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Investigation of the ESR Spectra of Adsorbed Radical-ions as a Method for the Study of the Oxidation-reduction Properties of Zeolites

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The influence of the conditions in the preliminary heat treatment of zeolites, of the degree of elimination of metal cations and aluminium, and of the nature of the cation introduced and the adsorbed molecule on the oxidation-reduction properties of zeolites is examined. It is shown that the available experimental data support the model postulating the formation in zeolites of centres of different strengths, the activity of which in the formation of radical-ions is determined by the type of zeolite and the conditions in its preliminary treatment.
The bibliography includes 33 references.

CONTENTS

I. Introduction 807
II. The oxidising and reducing properties of faujasites 807
III. The oxidising and reducing properties of mordenites 815
IV. Conclusion 821

I. INTRODUCTION

The study of the nature of the acid–base centres in zeolites is a fundamental problem the solution of which is necessary for understanding the mechanism of the action of this most important group of catalysts. Studies on amorphous aluminosilicates have already shown [1] that, apart from the usual Lewis and Brønsted centres, the surfaces of these catalysts contain the so called oxidation and reduction centres, the adsorption on which of condensed aromatic systems involves a one-electron transfer, and not the transfer of an electron pair, with formation of the corresponding adsorbed radical-ions (Fig. 1). However, the nature of these centres is not yet clearly understood. Nevertheless studies in recent years have shown that the oxidation-reduction centres can play a significant role in acid–base reactions catalysed by aluminosilicates.

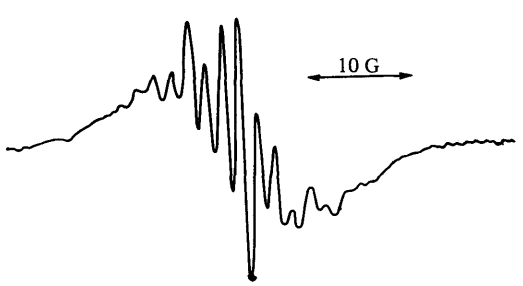


Figure 1. The ESR spectrum of anthracene adsorbed on an aluminosilicate from benzene solution [1].

The crystal structures of zeolites and the centres in these structures where cations may be located have now been quite thoroughly investigated. In recent years this situation stimulated detailed research on the oxidation-reduction centres in zeolites, which has led to new important generalisations in this field. The aim of the present review is to examine data obtained in studies, mainly by ESR, of the oxidation-reduction properties of different types of zeolites towards a wide variety of electron-donating and electron-accepting molecules.

It is not yet possible to classify the oxidation-reduction properties of zeolites according to any single characteristic of the adsorbent (the Si : Al ratio, the degree of elimination of cations or aluminium from the given type of zeolite) or according to the conditions in its preliminary treatment (heat treatment temperature, the amount of O_2 or H_2O determined). We shall therefore consider initially the oxidation-reduction properties of zeolites of types X and Y from which metal cations have been partly or completely eliminated. The review does not deal with studies in which the formation of radical-ions following the adsorption of hydrocarbons on zeolites has been observed under the conditions of external influences on the system, for example ultraviolet light or γ-radiation.

II. THE OXIDISING AND REDUCING PROPERTIES OF FAUJASITES

1. The Influence of the Degree of Elimination of Metal Cations, the Conditions in the Heat Treatment of Zeolites, and the Nature of the Adsorbed Molecule on the Oxidation-Reduction Properties of Faujasites

The adsorption of diphenylethylene, triphenylamine, quinoline, perylene, *p*-phenylenediamine, and aniline from 1 : 1 or 1 : 2 solutions in n-heptane or chloroform on type Y zeolites from which metal cations have been eliminated to different extents has been investigated [2]. The preliminary dehydration of the zeolite was carried out *in vacuo* at temperatures up to 500°C for 24 h. The substances were adsorbed in an atmosphere of pure N_2 at room temperature and the amount of adsorbed hydrocarbons was determined spectrophotometrically by measuring the concentration in the solution before and after the adsorption. Equilibrium in the adsorbate–zeolite system was attained after approximately 24 h. It was shown that the maximum degree of adsorption of triphenylamine on the NH_4Y zeolite activated at 500°C corresponds to 3.4×10^{20} molecules per gram of zeolite (one molecule per large cavity or approximately eight molecules per unit cell). The maximum number of triphenylamine radical-cations formed in the adsorption process is 1.2×10^{19} spins g^{-1}.

The authors[2] suggested that there exists definite steric hindrance to the approach of the $(C_6H_5)_2N$ molecule to the electron-accepting centre.

It is noteworthy that the concentration of neutral perylene molecules in the charge-transfer complexes formed in the perylene–iodine system[3] is also approximately 30 times higher than the concentration of the free perylene radicals produced. The alternative explanation is that the stabilisation of a single radical-cation formed may require several neutral molecules.

The influence of the temperature of activation of the zeolite towards adsorption and the formation of radical-ions has been studied for diphenylethylene[2]. It was observed that the equilibrium degree of adsorption of diphenylethylene, corresponding to ten molecules per unit cell of the zeolite, is already reached on the specimen activated at temperatures $\geq 200°C$. However, appreciable formation of radical-ions following adsorption was observed only on specimens heat-treated at approximately 400°C and the maximum concentration of radicals was noted on zeolites activated at temperatures $\geq 500°C$. In other words, for the adsorption of diphenylethylene it is sufficient to eliminate water molecules from the zeolite cavities, which occurs at 200°C, while the formation of electron-accepting centres requires higher activation temperatures (~400°C).

A similar dependence of the degree of adsorption and radical-cation concentration on the dehydration temperature of the NH_4Y zeolite was also observed for $(C_6H_5)_3N$. The degree of adsorption of $(C_6H_5)_3N$ is independent of the degree of elimination of metal cations from the type Y zeolite and corresponds to 3.4×10^{20} mol. g^{-1} or eight molecules per unit cell, which is characteristic of a specimen from which metal cations have been fully removed. However, the concentration of the triphenylamine radical-cations formed for low degrees of elimination of metal cations (up to 16 Na^+ ions from the unit cell) increases linearly with the degree of elimination of metal cations and the remains constant and equal to approximately 1.5×10^{19} spins g^{-1}.

