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Effect of Radioactive Emission on the Catalytic Properties of Solid Materials

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The general state of the problem of the radiation modification of the action of solid catalysts is discussed, in relation to various types of heterogeneous catalytic reactions, on the basis of 190 references.

CONTENTS

I. Introduction 436
II. Principal mechanisms of radiation damage 436
III. Effect of ionising radiation on the adsorptive power and the catalytic activity of solids 437

I. INTRODUCTION

Many research workers have turned their attention to the problem of radiation heterogeneous catalysis, for solid catalysts often undergo considerable activation on irradiation. On the other hand, attempts have been made to improve the chemical efficiency of the irradiation of a reaction system by the introduction of solids, since radiolytic reactions (other than chain processes) usually give low yields of the required product. Furthermore, study of the adsorption and catalytic properties of irradiated specimens will contribute to a better understanding of general aspects of heterogeneous catalysis, in particular the relation between the activity of a solid catalyst and defects in its crystal structure.

Because of the abundance of information on this aspect, the Review will not contain any detailed discussion of the mechanisms of the radiation-catalytic processes occurring in each individual case. We have tried to report the general state of the problem, with detailed consideration only of the clearest examples with the aim where possible of revealing general features inherent in various groups of phenomena.

It is necessary to distinguish cases in which preliminary exposure of the catalyst (in the absence of reactants), by producing radiation damage in the solid specimen, confers on it new catalytic properties from cases in which a considerable proportion of the radiant energy absorbed by the catalyst during the reaction is utilised in activating gas molecules adsorbed on its surface. In the latter case thermodynamically forbidden processes may occur[1]. The radiation modifcation of solid catalysts is in some way connected with the appearance of various kinds of interior and surface defects.

II. PRINCIPAL MECHANISMS OF RADIATION DAMAGE

The interaction of high-energy radiation with a solid result in various types of disturbance[2-5]: (1) vacancies are unoccupied lattice points; (2) interstitial atoms have been displaced from their usual position in the lattice and are located between lattice points (vacancies and interstitial atoms may be formed simultaneously by the Frenkel mechanism, i.e. by escape of an atom from a lattice point into an interstice; vacancies may arise also by a Schottky mechanism, when an atom that has vaporised from the crystal surface is replaced by an atom from a deeper layer; and vacancies may combine to form spherical pores or flat circular voids); (3) displacement peaks are regions containing up to 10^4 displaced atoms, such defects usually arising at the end of the path of the moving particles; (4) impurity atoms are chemically foreign atoms formed as a result of nuclear reactions occurring in the solid under the influence of the radiation; (5) the non-equilibrium electrons and holes produced by the ionisation of atoms and the excitation of electrons (ionisation effects) may be localised on biographic defects to form F- and V-centres respectively, and the ionisation effects may lead to coloration, luminescence, and the formation of free radicals; and (6) thermal peaks are high-temperature regions containing a few thousand atoms and reaching 1000 K, such defects being formed along the path of a fission fragment or a dislodged charged atom.

The various types of electromagnetic and corpuscular radiation are able in general to induce any type of disturbance in a solid, but the efficiency of formation varies. Furthermore, the mechanisms of the action of radiation on metals and on semiconductors are not identical[6]. Ionisation effects, which occur with almost all types of radiation, are very short-lived in metals, since they are rapidly reduced by radiationless transitions. Relatively stable changes occur only on the direct transfer of energy to the atomic framework of the lattice, with the generation of Frenkel pairs (interstitial atom + vacancy). Therefore the most intense effect is produced by bombarding metals with neutrons or heavy charged particles. Semiconductors and dielectrics, in contrast, are distinguished by the ease of formation of diverse stable defects.

The first of three possibilities when non-metals are irradiated[7] involves only direct ionisation, i.e. the production of non-equilibrium charge carriers. Such an effect is observed when X-rays, γ-rays, fast electrons, or positrons are used. The excess concentration of free current carriers of the same sign is given by the formula $\Delta n = g\tau$, where g is the rate of generation of carriers (which is proportional to the intensity of the γ-irradiation) and τ is their average lifetime[8,9]. Since τ is usually extremely short, specimens possess no radiation "memory". Under these conditions stable defects can appear only when electrons or holes are localised on biographic surface defects.

In the second case[7] irradiation (mainly neutron) initiates a nuclear reaction, which enriches the semiconductor with a donor or an acceptor impurity. This irreversible process, which is accompanied by a shift in the electron equilibrium, can become significant only when atoms having a sufficiently large capture cross-section for neutrons are present in the substance.

The third possibility is that the specimen possesses a brief "memory" owing to the appearance of interior structural defects of the Frenkel type. Atoms that have penetrated into interstices contribute new donor levels to the energy spectrum of the semiconductor, and vacancies contribute acceptor levels, which are responsible for the shift in the electron equilibrium [10]. It was suggested [11] that, as along as the energy parameter of the bombarding particle $\epsilon = mE/M$ is large in comparison with the forbidden gap E_e of the crystal (m is the mass of the electron, M the mass of the particle, and E the kinetic energy of the latter), it dissipates most of its energy on ionisation processes. When $\epsilon < E_e/8$, elastic collisions begin to predominate, leading to the displacement of lattice atoms. The number of atoms displaced in unit volume in unit time is [12] $N_d = \varphi n \sigma_d \bar{\nu}$, where φ is the density of incident particles, n the density of atoms, σ_d the cross-section of collisions leading to displacements, and $\bar{\nu}$ the mean number of atoms displaced by a primary atom, given by [13] $\bar{\nu} = 0.5[1 + \ln(E_m/2E_d)]$, in which $E_m = 4MM'E/(M + M')^2$, while E_d is the threshold energy of displacement of an atom and M' its mass. The displacement of atoms in dielectrics, in contrast to semiconductors, may be caused also by ionisation phenomena, which sometimes play a leading role. Various mechanisms of formation of these defects were suggested by Varley [14] and by Seitz [12].

Diffusion of the resulting vacancies and interstitial atoms produces an annealing effect as a consequence of their mutual annihilation. Thus after a certain time specimens of n-germanium that had been exposed to α-particles [15] acquired their original properties, but the annealing of specimens initially having p-conductance was only partial: the conductivity and the Hall coefficient did not return to the values characteristic of unexposed semiconductors. A series of theoretical studies have been made on the kinetics of the annealing of Frenkel pairs [16-19]. The saturation of radiation effects during prolonged exposure at high temperatures may be due to annealing.

III. EFFECT OF IONISING RADIATION ON THE ADSORPTIVE POWER AND THE CATALYTIC ACTIVITY OF SOLIDS

The influence of ionising radiation on the catalytic properties of solids should be interpreted in terms of one of the current theories of heterogeneous catalysis, which involve different concepts of the primary mechanisms of the interaction of the reactants with the catalytic surface. According to Balandin's theory [20] the activity of a catalyst depends on the presence in its lattice of atomic groupings (multiplets) arranged in definite fashion, on which reactant molecules are adsorbed and thus activated. If the changes in the lattice parameters produced by the ionising radiation contribute to the establishment of such a structure, the radiation will have a promoting effect on the solid catalyst; when exposure results in the degradation of active multiplets, poisoning of the catalyst is observed.

