steps of catalytic reactions is greatly assisted by the use of ionising radiation —a powerful agency for altering the concentration electrical charge carriers and for localising carriers on intrinsic defects of the surface.

An analogy has been observed between the active centres formed by conventional methods of catalyst preparation and the active centres of the radiation-induced defect type.

Thus, we may conclude that further developments in the relatively young science of radiation–catalytic processes are vital to the understanding of elementary acts in catalysis.

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