It is known[4] that in the NaY zeolite unit cell 32 Na^+ ions are located in the plane of the six-membered oxygen rings (S_{II}), 16 ions are in the hexahedral prisms (S_I), and eight ions are in the large cavities (S_{III}). It has been suggested[2] that the exchange of only the first 16 Na^+ ions leads to the formation of electron-accepting centres. The centres formed in the course of the elimination of Na^+ ions from the S_{III} sites and partial removal from the S_{II} site, which are readily accessible to triphenylamine molecules, participate in the formation of radical-cations. However, it should be noted that a number of studies have now been published where a different distribution of Na^+ cations in NaY zeolites is suggested on the basis of X-ray diffraction data. In particular, some authors believe that 2–4 Na^+ cations remain non-localised (S_{III}) or that in general all the Na^+ cations in the unit cell are located at the S_I and S_{II} sites.

Assuming that the removal of only eight of the 56 Na^+ cations from the zeolite unit cell leads to the formation of active centres, Stamires and Turkevich[2] obtained 2.8×10^{20} centres g^{-1}, which is approximately 20 times more than the maximum number of the triphenylamine radical-cations formed (approximately 1.5×10^{19} spins g^{-1}). The possible causes of this discrepancy were discussed above. The determination of the spin–spin and spin–lattice relaxation times of the $(C_6H_5)_3N^+$ radical–cations adsorbed on the HY zeolite and measurements of the temperature dependence of the spin susceptibility for different concentrations of these radical-cations led to the hypothesis that associated species comprising neutral $(C_6H_5)_3N$ molecules, solvent molecules, and the radical-cations $(C_6H_5)_3N^+$ are formed and that there is equilibrium between the paramagnetic and diamagnetic molecules:

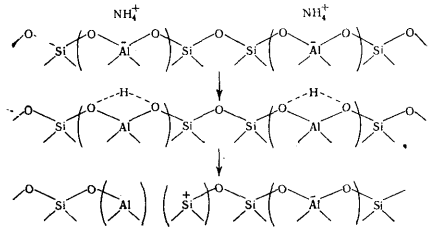
$$\underset{\text{2 radical-cations}}{2\,(C_6H_5)_3N^+} \rightleftarrows \underset{\text{diamagnetic ion}}{(C_6H_5)_3N^{2+}} + \underset{\text{neutral molecule}}{(C_6H_5)_3N} + Q \ .$$

The resolution of the hyperfine structure (HFS) spectrum of the triphenylamine radical-cation (triplet due to the ^{14}N nucleus with $I = 1$) depends on the number of $(C_6H_5)_3N$ molecules present in the zeolite pores which have reacted. It may be that this is associated with the interaction between $(C_6H_5)_3N^+$ and $(C_6H_5)_3N$ already mentioned, leading to the delocalisation of the unpaired electron and the disappearance of the HFS, or with the hindrance of the rotation of the radical by an excess of neutral molecules in the zeolite pores.

The influence of the solvent on the HFS of the $(C_6H_5)_3N^+$ ESR spectrum has been demonstrated by the following experiment. Triphenylamine was adsorbed from the gas phase at 200°C on a type Y zeolite from which metal cations had been eliminated and the ESR spectrum at room temperature was recorded at different time intervals (as the colour of the specimen changed). In all cases, a singlet line with slight asymmetry and a g-factor close to 2.00 was observed. The addition of n-heptane to zeolites at room temperature in a nitrogen atmosphere led to the immediate appearance of the HFS due to the nitrogen nuclei. On the other hand, the well resolved spectrum of the $(C_6H_5)_3N^+$ radical-cation adsorbed on the HY zeolite from solution in n-heptane is broadened and becomes anisotropic as a result of removal of the solvent or the reduction of the temperature at which the spectrum is recorded.

Stamires and Turkevich[2] noted that, in all cases where they observed a well resolved HFS of the spectrum of the adsorbed radical-cation, the subsequent adsorption of O_2 caused a reversible broadening of the ESR line. The fact that in the adsorption of the radical-cation the ESR method does not reveal the unpaired electron captured by the zeolite is probably due to the short relaxation time or the complete delocalisation of the electron in the zeolite lattice, where the varying crystal fields broaden the ESR line so much that it becomes impossible to observe.

It was shown[2] that iodine, one of the best acceptors in charge-transfer complexes, does not form these complexes at room temperature with donors such as aniline, naphthalene diphenylamine, and diphenylethylene, systems of this kind giving rise to an ESR signal only at elevated temperatures. Since the adsorption of the above substances on a zeolite freed from metal cations leads to the appearance of radical-cations already at room temperature, one may conclude that the electron-accepting centres of such an adsorbent exhibit at least the same activity as iodine. The following scheme for the formation of electron-accepting centres during the heat treatment of the NH_4Y zeolite was put forward on the basis of the results[2]:



Heat treatment of the ammonium-form of the zeolite leads to the formation of NH_3 and H^+ ions. The latter, interacting with the lattice oxygen, form the intermediate structure (B). With increase of heat-treatment temperature (~400°C), the elimination of OH groups begins, the latter giving rise to H_2O by reacting with H^+, and defects appear in the zeolite [structure (C)]. A complex involving charge transfer from an adsorbed molecule to a tricoordinate aluminium atoms is formed in the adsorption of triphenylamine. The stabilisation of the radical-cation produced is due to the rigid arrangement of the electron-accepting centres in the zeolite lattice. The formation of such centres probably does not disrupt the zeolite structure, since the degree of adsorption of triphenylamine is independent of the degree of elimination of metal cations and is equal to 3×10^{20} mol. g^{-1}, which is characteristic of the specimen freed from metal cations. The active centre with the tricoordinate aluminium atom possesses properties analogous to those of $SbCl_5$,[5] acting similarly to iodine, and is an electron trap. Such $(AlO)_{3/2}$ traps are distributed uniformly throughout the zeolite structure.