The electronic theory of catalysis [21] is based on the hypothesis that the free electrons and holes localised on surface defects play an active part in the primary acts of adsorption and activation of reactant molecules on a semiconductor catalyst surface. Since their equilibrium concentration depends unambiguously on the position of the Fermi level in the band structure of the semiconductor, any factor (including radiation) that displaces this level will cause a change in the catalytic properties of the specimen. These concepts form the basis of theoretical studies [22,23] on the influence of radiation on the adsorptive power and the catalytic activity of semiconductors. Experimental techniques have been described in detail [24] for the oxidation of carbon monoxide on nickel(II) oxide exposed to γ-rays. Some idea of the present state of the problem of the action of radiation on the adsorption and catalytic characteristics of solids can be obtained from reviews [25,26].

1. Adsorption

Investigation of the adsorption properties of irradiated specimens will give a clearer idea of the disturbances, produced than will examination of catalytic reactions, which usually have a complicated mechanism.

The chemisorption of hydrogen on zinc oxide (an n-type semiconductor) at 20°C hardly affects the electrical conductivity of the adsorbent, whereas chemisorption under the influence of γ-rays is accompanied by a considerable increase in conductivity [27]. The explanation given was that hydrogen is adsorbed in an uncharged form in the absence of radiation, whereas in a radiation field the free holes produced are captured by hydrogen molecules. This excludes recombination with the latter of the free electrons, which are involved in conduction. In contrast, the chemisorption of oxygen in the absence of radiation leads to a sharp fall in conductance, and, when it is switched on, additional chemisorption takes place with simultaneous increase in conductivity. The probable reason is that exposure converts oxygen into a form with a smaller negative charge, and also that the concentration of excess current carriers increases in the bulk of the zinc oxide. In the absence of irradiation neither hydrogen nor oxygen was chemisorbed on aluminium oxide (in contrast to zinc oxide) at 20°C, but in the presence of γ-rays the chemisorption of oxygen was more rapid than that of hydrogen [28]. This was attributed to the presence in aluminium oxide of a considerable number of efficienct centres, which captured some of the free holes necessary for the chemisorption of hydrogen.

The quantity of hydrogen chemisorbed on a γ-alumina surface was used [29] to determine the maximum density of adsorption centres ($\sim 5.5 \times 10^{12}$ cm^{-2}) produced by continuous cobalt-60 γ-rays at a dosage rate of 350 rad s^{-1}. On preliminary irradiation this quantity was $\sim 3 \times 10^{11}$ cm^{-2}. Electron spin resonance established the approximate equality of the concentration of radiation defects responsible for the adsorption of hydrogen and of paramagnetic centres produced by the irradiation of aluminium oxide. A study was made [30] of the effect of such radiation on specimens of γ-alumina differing in specific surface. The intrinsic volume of one adsorption centre was found for each case from the specific surface and the number of active centres (determined kinetically). The chemisorption rate constant for hydrogen increased on passing from small to large such volumes. The rate of chemisorption is given [31] by the equation

$$-\frac{dp}{d\tau} = \alpha K p^{\frac{1}{2}} I S (1 - \theta),$$

where p is the pressure of hydrogen, τ the time, α the surface density of adsorption centres, I the dosage rate, S the total area of the catalyst, and θ the proportion of adsorption centres occupied.

Despite the variation in the phase constitution and the specific surface of the adsorbents used, the initial rates of chemisorption of oxygen on the γ-irradiated aluminium

oxide were approximately the same [32], and the radiation efficiency of chemisorption of molecules was closely similar to the yield of pairs of excess current carriers. Termination of exposure led to cessation of radiation chemisorption, which indicated the short lifetime of the adsorption centres. The initial rate of chemisorption was directly proportional to the quantity of catalyst and the power of the γ-rays, but independent of the oxygen pressure [33]. The chemisorption was irreversible, the maximum number of chemisorbed molecules being 2.5×10^{12} cm^{-2}.

In the Reviewers' opinion the above publications leave no doubt that free current carriers generated by the radiation are involved in the adsorption of hydrogen and oxygen on semiconducting adsorbents, with the chemisorption of hydrogen involving free holes, and that of oxygen free electrons of the semiconductor. In both cases the initial rate of chemisorption is directly proportional to the power of the radiation. The fact that the initial rate of adsorption of oxygen, in contrast to that of hydrogen, is independent of the pressure is probably due to the more efficient adsorption of oxygen by the irradiated aluminium oxide [28].

Exposure of γ-alumina in equilibrium with carbon monoxide to cobalt-60 γ-rays at 300 K results in almost complete adsorption of the gas [34]. If irradiation was terminated before adsorption was complete, a post-radiation effect was observed: with rise in temperature from 300 to 375 K the initial rate of adsorption remained unchanged, but then began to fall, owing to thermal annealing of the active centres produced by the radiation. Adsorption of carbon monoxide, nitrous oxide, and oxygen at 77 K on γ-alumina exposed to γ-rays either previously or during adsorption (dosage rate 1000 rad s^{-1}) produced no change in form or intensity of the electron spin resonance spectrum [35]. Thus adsorbed gases do not interact with paramagnetic centres formed on irradiation, but heating γ-alumina with carbon monoxide or oxygen to 300 K was accompanied by a change in the e.s.r. signal. In contrast to carbon monoxide, the extra quantity of carbon dioxide adsorbed in the field of the γ-rays (300 rad s^{-1}) was $<10\%$ of the quantity adsorbed by aluminium oxide in the thermal process [36]. The activation energy of desorption of carbon dioxide from the surface was the same (4.5 kcal mole^{-1}) whether or not the adsorbents had been irradiated and whatever the dosage. When specimens on which carbon dioxide had been adsorbed by means of radiation were kept for 30 days or were heated, the bonding became stronger (the activation energy increased to 11 kcal mole^{-1}).

Several other cases have been noted of enhanced adsorptive power resulting from the irradiation of solids. Thus silica gel exposed to cobalt-60 γ-rays was a considerably more active adsorbent for nitrogen, hydrogen, carbon monoxide and dioxide, ammonia, and ethylene than before exposure [37], which was attributed to detachment of hydroxy-groups from the surface or direct interaction of the ionising radiation with gas molecules. Exposure of γ-alumina to cobalt-60 γ-rays (300 rad s^{-1}) had a favourable influence on the quantity of ethylene adsorbed and strengthened its bonding with the surface [38].

The system comprising benzene and silica gel exposed to γ-rays (640 rad s^{-1}) at the temperature of liquid nitrogen was studied in detail [39,40]. The radiation leads to the reaction

$$\equiv Si{-}O{-}H \rightarrow \equiv Si{-}O^{\cdot} + H$$

in the silica gel; the liberated hydrogen atoms either combine to form molecules or interact with benzene molecules to form $C_6H_7^{\cdot}$ radicals. The silica-gel radicals $-Si-O^{\cdot}$ are also able to react with benzene molecules and $C_6H_7^{\cdot}$ radicals:

$$\equiv Si{-}O^{\cdot} + C_6H_6 \rightarrow \equiv Si{-}O{-}C_6H_6^{\cdot}$$

$$\equiv Si{-}O^{\cdot} + C_6H_7^{\cdot} \rightarrow \equiv Si{-}O{-}C_6H_7 \ .$$

If hexane molecules had been present on the silica-gel surface their interaction with hydrogen atoms would have yielded $C_6H_{13}^{\cdot}$ radicals [41].