In the communication by the same workers, dealing with an ESR study of γ-irradiated zeolites of types X and Y, it is shown that such combined $(AlO)_{3/2}$ centres and traps capture the electrons liberated on γ-irradiation of the zeolite and a six-component HFS, due to the splitting of the levels of the captured electron in the field of the ^{27}Al nucleus ($I = 5/2$), is observed in the spectrum. The adsorption of $(C_6H_5)_3N$ from solution after γ-irradiation of a type Y zeolite freed from metal cations does not lead to the formation of triphenylamine radical-cations, since the electron-accepting centres have already been occupied by the electrons liberated by the γ-irradiation. However, annealing of the γ-irradiated preparations regenerates the active centres: the six-component spectrum of the captured electron vanishes and the spectrum characteristic of the $(C_6H_5)_3N^+$ radical-cation appears immediately after the adsorption of triphenylamine.

As will be shown below (subsection 2 of this Section), these results conflict with the data of Dollish and Hall[7], who observed the formation of the radical-cations of perylene when it was adsorbed on an irradiated HNaY zeolite (45% exchange).

It has been shown[8] that the hydrogen-form of a type Y zeolite (HY) possesses, after appropriate activation oxidation-reduction properties similar to those of Al_2O_3 or amorphous aluminosilicates. The authors investigated the formation of the radical-ions of tetracyanoethylene (TCE), 1,3,5-trinitrobenzene (TNB), *m*-dinitrobenzene (DNB), and perylene in the adsorption of these compounds from solutions in benzene on NaY, HNaY, and HY zeolites, Al_2O_3, and an industrial 13% Al_2O_3–SiO_2 catalyst. The specimens were subjected to preliminary activation in a stream of O_2 for 1 h at temperatures in the range 100° to 1000°C and, after cooling *in vacuo* and reheating in O_2 at a pressure of 20 cm, were conditioned for 16 h *in vacuo* (10^{-5} mmHg) at the given temperature.

Preliminary tests showed that the concentration of the TCE, TNB, and DNB radicals formed depends on the concentration in the solution and on the time of contact between the adsorbate and the catalyst. The dependence of the number of radicals on the concentration in the solution implies that an adsorption equilibrium is established between the adsorbate molecules in the solution and the corresponding radicals on the adsorbent surface. The slow increase of the concentration of radical-ions with time shows that the radicals are formed not only on the outer surface but also within the channels and cavities of the zeolite. The maximum concentration of the radicals was observed in adsorption from 0.1 M solution after contact for 48 h. Additional ultraviolet irradiation of the adsorbate solution–zeolite system for 1 h led to an increase of the concentration of radical-ions by a factor of 1.5 for TCE and by factors of 2 and 3 for TNB and DNB respectively. Ultraviolet irradiation probably increases the electron-donating activity of weak centres. Presumably the fraction of such centres increases with the electron-affinity of the adsorbed molecule. The effect of irradiation in the case of TCE, a fairly strong electron-acceptor, is therefore significantly smaller than for the relatively weak acceptors such as TNB and DNB. These results indicate a fairly wide range of energies of the electron-donating (reduction) zeolite centres. In all subsequent experiments, the concentration of the radical-ions formed was determined after keeping a 0.1 M adsorbate solution in contact with the zeolite for 48 h and after additional ultraviolet irradiation of the system for 1 h.

It has been shown[8] that the adsorption of TCE by the HY zeolite dehydrated at 150–400°C is accompanied by the appearance of a nine-line ESR spectrum with $g = 2.0027$ and an HFS constant of approximately 4.9 G, which is characteristic of the TCE radical-anion. At dehydration temperatures above 400°C, the HFS disappears and the observed singlet is analogous to the ESR signal of the TCE polymer[9]. The singlet is observed also in the adsorption of TCE on the NaY zeolite over the entire range of dehydration temperatures. The dependence of the concentration of the TCE radical-anions on the heat-treatment temperature of HY and NaY is characterised by two maxima in the region of temperatures of approximately 250° and 650°C.

Table 1. The concentration of TCE radical-anions (spins g^{-1}) on various adsorbents[8].

Activation temperature	Adsorbent			
	HY	NaY	Al_2O_3	13% Al_2O_3–SiO_2
250°	$3 \cdot 10^{17}$	$3.5 \cdot 10^{17}$	$4.5 \cdot 10^{18}$	$6.5 \cdot 10^{17}$
660°	$4.2 \cdot 10^{18}$	$3.1 \cdot 10^{17}$	$9.0 \cdot 10^{18}$	$9.8 \cdot 10^{17}$

Table 1 presents data characterising the reducing properties of the adsorbents investigated in the formation of TCE radical-anions.

It has been shown[8] that the concentration of TCE radical-anions is independent of the degree of exchange of Na^+ for NH_4^+ and amounts to approximately 3×10^{17} spins g^{-1} when the preliminary dehydration of the zeolite has been carried out at 250°C. However, a sharp non-linear increase of the concentrations of TCE, TNB, and DNB radical-anions, starting from 35% exchange, was observed on specimens activated at 650°C. It is interesting to note that the oxidising activity of the type Y zeolite in the formation of triphenylamine radical-cations[2] reaches a maximum for approximately the same degree of elimination of metal cations (approximately 30%), remaining constant on further increase of the degree of exchange. One cannot rule out the possibility that the removal of the first Na^+ ions leads mainly to the formation of oxidation centres

and further elimination of metal cations (after approximately 30% exchange) is accompanied by a sharp increase of the number of reduction centres.

The oxidising properties of type Y zeolites have been studied[8] in relation to the adsorption of perylene from a saturated benzene solution (approximately 6.5×10^{-3} M) at room temperature. The maximum concentration of the perylene radical-cations was reached after the solution has been in contact with zeolite for 5 days and did not change after additional ultraviolet irradiation. In the presence of O_2, the adsorption of perylene on the HY zeolite at room temperature gives rise to an ESR spectrum characteristic of the perylene radical-cation. It was noted that the HFS of the spectrum and its relatively slight time variation are analogous to the changes observed in the adsorption of perylene on amorphous aluminosilicate.