Preliminary irradiation also affects the adsorption properties of solids, though usually to a less extent. Silica gel after treatment with γ-rays, for example, acquires an appreciable ability to adsorb hydrogen [42]. This is accompanied by the appearance of colour centres, which were identified [42] with holes associated with excess of oxygen in the silica. The adsorption of hydrogen involved interaction of these holes with electrons of the gas molecules, with consequent decolorisation of the colour centres. Reactor radiation, hard X-rays, γ-rays, and exposure to slow electrons from a high-frequency discharge promoted the adsorption of gases by silica gel [43] in the sequence—carbon dioxide < oxygen < hydrogen—but with proton beams and α-rays the adsorption capacity increased from hydrogen to carbon dioxide and oxygen. No stimulation of the adsorption of argon by radiation was detected. The absorptive capacity of irradiated silica gel for hydrogen increased with its contamination by aluminium [44]. That of beryllium oxide for hydrogen was only slightly enhanced by exposure to γ-rays [45]. Exposure of γ-alumina to fast neutrons impared its adsorptive properties for krypton [46], and to n,γ-rays those for benzene and water vapour [47]. Treatment of nickel oxide in a nuclear reactor increased the subsequent sorption of hydrogen and oxygen [48].

It may be concluded from the above results that the enhancement of the adsorptive power of oxides produced by radiation is in many cases due to the appearance of non-equilibrium current carriers in their interior and on the surface. However, whereas free electrons or holes are the main agents in the continuous exposure of adsorbents, the centres of adsorption after preliminary irradiation are charge carriers produced by the radiation and trapped by biographic or radiation surface defects. Thus analysis of numerous e.s.r. spectra of irradiated sorbents before and after the adsorption of oxygen, carbon monoxide, and other electron acceptors indicates [49] that paramagnetic centres formed in a solid by the trapping in structural defects of electrons generated by the radiation are transformed into molecular ions—O_2^-, CO^-, CO_2^-, etc.

2. Isotopic Exchange and Ortho–Para Conversion of Hydrogen and the Isotopic Exchange of Oxygen

Isotope exchange is one of the simplest reactions, with a comparatively simple experimental technique. Together with the ortho–para conversion of hydrogen such exchange has therefore been used quite often as a model reaction.

Electron diffraction revealed structural disturbances in the metal lattices after the pretreatment of platinum and nickel catalysts with accelerated argon ions, which affected the rate of exchange between hydrogen and deuterium [50]. Preliminary bombardment of magnesium oxide with neutrons increased the rate of this exchange and of the ortho–para conversion of hydrogen [51,52], which e.s.r. data showed to be due to the appearance of electrons localised on surface radiation defects. On the other hand, these reactions were slower on specimens of alumina that

had first been irradiated with neutrons. If, however, the aluminium oxide contained small additions of salts of transition metals, n,γ-radiation had a considerable activating influence for the ortho–para conversion of hydrogen[54]. Enhanced catalytic activity towards deuterium–hydrogen exchange was observed[55] in irradiated powdered oxides—ZnO, MgO, V_2O_5, $BaTiO_3$, $CaSiO_3$, $KAlSi_3O_8$, etc.—whose treatment with neutrons in a nuclear reactor resulted in a considerable change in the rate of the process, whereas γ-irradiation was far weaker in increasing the rate, and sometimes had hardly any effect.

The rate of exchange on titanium dioxide at the temperature of liquid nitrogen increased by a factor of 10^4 after γ-irradiation (dosage rate 120 rad s^{-1}, integral dose 1.7×10^7 rad).[56] When the temperature of the irradiated catalyst rose to 0°C, its activity dropped sharply and the e.s.r. signal became weaker.

Parallel variation of the e.s.r. spectrum and of the catalytic activity towards deuterium–hydrogen exchange was established also for the pretreatment of silica gel with γ-rays (integral dose from 2×10^5 to 2×10^7 rad).[57] The activity of the catalyst increased with the radiation dose, the duration and temperature of the heat-treatment preceding irradiation, and also the contamination of the specimens with aluminium. The considerably more rapid annealing of catalytic activity in hydrogen than in a vacuum was attributed to irreversible adsorption of hydrogen on active centres of the catalyst, which, according to optical and e.s.r. spectroscopy, were holes stabilised on oxygen atoms adjacent to aluminium atoms. After γ-irradiation (dosage rate 1.2×10^{17} eV g^{-1} min^{-1}) the activation energy of deuterium–hydrogen exchange had fallen from 9 to 2 kcal $mole^{-1}$, which was regarded[58] as due to a change in the reaction mechanism. The increase in the rate of exchange between hydrogen and deuterium observed in ethylene was attributed[59] to the appearance of unpaired electrons in the γ-irradiated aluminosilicate catalyst (dosage rate 100 rad s^{-1}, integral dose 1.5×10^6 rad). Their concentration was determined by e.s.r. as 4×10^{18} spins g^{-1}. The enhancement of the catalytic activity of aluminosilicate cracking catalysts towards this reaction after their γ-irradiation was accompanied by an increase in optical absorption by the specimens, both parameters increasing with the radiation dose. However, no direct relation was detected between the numbers of active centres and colour centres during annealing.

γ-Irradiation (2×10^7 eV g^{-1} min^{-1} for 0.5 h) had a promoting effect on the subsequent catalysis for γ-alumina of deuterium–hydrogen exchange at −78°C.[61] It is significant that radiation treatment of specimens already subjected to thermal activation at 400°C and of unactivated specimens increased their activity by factors of 7 and 1000 respectively, although in the latter case the radiation effect underwent more rapid annealing. The active centres were identified[61] with electrons or holes localised on structural defects, which was supported by results[62,63] recording the appearance of signals due to paramagnetic resonance absorption in γ-alumina after its treatment with γ-rays. The conclusion that short-lived radiation defects are not involved in deuterium–hydrogen exchange is inconsistent with data[64] indicating a sharp fall in catalytic activity of the γ-alumina after the γ-rays had been switched off. The initial reaction velocity in a system comprising 10% of hydrogen, 10% of deuterium, and 80% of helium over aluminium oxide was increased by irradiation by a factor of 1000 at 50°C, but only by factors of 4–5 at 150°C, owing to thermal annealing of the radiation active centres in the catalyst[64]. Investigation of the influence of β- and γ-rays, and also of ultraviolet radiation, on isotope exchange between benzene and heavy water on the surface of platinum dioxide[65] showed that the reaction was accelerated only by the action of radiation on the reaction mixture.

The effect of the temperature of preliminary conditioning of a catalyst on the magnitude of the radiation effect[61] has been observed by many other workers. Thus the rate of the ortho–para conversion of hydrogen on the surface of magnesium oxide that had been thermally activated at 675°C remained unchanged after irradiation of the catalyst by cobalt-60 γ-rays[66], but if the specimen had been activated at 500°C, its subsequent irradiation trebled the activity. When the system was irradiated during the reaction, the rate of the latter increased tenfold. It was concluded[66] that the action of the radiation involves neither an increase in the adsorption of hydrogen nor its radiolysis.

A detailed investigation on α-alumina that had been exposed to cobalt-60 γ-rays (10^{18} eV g^{-1} h^{-1}) at 77 K showed[67] that specimens that had been activated at 560°C exhibited no e.s.r. signal and their catalytic activity remained unchanged after irradiation, which caused a signal to appear. Hence unpaired electrons produced during irradiation are unable to influence the course of the reaction, which supports the view[67] that the action of coupled electrons is necessary for the dissociation of hydrogen molecules. However, the activity of a specimen that had been preheated at 200°C—insufficient for its activation—and then irradiated reached that of a specimen that had been activated at 550°C.

It can thus be accepted as fully proved that the radiation sensitivity of catalysts for deuterium–hydrogen exchange diminishes with rise in the temperature of their thermal activation. A study of the effect of neutron irradiation or bombardment with α-particles on the catalytic properties of strongly activated γ-alumina specimens even revealed a negative radiation effect[68]. This work also showed that poisoned catalysts—water, hydrogen, and acetylene were used as poisons—were more sensitive to radiation. A mechanism is therefore quite likely in which irradiation, like high-temperature evacuation, removes from the catalyst surface foreign gases blocking the active centres.

Several papers have recently appeared[1] on the action of radiation on homomolecular oxygen isotope exchange. Although this reaction does not take place on silica gel, it occurs at an appreciable rate on specimens exposed to integral doses $\geqslant 7 \times 10^6$ rad of cobalt-60 γ-rays[69,70]. The degree of conversion increases with the total catalytic surface area and the radiation dose. This effect was attributed to the formation of active centres of the type $\geq Si^{\cdot}$ or $\geq SiO^{\cdot}$ in the silica. After the action of γ-rays on lanthanum, samarium, and gadolinium oxides the rate of the process increased hundredfold[71]. More detailed study of the reaction on gadolinium oxide exposed to cobalt-60 γ-rays (integral dose 4×10^5 to 1.8×10^7 rad) at −85°C revealed an interesting relationship[72]: with increase in the integral dose the catalytic activity increased, and then somewhat diminished; after repeated growth in activity, the latter became independent of the radiation dose. The decrease in catalytic activity on exposure to doses exceeding 1.2 Mrad was explained by the association of primary defects. The secondary increase in activity was probably due to an increase in the number of association complexes.

Under a pressure of 20 mmHg at temperatures of 300° to 400°C the rate of exchange of oxygen on neodymium

oxide was approximately the same in a field of cobalt-60 γ-emission (200 rad s^{-1}) as in the absence of irradiation. Below 300°C there was hardly any change on the unexposed sesquioxide, but under irradiation the rate increased as the temperature fell from 300 to 20°C. This is because at low temperatures the reaction velocity on biographic active centres became incomparably smaller than the rate on radiation defects. At high temperatures the exposure of various oxides to cobalt-60 γ-rays did not lead to their activation, but at low temperatures their activity increased initially in proportion to the radiation dose, and then ceased to depend on it[74]. The radiation susceptibility diminished on passing from dielectrics to intrinsic semiconductors, and disappeared completely in substances having a forbidden gap <2 eV.[74] Similar results were obtained with preliminary radiation modification of the oxides. The activity of specimens that had been irradiated in an atmosphere of oxygen exceeded the activity of those that had been exposed in a vacuum.

In spite of the many experimental results on isotope exchange, it is still difficult to reach any conclusions on general aspects of the process or on its mechanism. Only the dependence of the radiation susceptibility of catalysts on the width of the forbidden gap[74] is of universal character, as we shall see later.

3. Decomposition of Hydrogen Peroxide and Certain Other Compounds

Study of the effect of radiation on the rate of decomposition of hydrogen peroxide was initiated[75] by recording the decrease in the catalytic activity of platinum during the reaction occurring in an X-ray field. Radiation poisoning of platinum is produced also by pretreatment with γ-rays[76]. Other workers also found[77,78] that exposure of platinum catalysts deposited on semiconductor carriers to a mercury–quartz lamp has an adverse influence on their catalytic properties in a subsequent reaction. Especially strong deactivation was observed when the dielectric silicon dioxide was used as carrier. However, direct γ-radiation of the hydrogen peroxide–platinum reaction system resulted in an appreciable increase in the rate of decomposition of the peroxide[79].

Another study[80] demonstrated the role of the carrier in the activation of a silver–silver oxalate catalyst by γ-rays (integral doses 2×10^3, 1.2×10^5, and 2.4×10^5 rad). The activity of the catalyst had changed little after irradiation, but was increased by subsequent heating. The explanation offered was that radiolytic silver, formed in the carrier on exposure, accelerated thermal decomposition of the salt with the separation of active silver. Introduction of a β-ray source (the sulphur-35 isotope) into the carrier of an iron phthalocyanine–barium sulphate catalyst improved the stability of the catalyst: the number of moles of hydrogen peroxide decomposed per mole of iron phthalocyanine decomposed increased in direct proportion to the specific radioactivity of the specimen[81]. Thus with catalysts of specific radioactivity 10.2 and 238.0 mc g^{-1} the stability increased by 9% and 45% respectively.

The decomposition of hydrogen peroxide on neodymium oxide was accelerated after pretreatment of the latter in a nuclear reactor[82]. The active centres thus formed were so stable that annealing the catalyst at 110°C for 24 h, though lowering the activity, did not bring it down to that of the unirradiated specimen. The rate of decomposition of hydrogen peroxide on nickel oxide and the quantity of excess oxygen adsorbed both increased in parallel with the energy absorbed from cobalt-60 γ-rays (integral dosage $10^7 - 8 \times 10^9$ rad).[83] With a dose of 10^8 rad the catalytic activity of the nickel oxide was double that of unirradiated specimens. The electrical conductivity of the oxide simultaneously diminished.

Many workers choose the decomposition of formic acid as model reaction. Thus the catalytic activity of copper and silica gel is somewhat improved after bombardment with fast neutrons[84]. An interesting study was made of this reaction[85,86] occurring at a high temperature on a single crystal of silver pre-irradiated with accelerated argon ions. Electron diffraction showed that the radiation treatment led to the formation of point defects and dislocations in the crystal lattice. Two competing processes—increase in the activation energy of decomposition and enhancement of the reproducibility coefficient†—were involved. Depending on which face of the single crystal was subjected to ion bombardment, one of these processes predominated, and thereby determined the sign of the radiation effect.