The concentration of the perylene radical-cations depends almost linearly on the activation temperature of the HY zeolite over the temperature range 150–660°C. The maximum concentration observed on the specimen activated at 660°C corresponds to approximately 1.7×10^{19} spins g^{-1} or approximately 3.1×10^{16} spins m^{-2}. The adsorption of anthracene under the same conditions involves the formation of a number of radical-cations smaller by a factor of approximately 4. This finding shows that the yield of radical-cations is determined mainly by the ionisation potential of the adsorbate molecule and not by its size (at least for perylene and anthracene). When the activation temperature exceeds 700°C, a sharp decrease of the concentration of perylene radical-cations is observed, being due to the disruption of the zeolite structure, which is revealed by X-ray diffraction.

Table 2.

Adsorbent	Concentration of TCE radical-anions, 10^{-15} spins m^{-2}	Concentration of perylene radical-cations, 10^{-15} spins m^{-2}
HY	8	31
Al_2O_3	45	7
13% Al_2O_3–SiO_2	3	2

Table 2 presents the oxidising and reducing activities of the HY zeolite, an amorphous aluminosilicate (13% Al_2O_3–SiO_2), and Al_2O_3 expressed in terms of the number of perylene radical-cations and TCE radical-anions referred to 1 m^2 of the adsorbent surface for an activation temperature of 660°C.

It is suggested that two types of reduction (electron-donating) centres exist on the HY surface. The relatively weak centres correspond to the activity maximum for an activation temperature of 250°C. These centres reduce the TCE molecules to the radical-cations, but are too weak to reduce the TNB and DNB molecules. It is significant that the activity of the weak centres is independent of the degree of exchange of Na^+ ions for NH_4^+. It is suggested[8] that such centres may be hydroxy-groups as happens in Al_2O_3 activated at low temperatures.

An increase of activation temperature to 660°C is accompanied by the dehydroxylation of the HY zeolite and leads to the formation of strong electron-accepting and electron-donating centres responsible for the oxidation-reduction properties of the zeolite, i.e. the mechanism is the same as that proposed by Stamires and Turkevich[2] (see above).

The fact that the maximum concentration of the radical-ions formed is significantly smaller than the possible number of oxidation-reduction centres is due, according to the authors[8], to the inaccessibility of some of these centres to the adsorbed organic molecules. It is postulated that, for low degrees of exchange (<35%), mainly Na^+ cations at the S_I sites, inaccessible to TCE molecules, are substituted and the activity of the HNaY zeolite in the formation of radical-anions does not therefore change. For degrees of exchange >35%, Na^+ ions at the S_{II} sites, accessible to TCE molecules, begin to exchange, which leads to a sharp increase of the reducing activity of the zeolite. However, subsequent investigations showed that this explanation is not the only one possible. It was shown previously[10] that the oxidising and reducing properties of activated Al_2O_3 are to some extent interrelated. It was of interest to discover whether this relation between the oxidising and reducing properties holds for zeolites.

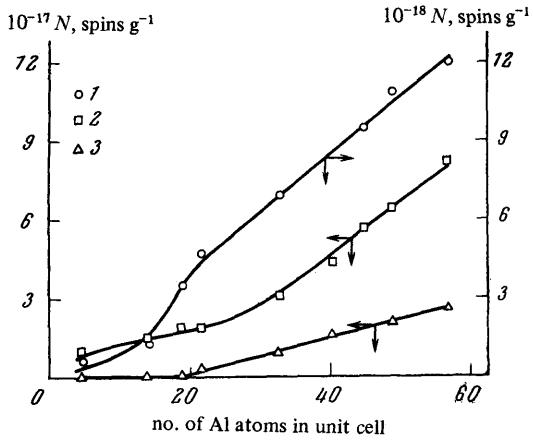


Figure 2. Variation of the concentration (N) of anthracene (curve *1*), TCE (curve *2*), and TNB (curve *3*) radical-ions with the number of aluminium atoms in the unit cell of a type Y zeolite[10].

A detailed study has been made[11] of the dependence of the oxidising and reducing properties of the HY zeolite on the Al : Si ratio. The adsorbates employed were 0.1 M benzene solutions of TCE, TNB, and DNB and 0.005 M benzene solutions of naphthalene, anthracene, and perylene. Fig. 2 illustrates the dependence of the concentration of the radical-ions of anthracene, TCE, and TNB on the number of aluminium atoms per unit cell of the type Y zeolite activated at 600°C. The decrease of the redox activity of the zeolite with decreased aluminium content is consistent, according to the authors, with the mechanism of the formation of electron-donating and electron-accepting centres already examined. The linearity of the plots in Fig. 2 shows that the activity of the zeolite is due to highly localised centres and not to the collective effect of several centres incorporating Al^{3+}.

We may note that this treatment of the experimental data is by no means self-evident. The point is that, even for maximum degrees of elimination of aluminium, the residual aluminium in the zeolite is quite sufficient for the formation of the same number of oxidation-reduction centres as in the specimens from which aluminium has not been removed. However, since the yield of radical-cations nevertheless falls with decrease of the aluminium content in the zeolite, one must suppose that not all the aluminium atoms in the crystal lattice are equivalent in relation to the formation of the oxidation-reduction centres. However, the aluminium elimination process is probably not homogeneous, i.e. some aluminium atoms are removed first. The linearity of the plots in Fig. 2 in such a case is rather unexpected.

It has been shown [11] that preliminary adsorption of anthracene and perylene on the HY zeolite causes a tenfold increase of the concentration of TNB radical-anions compared with the yield of these species in adsorption on a clean zeolite surface.

Almost the same increase of the yield of TNB radical-anions after the preliminary adsorption of electron-donating molecules (anthracene and perylene) was observed on the HY zeolite activated *in vacuo* and on the dealuminated HY zeolite. However, the effect is not observed when naphthalene is the first substance to be adsorbed. The preliminary adsorption of TNB likewise does not increase the yield of the anthracene radical-cations. Table 3 presents data illustrating the influence of the preliminary adsorption of various aromatic hydrocarbons on the yield of TNB radical-anions.