Preliminary irradiation of a catalyst comprising a mixture of aluminium and silicon oxides in a nuclear reactor somewhat lowered the rate of cracking of cumene at 300–450°C.[87] However, if the specimen had been "alloyed" with zinc and vanadium additions before exposure, the rate of the process was more than doubled, which indicated that impurity centres played an active part. A possible mechanism of interaction between corpuscular radiation and impurity atoms was illustrated[88] by the decomposition of nitric oxide on catalysts consisting of alumina (a dielectric), nickel monoxide (a *p*-type semiconductor), and tin dioxide (an *n*-type semiconductor) with additions of boron and lithium oxides. After exposure to neutrons (dosage rate 10^{11} n cm^{-2} s^{-1}) for 3 h and standing for 1 month, the tin dioxide showed an increase, and the nickel monoxide a decrease, in catalytic activity. The reaction velocity had diminished on the catalyst comprising 90% Al_2O_3 + 10% Li_2O, but had increased on 90% Al_2O_3 + 10% B_2O_3. This was attributed to a change in the electronic properties of the oxides, both directly under the influence of the neutron irradiation and as a result of interaction with α-particles generated in the course of the nuclear reaction of lithium-6 and boron-10 atoms with neutrons.

Pretreatment of a copper catalyst with neutrons (integral flux 3×10^{18} n cm^{-2}) lowered the activation energy of the dehydrogenation of cyclohexane from 41 to 17.5 kcal $mole^{-1}$ and accelerated the process fivefold[89]. This was attributed to the appearance of foreign (probably nickel) atoms in the specimen as a consequence of a nuclear reaction. No change in activity was observed when a copper catalyst was exposed to γ-rays. The emission from a nuclear reactor changed the catalytic activity of oxides of certain amphoteric elements in the thermal decomposition of light and heavy water[90]. This phenomenon was regarded as due to change in both electronic and structural characteristics of the specimens.

The decomposition of *n*-hexane was investigated on a potassium–chromium–alumina catalyst ($Al_2O_3 : Cr_2O_3 : K_2O$ = 90.7 : 5.6 : 3.7 mole %) irradiated in a nuclear reactor with slow neutrons [flux(0.8 and 1.2) $\times 10^{13}$ n cm^{-2} s^{-1}] and with γ-rays[91]. After the radiation treatment the yield of hydrogen diminished, while that of gaseous hydrocarbons somewhat increased, indicating more intense cracking.

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† A reproducibility coefficient is not actually mentioned in Refs. 85 and 86 (Ed. of Translation).

Roasting the exposed catalysts did not destroy the radiation effect, but the latter disappeared completely when the experiment was repeated. The parallelism between the rate of cracking and the concentration of the radioactive chromium-51 isotope produced suggested that the latter had a promoting effect. This is confirmed by results[92] for the reaction occurring on γ-alumina to which chromium or chromium-51 (a source of γ-rays) had been added: the rate of cracking increased on introduction of the latter.

The favourable effect of induced radiation was clearly shown by a study[93] of the decomposition of n-butane (dehydrogenation, cracking, isomerisation) on alumina catalysts containing 10% of vanadium(V), molybdenum(VI), and tungsten(VI) oxides respectively, after irradiation with slow neutrons (flux 10^{13} n cm^{-2} s^{-1}) in a nuclear reactor. Before irradiation the activity of these catalysts decreased in the above sequence. The catalytic activity of the first of them was unaffected by the neutron treatment (whether for 3 days or for 1 month). Prolonged irradiation of the aluminium–molybdenum oxide catalyst resulted in the appearance of the molybdenum-99 isotope, a source of β- and γ-rays, which led to a slight increase in the degree of conversion of the butane. Interaction of the aluminium–tungsten oxide catalyst with neutrons was accompanied by formation of the tungsten-185 and -187 isotopes, whose induced radioactivity far exceeds that of molybdenum-99. This was regarded as the reason why the activity of the specimens had more than doubled.

Preliminary γ-irradiation of catalysts also changed the rate of decomposition. Thus an appreciable increase in the rate for isopropylbenzene on aluminosilicate catalysts was accompanied[94] by the appearance of colour centres, formed by aluminium atoms on each of which a hole was localised. These centres were probably responsible for accelerating the reaction. An increased rate of dealkylation of isopropylbenzene was observed also after γ-irradiation of pure silica gel[95]. Here biographical defects in the catalyst surface, which trapped free holes formed under the influence of the radiation, were regarded as the active centres. The radiation treatment of silica on which a gas had been adsorbed showed that dealkylation resulted from the direct capture of free holes by the semiconductor. This yet again indicates an electronic mechanism for the radiation promotion of silicon dioxide.

Preliminary irradiation of magnesium oxide with γ-rays from a caesium-137 source (integral dose 2.5×10^7 rad) led to a decrease in the rate of decomposition of potassium perchlorate accompanied by a fall in the threshold temperature at which this reaction becomes possible[96]. Radiation was shown to produce a contraction in the crystal lattice of the oxide with the generation of free electrons. Recombination of the latter with free holes involved in the process had an adverse effect on the activity of the oxide.

Studies of decomposition occurring on solid catalysts under the influence of continuous irradiation usually attempt to elucidate how the rate of homogeneous radiolysis changes on the introduction of catalysts possessing various properties. It will be shown that such an approach enables the maximum amount of information to be extracted on the primary steps of interaction on the catalyst surface.

The rate and the degree of decomposition of potassium oxalate in aqueous solution under the influence of γ-rays increased considerably in the presence of a suspension of zinc oxide[97]. The dependence of the rate of γ-radiolysis of pentane in the presence of silica gel, magnesium oxide, or aluminium oxide on their surface coverage by the initial gas suggested[98–101] the active transfer of the emission energy absorbed by the solid to the adsorbed molecules. It was assumed that use was made of the energy evolved on the annihilation of electron–hole pairs generated in the oxides by the radiation, this process involving holes localised on adsorbed pentane molecules and free electrons.

The importance of short-lived radiation defects was confirmed[102] by the hundredfold increase in the yield of hydrogen from the γ-radiolysis of water when the process occurred on a silica-gel surface. Electron spin resonance showed that the emission was unable to create permanent defects in the catalyst but only excited states, whose energy was consumed in the decomposition of adsorbed molecules. A strong dependence of radiation-chemical yields on the surface coverage of solids by the starting material was observed also in the γ-radiolysis of heptane on aluminosilicate, aluminium–tungsten, and aluminium–molybdenum catalysts[103–105] and in the decomposition of isopropylbenzene on aluminium silicate[106,107]. The equality of the rates of homogeneous and heterogeneous processes when surface coverage by the initial molecules exceeds a monolayer indicates that the emission energy is transferred only to the first adsorbed layer. The ability of solids to transmit emission energy to adsorbed molecules is strongly dependent on their chemical nature. Thus the rate of the γ-radiolysis of ammonia on a zeolite in the sodium form exceeded considerably the rate of the homogeneous process[108–110], but when the calcium form was used the yield of hydrazine was the same in the two cases.

The view that a catalyst is an energy converter, transforming one type of motion (e.g. the kinetic energy of substrate molecules) into a different form important for the activation of molecules (e.g. into the vibrational energy of molecules), was expressed as early as the 1920s.[111] This concept formed the basis of the first theoretical interpretation of the phenomena involved in the effect of radiation on the catalytic properties of solid materials[112]. The hypothesis[113] that the radiation-catalytic activity of solids is determined by their heat capacity, increase in which should be accompanied by a decrease in activity, has not found experimental confirmation.

The rate of decomposition of carbon dioxide exposed to cobalt-60 γ-rays, X-rays, and strontium-90 β-rays is sharply increased by the introduction of silica gel, alumina, and magnesium oxide into the system[114,115]. Radiation-chemical yields are extremely slightly dependent on temperature and on the nature of the emission. Investigation of this reaction occurring under the influence of γ-rays (2.8 Mrad h^{-1}) on oxides having different electronic characteristics led to the conclusion[116] that the intensity of heterogeneous radiolysis diminishes from intrinsic to n-type and then to p-type semiconductors. The high-temperature γ-radiolysis of water vapour accelerated considerably in the presence of zinc oxide, with a forbidden gap of 3 eV; the effect of vanadium pentoxide, with a gap of 0.5 eV, was hardly noticeable[117].

The deduction that energy is transmitted to the adsorbed substance more efficiently in the case of dielectrics and semiconductors is supported by many investigations. Thus the degree of decomposition of azoethane fell on passing to catalysts having a narrow energy gap, to magnesium(II), silicon(IV), titanium(IV) oxides, (8.7, 8.0, and 3.0 eV respectively), etc.[118,119] This problem was examined in detail in studies[120,121] of the dehydrogenation of cyclohexane on dielectric oxides (silica, alumina, aluminium silicate), n- and p-semiconductors (zinc and nickel monoxides), and metals (nickel, 7% platinum/

/silica). In the thermal process the specific activities of the catalysts formed the sequence

$$Pt/SiO_2,\ Ni > NiO > ZnO,\ Al_2O_3 \cdot SiO_2 > MgO,\ ZrO_2,\ Al_2O_3,\ SiO_2.$$

Under the influence of continuous γ-irradiation (3.4×10^{16} eV g^{-1} s^{-1}) the relation between the activities was inverted: materials having a wide forbidden gap were the most active. It is significant that, in contrast to semiconductors and metals, radiation-active dielectrics showed the presence of paramagnetic centres and $C_6H_7^{\bullet}$ radicals when cyclohexane was adsorbed during irradiation. The dependence was interpreted[120,121] on the hypothesis that the cyclohexane molecule is activated by the energy evolved on recombination of a free electron with a hole previously trapped by the molecule. This energy is equal to the difference between the width of the forbidden gap and the heat of adsorption of the gas molecule, so that substances having a wide energy gap should possess the maximum activity. The conclusion that free current carriers—not stable defects—play the main part in the decomposition of cyclohexane is supported by the fact[122] that the degree of decomposition of the initial gas on an aluminosilicate catalyst (10% Al_2O_3) under direct γ-irradiation exceeds considerably the extent of decomposition on a previously irradiated specimen.

While completely accepting the viewpoint of the authors[120,121], the Reviewers would like to stress that it would have been wrong to base prediction of the radiation-catalytic activity of solids solely on the width of the forbidden gap, without regard to the heat of adsorption of the molecules. Furthermore, the recombination of electron–hole pairs on adsorbed molecules may meet serious competition from their recombination on other local centres (impurities, defects), which are present in abundance on solid surfaces.

4. Decomposition of Alcohols and Isomerisation of Hydrocarbons

Although the catalytic decomposition of alcohols usually takes place by a fairly complicated mechanism, study of this particular class of reactions has revealed several interesting laws governing the interaction of reactants with the surface of irradiated catalysts. The dehydration of n-decanol and isomerisation of the resulting dec-1-ene were studied[123,124] on samples of alumina that had been subjected to preliminary irradiation. X-Rays had a favourable effect on the degree of conversion, treatment with cobalt-60 γ-rays and reactor n,γ-radiation lowered the catalytic activity of the oxide, and exposure to fast neutrons produced no observable change. Interesting results were reported[125] for this reaction occurring on alumina that had been exposed to neutrons (8×10^{12} n cm^{-2} s^{-1}) for 1–10 days. Catalysts that had been irradiated for a few days exhibited a negative radiation effect. The yield of unsaturated hydrocarbons increased as the duration of neutron bombardment was lengthened. This was attributed to the occurrence of two competing processes—the negative influence of the direct interaction of neutrons with active centres in the alumina and the promoting effect of the high-energy radiation emitted from the short-lived aluminium-28 and oxygen-19 isotopes formed in the specimens as a result of a nuclear reaction.

The catalytic activity of silica in the isomerisation of butene and the conversion of cyclopropane into propene was increased by preliminary irradiation with X-ray bremsstrahlung[126]. The rate of the second process diminished when the catalyst was heated to 100°C, and fell sharply at 200°C, whereas the activity of the silica towards the first reaction became appreciably lower only at 400°C. This was explained by the generation of two types of active centres on the surface. The great thermal stability of the radiation active centres involved in the isomerisation of butene was noted also in the neutron pretreatment of silica gel, aluminium silicate[127], and also potassium aluminate catalysts[91], which exhibited a fifty-fold radiation activation.

Study of the thermal dissociation of ethanol on neutron-treated zinc oxide—(2.3 and 3.9) $\times 10^{13}$ n cm^{-2} s^{-1}—showed[128] that increasing the duration of the radiation intensified dehydrogenation and tended to suppress dehydration. This effect was attributed[129] to the appearance of gallium as donor impurity in the zinc oxide, which raised the Fermi level and should thus[21] lead to a similar change in selectivity of the catalyst. The shift in the decomposition of propan-2-ol towards dehydrogenation after the irradiation of yttrium[130] and neodymium[131] oxides with thermal neutrons (1.2×10^{13} n cm^{-2} s^{-1}) was explained by production of the radioisotopes—yttrium-90, terbium-166 and neodymium-147, neodymium-149.

Many studies have confirmed the decisive role of the electronic properties of irradiated catalysts in the decomposition of alcohols. For example, the rate of dehydrogenation of ethanol on copper(II) oxide increases after its γ-irradiation, with an increase in the electrical resistance, but on copper(I) oxide it falls in parallel with the latter[132]. Continuous exposure of zinc oxide (an n-semiconductor) to γ-rays (4.5×10^5 r h^{-1}) activated it for the dehydrogenation of methanol, whereas chromic oxide (a p-semiconductor) was poisoned under the same conditions[133] (the increase in the rate of this reaction on zinc oxide when γ-irradiation was begun has been confirmed[134,135]). Exposure of two preparations of tungsten disulphide differing in stoichiometric composition[136]—$WS_{1.99}$ (an n-semiconductor) and $WS_{2.3}$ (a p-semiconductor)—to a flux of slow neutrons (1.2×10^{13} n cm^{-2} s^{-1}) and to γ-rays (10^4 r s^{-1}) in a reactor led to the formation in the bulk of the specimens of the tungsten-187, tungsten-185, and sulphur-35 isotopes (β- and γ-sources), which activated the disulphides for the dehydration of n-decanol; the electrical conductivity of the first preparation fell, whereas that of the second preparation increased.