Table 3.

Adsorbate	Ionisation potential, eV	Maximum concn. of radical-cations per gram of zeolite	Average number of radical-cations required for the formation of one TNB radical-anion
Perylene	6.83	$5 \cdot 10^{19}$	2.7
Anthracene	7.23	$1.2 \cdot 10^{19}$	2.7
Naphthalene	8.1	$6 \cdot 10^{17}$	—
Benzene	9.25	$1 \cdot 10^{17}$	—

Evidently approximately one TNB radical-anion is formed additionally for each three anthracene or perylene radical-cations. This implies that only one of the three oxidation-reduction centres is involved in the increase of the yield of TNB radical-anions by virtue of its structure and energy relations. One can also suppose that the increased yield is due to the cooperative interaction of three neighbouring oxidation centres with one reduction centre. The latter hypothesis is supported by the finding that the increased yield is almost independent of the degree of elimination of aluminium from the zeolite.

Flockhart et al. [11] believe that such a large increase (by an order of magnitude) in the concentration of radical-anions as a result of the formation on the zeolite surface of radical-ions of opposite sign cannot be accounted for solely on the basis of the model proposed previously, which assumes that some of the active centres are inaccessible to the adsorbate molecules. A more likely hypothesis is that centres having different strengths exist. Possibly the observed tenfold increase in the concentration of radical-anions characterises the number of electron-donating centres whose strength is insufficient to reduce the TNB molecule to the radical-anion. The electron-donating capacity of such centres increases following the adsorption of anthracene or perylene on neighbouring oxidation centres. The independence of the increase in the yield on the degree of elimination of aluminium apparently shows that it is mainly aluminium atoms responsible for the strong electron-donating centres which are removed during the aluminium elimination process.

Naphthalene, which has a higher ionisation potential than anthracene and perylene, is adsorbed on energetically stronger oxidation centres, which do not interact with the nearest reduction centres. Preliminary adsorption of naphthalene does not therefore lead to an increase of the yield of TNB radical-anions.

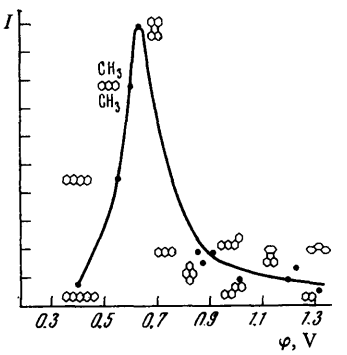


Figure 3. Variation of the integral ESR signal intensity (I) with the half-wave potentials (φ) of various aromatic hydrocarbons adsorbed on 22% Al_2O_3–SiO_2 (the potentials have been measured relative to Ag–0.1 N Ag^+ in acetonitrile) [11].

It is noteworthy that the conclusion concerning the formation of oxidation-reduction centres of different strengths had been made earlier [12], but in relation to amorphous aluminosilicates. The author obtained an experimental relation between the concentration of the radical-cations of different aromatic hydrocarbons formed in the experiment and the half-wave potential of the adsorbate (Fig. 3). He attempted to describe this relation theoretically and showed that the best agreement between the theoretical and experimental curves is observed when account is taken of the distribution of the oxidation centres of the aluminosilicate with respect to strength. Since such distribution is unknown *a priori*, the author postulated a Boltzmann distribution in the calculation of the theoretical curve. Furthermore, the possibility of the formation of doubly charged cations was postulated for adsorbates with low ionisation potentials (tetracene and pentacene).

2. The Nature of the Influence of Molecular Oxygen on the Formation of Radical-ions

In the investigations discussed above [2,8,10], the problem of the influence of O_2 on the oxidising and reducing properties of zeolites was not specially studied. Flockhart and coworkers [8,10] carried out the preliminary heat

treatment and the adsorption of hydrocarbons in the presence of O_2. Although Stamires and Turkevich[2] carried out the preliminary dehydration *in vacuo*, their method for the impregnation of the adsorbent with the adsorbate solution (in an atmosphere of dry nitrogen) did not rule out the access of traces of O_2 into the system.

Dollish and Hall[7] studied the influence of the preliminary heat treatment of the NH_4Y, NH_4X, NaY, and CaY zeolites and of O_2 on the yield of radical-anions in the adsorption of perylene and triphenylamine from benzene solutions. They investigated zeolite specimens activated in four different ways: (*a*) by evacuation at 550°C; (*b*) by heat treatment in a stream of O_2 for 17 h at 550°C with subsequent evacuation at the same temperature for 17 h; (*c*) by heat treatment in a stream of O_2 at 550°C with subsequent slow cooling in O_2 to room temperature and evacuation at room temperature; (*d*) by heat treatment in a stream of O_2, evacuation for 6 h, treatment in a stream of H_2 for 24 h, and evacuation for 6 h, all the treatments being carried out at 550°C. Table 4 presents the experimental data for the influence of the preliminary treatment of the zeolites on the yield of radical-ions. In all cases, the surface coverage by the adsorbate was 7×10^{20} mol. g^{-1} (4×10^{20} mol. g^{-1} for triphenylamine).

Table 4. The influence of the preliminary treatment of zeolites on the concentration of radical-ions (10^{17} spins g^{-1}).

Adsorbent, % exchange, adsorbate	NH_4Y			CaY		NH_4X*	NaY
	45%	79%	79%	36%	79%	48%	
Type of treatment	perylene	perylene	tri-phenyl-amine	perylene	perylene	perylene	perylene
a	1.3	6.2	1.0	0.3	0.6	0.3	not detected**
b	9.5	32.3	8.1	0.3	9.1	1.0	not detected
c	36***	58****	20****	0.4***	15***	2.6***	—
d	1.0	1.8	0.7	—	0.3	—	—

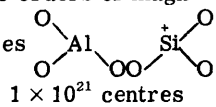
*Heat-treated at 500°C owing to its lower thermal stability.

**Exposure to dry air for 24 h leads to the appearance of a signal equivalent to 0.9×10^{17} spins g^{-1}.

***Exposure to air for 24 h does not alter the concentration of the radical-ions or alters it only slightly (≤15%).

****Exposure to air for 24 h increases the concentration to 1.2×10^{19} spins g^{-1}.

The influence of O_2 on the yield of perylene radical-cations was studied in detail on an NH_4Y specimen with 45% exchange, treated by method *a*. The results show that the adsorption of a single O_2 molecule induces the formation of a single perylene radical-cation. The same stoichiometry was obtained also from the determination of the amount of H_2O formed after the reduction with hydrogen (method *d*). In order to elucidate the nature of the chemisorbed oxygen, the NH_4Y specimen with 45% exchange, treated by method *a*, was irradiated by X-rays *in vacuo*. The ESR spectrum of this specimen consisted of the sextet characteristic of the electron captured by an aluminium-27 ion[6] and of the spectrum of the O_2^- radical-ion. The concentration of these species was 1×10^{16} and 4×10^{16} spins g^{-1} respectively. Contact between the irradiated specimen and the perylene solution led to the disappearance of both signals and the appearance of the spectrum of the perylene radical-cation equivalent to 1.3×10^{18} spins g^{-1}. Table 4 shows that the yield of the perylene radical-cations on a non-irradiated NH_4Y specimen with 45% exchange is 1.3×10^{17} spins g^{-1}. These data demonstrate the important role of the oxygen chemisorbed irreversibly at 550°C in the formation of radical-ions. Since ESR signals due to O_2^- are not observed on the non-irradiated specimens, the authors assume that oxygen is chemisorbed in the form of some other species. However, such oxygen must react with perylene to form the ion pair $Pn^{+}O_2^-$. Nevertheless, the formation of the radical-cations is not accompanied by the appearance of an ESR signal due to O_2^-, which is perhaps a common feature of all donor–acceptor systems.

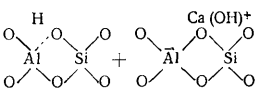
Dollish and Hall[7] discuss in detail the possible reasons why the maximum observed concentration of radical-cations is smaller by approximately two orders of magnitude than the number of anionic vacancies  in the 79% NH_4Y zeolite (approximately 1×10^{21} centres g^{-1}). Comparison of the sizes of the large cavities (approximately 13 Å), the diameters of the large channels (8–9 Å for NaY), and the sizes of the triphenylamine (approximately 10 Å) and perylene (6.5 × 9.1 Å) molecules led the authors to the conclusion that steric hindrance lowers the yield of radical-ions in the adsorption of such comparatively large molecules.

The influence of air and water vapour on the concentration of benzene, anthracene, naphthalene and diphenylamine radical-ions adsorbed *in vacuo* on a type Y zeolite from which cations have been removed has been investigated[13]. The preliminary treatment of the zeolite involved heat treatment for 4 h in air at 600°C followed by evacuation at 470–500°C. Benzene and naphthalene were adsorbed at room temperature and diphenylamine and anthracene at 85–90°C. It was shown that the ESR signal of the benzene radical-cation appears only after irradiation of the benzene molecules adsorbed on the zeolite with ultraviolet light for 20 h.

Naphthalene, anthracene, and diphenylamine radical-ions are formed without additional ultraviolet irradiation. It is suggested that the radical-ions are apparently formed via charge transfer to the electron-accepting centre formed when cations are eliminated from the zeolite, since adsorption on the metal cation-containing specimen does not lead to the formation of radical-ions. The formation of radical-ions from adsorbates with a high ionisation potential (benzene) requires an additional activation of the adsorbed molecule by ultraviolet radiation. The admission of water vapour gradually decreases the intensity of the ESR signals from anthracene and diphenylamine by a factor of 1.5–2. However, prolonged exposure of the specimen to water vapour does not lead to the complete disappearance of the signal. The influence of water has been explained by the reverse reaction involving the conversion of the radical-ion into a neutral molecule under the conditions of strong specific adsorption of water molecules by the zeolite. The admission of air increases the intensity of the ESR signals of the adsorbed anthracene and diphenylamine radical-ions which is probably due to the effect of oxygen.

3. The Influence of the Nature of the Cations and Their Location in the Zeolite Structure on the Oxidising and Reducing Properties of Faujasites

In the studies already mentioned[7-11], the formation of radical-ions was also observed on different cationic forms of zeolites of types X and Y. The appearance of an ESR signal (singlet) in the adsorption of TNB on CoY, NiY, and LaY has been noted[11]. The adsorption of TNB on CaY leads to the appearance of an ESR signal with a HFS. Dollish and Hall[7] investigated the influence of the degree of exchange of Na^+ for Ca^{2+} on the yield of perylene radical-cations. They found (Table 4) that, for low degrees of exchange ($\leqslant$36%), the activity of the CaY zeolite in the formation of radicals is very low even in the presence of O_2. However, for high degrees of exchange ($\geqslant$79%), the activity of CaY becomes comparable to that of the NH_4Y zeolite. For low degrees of exchange, Ca^{2+} ions occupy S_I sites in the hexagonal prisms connecting neighbouring cubo-octahedra and capable of accommodating 50% of the ions. Centres of another type are located in the plane (or close to it) of the six-membered rings in the large zeolite cavities. In the initial zeolite, there is on average one Na^+ ion for each ring of this kind. The complete exchange of the singly-charged Na^+ ions for the doubly-charged Ca^{2+} ions should lead to the formation of a positively charged centre and a centre with a partial negative charge (a cationic vacancy). In the presence of small amounts of water, the structure of the CaY zeolite can be represented schematically as follows:



Dehydation results in the formation of centres in CaO analogous to those postulated for a type Y zeolite from which cations have been removed [see structure (C) in the scheme presented in Subsection 1 of the present Section].