Among investigations on the decomposition of alcohols on solids into which radioactive isotopes had been introduced during preparation, note must be taken of a series of papers by Balandin, Spitsyn, and their coworkers. The increases in the degree of dehydration at 350°C of alcohols on magnesium sulphate catalysts containing the radioactive sulphur-35 isotope, in comparison with specimens to which non-radioactive sulphur had been added, were respectively 200%, 121%, 42%, and 26% for n-pentanol, n-hexanol, n-decanol, and n-dodecanol[136,137].

The effect of internal β-emission on the catalytic properties of solid materials was thoroughly studied[138–141] with as example the dehydration of cyclohexanol on magnesium sulphate to which had been added sodium sulphate and calcium chloride containing either non-radioactive sulphur and calcium or their radioactive isotopes sulphur-35 and calcium-45. The non-radioactive additives diminished significantly the catalytic activity of the magnesium sulphate, whereas the radioactive additions, while themselves not catalysing the reaction, increased considerably the degree of dehydration. Activation energies for the reaction on the radioactive specimens were somewhat

lower. A linear relation was observed between the activity and the dosage rate of self-irradiation of the catalysts: the degree of conversion of the alcohol increased in parallel with the specific activity of the specimens.

The mechanism of the influence of internal radioactive emission on the catalytic properties of solids evidently differs from that of external radiation. For example, the degree of dehydration of n-dodecanol on alumina diminished on continuous irradiation of the system with electrons, but introduction of a source of electrons (calcium-45) into the catalyst increased sharply the activity of the specimen[123]. The same conclusion can be reached by comparing the above results[138-141] with data[142] indicating that exposure of the cyclohexanol–magnesium sulphate system to external X-rays does not increase the degree of dehydration of the alcohol, although it produces high-energy electrons within the catalyst. Electron-microscopic investigation[143] of non-radioactive specimens of potassium, magnesium, and barium sulphates and of molybdenum trioxide, as well as specimens containing various quantities of radioactive sulphur and molybdenum isotopes, showed that the radioactive substances had considerably more developed surfaces. However, this alone is insufficient to explain the enhanced catalytic activity of radioactive specimens. The catalytic activity of specimens of magnesium sulphate containing sodium sulphate labelled with radioactive sulphur, calculated per unit surface for the dehydration of cyclohexanol, increased with the β-radioactivity[144].

Among the investigations on the decomposition of alcohols under the influence of continuous external γ-irradiation we would like to note a series of papers by Vladimirova, Zhabrova, and their coworkers. The view that dielectrics are the most active in transmitting the energy of the radiation was again confirmed[145-147]: the rate of decomposition of methanol on silica and alumina exceeded the rate of the homogeneous process by a factor of 10; the rates on the semiconducting zirconium(IV), zinc(II), magnesium(II), and nickel(II) oxides by factors of 2–3; and on metals the intensification of the reaction was hardly appreciable; but the presence of activated carbon slowed down the reaction. The radiation-catalytic activities of diamond and graphite—the same chemical substance in different electronic modifications—were compared[148]. Diamond (natural and synthetic), having a forbidden gas of 7 eV, contributed to reaction velocities exceeding the rate of the homogeneous radiolysis of methanol by a factor of 100. Graphite, whose conductance is almost metallic, was not a radiation catalyst.

With the smallest (0.7%) surface coverage of silica gel the yield of decomposition products from methanol was the highest, exceeding hundredfold the yield of homogeneous radiolysis, but with a monolayer the increase was only tenfold[149]. A more detailed investigation[150,151] revealed the interesting fact that, with the same quantity of methanol on silica and alumina surfaces, their catalytic activity was independent of the specific surface and the size of the globules. This indicates yet again that free current carriers, generated by radiation inside the solid, are involved in the decomposition of adsorbed molecules, and that their diffusion from the interior to the surface is more rapid than the primary steps in the radiation-catalytic reaction. The increase in the rate of the process observed with decrease in the quantity of substance adsorbed shows that catalytic activity is determined solely by the relation between the quantity of the compound adsorbed and the excess quantity of current carriers.

Analysis of numerous experimental data suggests that the mechanism of the decomposition of methanol is[28]

$$\text{Tв solid} \xrightarrow{\text{rad.}} K^+ + A^-$$

$$CH_3OH + K^+ \rightarrow \underset{\substack{\text{physical}\\ \text{adsorption}}}{CH_3OH^+}$$

$$\underset{\text{chemical}}{CH_3OH^+} + \ominus \rightarrow \dot{C}H_2OH + H$$

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

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

$$H + H \rightarrow H_2 \ .$$

The energy evolved on the annihilation of an electron and a hole is consumed in the formation of a hydroxymethyl radical. These radicals recombine to form a molecule of ethylene glycol, and decompose to give a formaldehyde molecule.

5. Catalytic Hydrogenation

The hydrogenation of ethylene is most often chosen as model reaction, since in many cases this process does not require a high temperature. As early as 1932 a 5% increase in rate was recorded for this reaction taking place on a copper catalyst exposed to X-rays at room temperature[152].

Preliminary γ-irradiation of copper produced slight deactivation, whereas the catalytic activity of zinc oxide decreased by 80%.[153] This was attributed to a change in the charge structure of the semiconductor surface. The rate of hydrogenation of ethylene falls after zinc oxide has been exposed to γ-rays[55]. The decrease in catalytic activity of the oxide is not accompanied by change in the activation energy of the reaction, and heating the specimens restores their original properties. The active centres were assumed[154] to be interstitial Zn^+ cations, which are converted by ionising collisions with secondary electrons into inactive Zn^{2+} cations; heat-treatment promotes the reverse process. In contrast to zinc oxide, silica gel, which is not a catalyst for this reaction, was appreciably activated after γ-irradiation for 20 h.[155]

Considerable increase in catalytic activity of copper, nickel, and platinum catalysts in the hydrogenation of ethylene was observed after their bombardment with accelerated positive argon ions[156-158]. Electron diffraction recorded significant structural disturbances in the crystal lattices. Heating the metals at 550°C annealed the defects and lowered the reaction velocity to values characteristic of unirradiated catalysts. On the other hand, structural defects generated in copper by α-particles from a polonium-210 source caused a decrease in catalytic activity independently of the environment (hydrogen, vacuum) in which irradiation had occurred[159].

Examination of the effect of fast neutrons on the catalytic properties of zinc oxide showed[160] that the sign and the magnitude of the radiation effect depend on the chemical and thermal treatment of the catalysts preceding irradiation. The activity in the hydrogenation of cyclohexene of platinum catalysts deposited on aluminium silicate was unaffected by preliminary exposure to γ-rays[161]. However, the rate of this reaction was increased by the exposure of platinum–silica catalysts to a quartz–mercury lamp[162], the maximum increase in activity (double) being observed on illumination for 3–4 h. After exposure for 6 h the rate of the process returned to its initial value.

Passage of the catalytic activity through a maximum was recorded in the hydrogenation of nitrobenzene when a nickel catalyst was subjected to X-rays and β-particles [163]. This work also showed that the treatment of palladium with accelerated electrons increases the rate of hydrogenation of *p*-nitrotoluene in glacial acetic acid. The same result was obtained when platinum was exposed to β-rays of energy 3 MeV, whereas those of energy 2 MeV and X-rays produced no appreciable change. The radiation effect was attributed [163] to the appearance of defects in the structure of the catalysts.