A wider assortment of cationic forms of type Y zeolites was studied by Hirschler et al.[14] In order to elucidate the possibility of the formation of radical-ions on adsorption of molecules with a high ionisation potential (>9.0 eV), the authors studied the adsorption of olefins (oct-1-ene, pent-1-ene, etc.), benzene, and methylbenzenes on cationic forms of a type Y zeolite containing lanthanides as well as CaY and CeX. The zeolites were dehydrated in air at 500°C and the hydrocarbons were adsorbed from solutions in carbon tetrachloride. The authors concluded that the ESR spectra of the radical-cations observed in the adsorption of olefins cannot be accounted for solely by electron transfer from the adsorbed molecule to the adsorbent. On the basis of the gas-chromatographic analysis of the products of the reaction of pent-1-ene with the zeolite, the authors suggested that the radical-cations are formed from polymerisation products.

The influence of the amount and nature of the added cations on the ability of type X and Y zeolites to form radical-cations in the adsorption of anthracene and naphthalene has been investigated[15]. In addition to the sodium-form of the zeolites and the form freed from metal cations, a study was made of the magnesium, lanthanum, and yttrium cationic forms with different degrees of exchange. The zeolites were heat-treated for 6 h in a stream of dry air and then for 1 h in a stream of helium at 550°C. Naphthalene and anthracene were adsorbed from benzene solutions at room temperature. The formation of radical-cations in the adsorption on the NaY zeolite was not observed. In contrast to the results obtained by Hirschler et al.[14], Zhavoronkov[15] did not observe ESR signals in the adsorption of benzene on zeolites containing triply-charged cations. The adsorption of anthracene on cationic forms of a type X zeolite (with degrees of substitution of sodium by magnesium and lanthanum of 44 and 22% respectively) also did not lead to the appearance of an ESR signal. The latter result is, incidentally, not surprising, since the degree of substitution of cations was too low. The formation of radical-cations was observed in the adsorption of naphthalene and anthracene on type Y zeolites containing doubly- and triply-charged cations, the anthracene signal being more intense.

With increase of the degree of exchange of sodium for magnesium, lanthanum, and yttrium cations, the concentration of the radical-cations arising on adsorption of anthracene greatly increases, particularly on LaY and YY zeolites for degrees of exchange of 20–30%. In the range of 30–50% exchange, the concentration of radical-ions increases only slightly, but rises by an order of magnitude on passing to specimens obtained with non-equivalence of the exchange of sodium for triply-charged cations. Such non-uniformity in the increase of the concentration of the paramagnetic species as a function of the degree of exchange may be associated with the non-equivalence of various sites occupied by the sodium cations in the zeolite introduced by the exchange process. It is important to note that the concentration of the radical-ions formed on the specimen freed from cations and on zeolites with triply-charged cations for degrees of exchange in the range 20–30% are approximately the same, while for the magnesium-form the concentration is several times smaller. Zhavoronkov et al.[15] note different types of behaviour of X and Y zeolites with adsorbed anthracene in relation to atmospheric oxygen. Contact of type Y zeolites with air for several days hardly alters the concentration of the anthracene radical-cations formed. On the MgX, LaX, and NaY zeolites, radical-cations are also not formed immediately after adsorption, but exposure of these specimens to air for several days leads to the formation of paramagnetic centres at concentrations of 4.7×10^{16}, 5.7×10^{15}, and 1.6×10^{16} spins g^{-1} respectively.

Zhavoronkov et al.[15] do not discuss the role of the cations introduced into the zeolite in electron-transfer reactions. Richardson[16] and Neikam[17] investigated this problem. Richardson[16] used the ESR method to determine the degrees of ionisation of anthracene, naphthalene, perylene, and pyrene adsorbed on faujasites in which approximately 60% of the Na^+ ions had been replaced by K^+, Li^+, Ba^+, Sr^{2+}, Ca^{2+}, Mg^{2+}, Ag^+, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+} ions. The specimens were first dehydrated in air for 12 h at 400°C and the hydrocarbons were adsorbed from 0.01 M benzene solutions.

According to Richardson[16], the adsorption is accompanied by electron transfer from the adsorbate to the cation. The number of radical-cations varies exponentially with the difference between the ionisation energy of the adsorbate and the electron affinity of the cation. The conclusion that the cations are involved in the oxidation of anthracene to the radical-cation was reached on the basis of the following experiment. A series of specimens of the magnesium-form of the zeolite containing 2% of copper were heated for 2 h at 100°C. An ESR signal without the HFS characteristic of dehydrated Cu^{2+} ions was observed for these preparations and the adsorption of anthracene did not lead to the formation of radical-cations. The remaining specimens of this series were dehydrated at increasing temperatures and the ESR signals due to the Cu^{2+} ions

were recorded also after the adsorption of anthracene. It was shown that the HFS characteristic of dehydrated Cu^{2+} ions and the spectrum of the anthracene radical-cations appear only after heat treatment above 300°C. The author's attempt to measure the changes in the intensity of the Cu^{2+} signal intensity due to electron transfer from anthracene to Cu^{2+} was unsuccessful, since the number of electrons involved in the reaction is too low to cause an appreciable decrease of the Cu^{2+} signal.

However, this experiment probably cannot be regarded as a direct confirmation of the involvement of cations in the oxidation of anthracene to the radical-cation. The results indicate only an agreement between the dehydration temperatures necessary, on the one hand, for the appearance in the spectrum of the HFS due to the Cu^{2+} ions and, on the other hand, for the formation in the zeolite of centres capable of oxidising anthracene. We believe that there are no grounds in this instance for the hypothesis that the changes in the environment of Cu^{2+} ions on dehydration, accompanied by the appearance of the HFS, need necessarily lead to the formation of anthracene radical-cations.

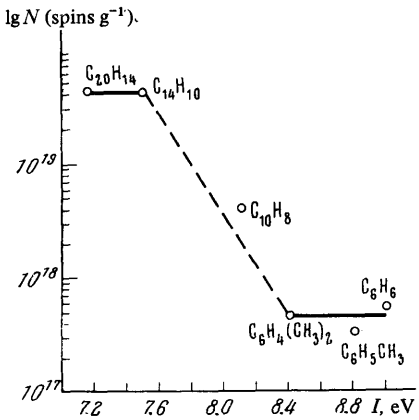


Figure 4. The yield of radical-ions ($\lg N$) on the 13.3% CeY zeolite as a function of the ionisation potential of the adsorbate [17].