The view that preliminary electromagnetic irradiation and exposure to a flux of light charged particles are unable to affect rates of hydrogenation appreciably is supported also by the hydrogenation of petroleum [164] and unsaturated hydrocarbons [165] on metals. Most investigators therefore relate the change in the rate of hydrogenation to the appearance of structural defects in the specimens. Thus work in which the rate of hydrogenation of acetone was trebled on neutron-irradiated specimens of nickel showed [166] that on thermal annealing the radiation activity of the catalysts disappears over a temperature range in which the number of point defects decreases sharply. Variation in the concentration of free current carriers probably also plays an important part in semiconductors subjected to γ-rays during the reaction. The positive radiation effect in the hydrogenation of carbon monoxide was found [167] to depend on the excess quantity of zinc in its oxide, which determined the electronic properties of the catalyst. The rate of this reaction trebled on zinc oxide at 160°C. [168] With rise in temperature the radiation effect diminished, and at 230°C disappeared altogether, probably owing to an increased rate of annealing of electron–hole pairs.

The influence of reactor radiation on the rate of the liquid-phase hydrogenation of dimethylprop-2-ynol and butynediol was studied by Sokol'skii et al. A comparison was made of the activities of platinum and osmium–platinum blacks obtained from the oxides with and without preliminary irradiation [169]. The considerably higher activity of the former was attributed to the increased degree of dispersion of the metals detected by X-ray diffraction. A similar pattern was observed in the hydrogenation of butynediol in ethanol on platinum and palladium catalysts [170]. This effect is due also to the appearance of impurity rhodium, silver, and cadmium atoms inside the platinum [171]. In the hydrogenation of the dimethylpropynol in dioxan on palladium catalysts obtained from the oxides exposed to neutrons and to α-particles the reaction velocity increased by 100% and 60% respectively; the rate of the process in ethanol was independent of irradiation of the oxide [172].

Pretreatment in a nuclear reactor had a beneficial effect on the catalytic activity of 5% and 0.5% of platinum, palladium, and rhodium on γ-alumina in the hydrogenation of the dimethylpropynol in caustic soda [173,174]. The largest increase in activity was observed with the 0.5% platinum catalyst, when preliminary irradiation of the metal together with the carrier increased the activity of the catalyst by a factor of 5.2, but radiation treatment of the carrier separately before deposition of the active metal led to a fiftyfold increase in the rate of the process. A similar phenomenon, though less well defined, was observed also with the palladium and rhodium catalysts. Raising the temperature of the reaction diminished the radiation effect. The change in the electronic and structural properties of the carrier under the influence of radiation probably also played a part here.

Continuous β-irradiation of a platinum plate (of thickness equal to the range of a β-particle) doubled the rate of hydrogenation of benzene, which took place on platinum black deposited on the opposite side of the plate [175]. This was due to migration to the surface of defects generated inside metal by the radiation.

6. Catalytic Oxidation

Pretreatment of platinum black with X-rays in a moist atmosphere for 2 h increased by 16% the rate of conversion of sulphur dioxide into the trioxide at 260°C; [176] if the reaction temperature was raised to 400°C, only 1.3% activation of the catalyst was observed. Radiation treatment in dry air did not affect the catalytic activity. A similar result was obtained by workers [177] who observed an increased content of oxygen, formed by the radiolysis of air, in platinum that had been exposed to X-rays in a moist medium.

Preliminary bombardment of vanadium pentoxide with thermal neutrons (10^{18} n cm^{-2} s^{-1}) diminished its activity in the oxidation of sulphur dioxide [178]. Since this reaction took place above 500°C, the radiation effect was due to the production of stable defects, probably with the appearance of silver-110 atoms—γ- and β-sources—inside the catalyst. The rate of this process decreased on the pure pentoxide also when the latter was exposed to γ-rays during the reaction [179]. The magnitude of the radiation effect is a function of the initial properties of the catalyst. Under the influence of continuous exposure to X-rays the catalytic activity of pure titanium dioxide, which has little effect on the oxidation of sulphur dioxide, increased by 18.4%; irradiation of the more effective catalyst TiO_2 + NH_4VO_3 accelerated the reaction by only 12%, but the most active catalyst TiO_2 + V_2O_5 was poisoned [180]. Similar results were obtained for the conversion of ethanol into formaldehyde on vanadium pentoxide [181].

An electromagnetic radiation field usually has a marked effect on the ability of semiconductors to catalyse oxidation. Examples are the oxidation of propane on zinc oxide under the influence of X-rays [182] and also the oxidation of various hydrocarbons on dielectrics (silica gel, alumina, aluminium silicate) subjected to γ-rays [183]. Both effects were explained by the excitation of free current carriers in the solid. This is indicated also by the invariability of the rate of oxidation of hydrogen on platinum when the system is introduced into an X-ray field [184], since the electronic properties of a metal show little response to the influence of X-rays.

Many workers have dealt at length with the conversion of carbon monoxide into the dioxide. The effect of neutron bombardment (fluxes of thermal and fast neutrons respectively 2×10^{11} and 7×10^{9} n cm^{-2} s^{-1}) of nickel oxide with 2.5 mole % of lithium oxide on the rate of this reaction has been studied [185,186]. The further intensification of the process when conducted directly in a nuclear reactor instead of on previously irradiated specimens indicates the definite roles both of short-lived defects and of stable disturbances resulting from the nuclear reaction $^{6}Li(n,\alpha)^{3}H$. A definite correlation was detected between the catalytic activity and the hole conductance of nickel oxide. Pretreatment of nickel and zinc monoxides with γ-rays had no appreciable influence on their activity [187]. However, other workers showed [188] that the γ-irradiation of nickel

monoxide in a vacuum had an adverse effect on its catalytic properties, but in an atmosphere of oxygen a beneficial effect. This was explained by the radiation-stimulated migration of activated oxygen deep into the lattice of the catalyst.

The electron bombardment—$(3-12) \times 10^{12}$ el cm^{-2} s^{-1}—of cuprous oxide led to its deactivation, in spite of an increase in the specific surface[189]. This phenomenon is connected with decrease in the concentration in the mobility of free holes in the bulk of the catalyst. Over the temperature range 80–300°C the activation energy of the oxidation of carbon monoxide on alumina under the influence of X-rays was zero, but with further rise in temperature it reached 18 kcal $mole^{-1}$, coinciding with the activation energy of the thermal process[190].

As we have been able to see, ionising radiation is a powerful factor influencing the adsorption and catalytic properties of solids. In spite of a vast quantity of experimental results accumulated by the present time, however, scientists are still far from a generally accepted interpretation of this phenomenon, and still farther from being able to use radiation to control the activity and the selectivity of catalysts. An increasing number of authors interpret radiation effects on the basis of an electronic theory of catalysis. Such an approach permits the most productive utilisation of existing theoretical ideas on the interaction of electromagnetic and corpuscular radiation with solids.

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