Neikam [17] investigated the activity of the lanthanide cationic forms of type Y zeolites in the formation of benzene, toluene, *p*-xylene, naphthalene, anthracene, perylene, and coronene radical-ions. The hydrocarbons were adsorbed from solutions in carbon tetrachloride on the zeolite activated at 500°C in air or in an oxygen atmosphere. It was shown that the concentration of the radical-ions formed following adsorption on the CeY zeolite is approximately an order of magnitude higher than on the LaY, SmY, and DyY zeolites. The adsorption on GdY leads to the appearance of very weak ESR radical-ion signal ($<10^{16}$ spins g^{-1}). The important role of O_2 in the formation of active centres was demonstrated by comparative experiments in which the 13.3% CeY zeolite was activated in helium, molecular hydrogen, or air. Fig. 4 illustrates the variation of the logarithm of the concentration of the radical-ions (for the 13.3% CeY zeolite) with the ionisation potential of the adsorbed molecule.

The theoretical interpretation of this relation is based on the hypothesis [16] that the concentration of the radical-cations formed on adsorption ($N^{\ddagger}$) obeys the Boltzmann distribution: $[N^{\ddagger}] = N_0 e^{-\Delta E/kT}$, where N_0 is the number of adsorbed molecules and $\Delta E = I + A + W$. The ionisation potential of the adsorbate (I), the electron affinity of the adsorbent (A), and the charge-transfer energy (W) correspond to the following processes: $Ar \rightarrow Ar^{\ddagger} + e(I)$ $S^{+} + e \rightarrow S(A)$, and $S + Ar^{\ddagger} \rightarrow S \ldots Ar^{\ddagger}(W)$. S and R denote the adsorbent and adsorbate respectively. It is readily seen that, when A and W vary only slightly for different adsorbates, the relation between $\lg[N^{\ddagger}]$ and I should be linear. Physically, this implies the energetic homogeneity of the electron-accepting zeolite centres.

The data presented in Fig. 4 show that this is not the case. The presence of two regions with a constant concentration of the radical-cations formed, separated by a transition region, demonstrates the energetic inhomogeneity of the electron-accepting zeolite centres. It follows from Fig. 4 that approximately 4×10^{17} centres in the 13.3% CeY zeolite have sufficient energy for the oxidation of molecules with $I \leq 9.0$ eV and approximately 4×10^{19} centres are capable of oxidising molecules with $I \leq 7.5$ eV. Centres of the third type correspond to the oxidation of naphthalene ($I \simeq 8.1$ eV). The author [17] explains on the basis of this model the similarity of the concentrations of anthracene and perylene radical-cations oxidised by centres with energy ≤ 7.5 eV. Such agreement is also observed for benzene, toluene, and *p*-xylene, which may be oxidised to radical-cations only on centres whose energy is approximately 9.0 eV. We may note that the concentration of perylene radical-cations on a type Y zeolite freed from cations is approximately four times higher than the number of anthracene radical-cations [8] (Table 3).

The distribution of active centres with respect to energies depends on the cerium content in the zeolite. A decrease of the cerium content from 13.3% to 8.7% reduces the number of weak centres (7.5 eV) by a factor of 4 and the number of strong centres (9.0 eV) by a factor of 50. ESR signals were not observed in the adsorption on the 8.7% CeY zeolite of molecules whose ionisation potential is higher than that of naphthalene. On the basis of these data and the measurements of the magnetic susceptibility of the CeY zeolites, the author [17] concludes that the strong electron-accepting centres (9.0 eV) are distributed within the small cavities of the zeolites and include a pair of Ce^{4+} cations. However, it is suggested that the Ce^{4+} cations themselves, formed from Ce^{3+} when the zeolite is heat-treated in the presence of O_2, do not function directly as electron acceptors. The role of the Ce^{4+} cations reduces to an increase in the electron affinity of the active centres already formed in the zeolite under the influence of chemisorbed oxygen during heat treatment.

Fig. 5 and the data in Table 5 illustrate the relation between the concentrations of the radical-cations formed and the number of adsorbed molecules. For perylene, curves *1* and *2* in Fig. 5 coincide.

Comparison of the sizes of the adsorbed molecules with the diameters of the windows in the large zeolite cavities (7.5 Å) and allowance for the yield of the radical-cations led Neikam [17] to the conclusion that the weak oxidation centres (7.5 eV) are located on the outer zeolite surface. The low concentration of the coronene radical-cations (compared with perylene) indicates, according to the author, that the size of the adsorbed molecule is an important factor in the formation of radical-cations also in adsorption on the outer surface. The author believes

that the results obtained by Stamires and Turkevich [2] for a type Y zeolite from which metal cations had been eliminated also confirm the conclusion that the oxidation centres are located on the outer surface.

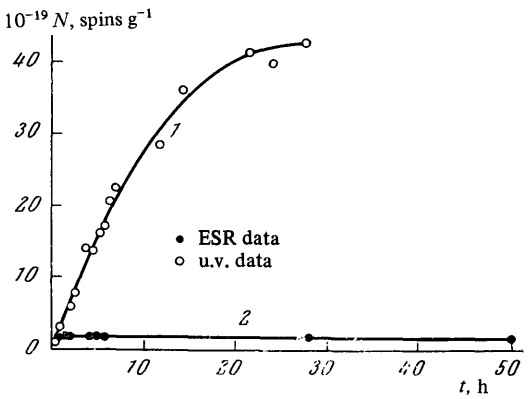


Figure 5. Variation of the degree of adsorption of anthracene and the concentration of the radical-cations formed (N) with contact time (t): 1) degree of adsorption based on the analysis of ultraviolet spectra; 2) the concentration of radical-cations based on ESR data (13% CeY zeolite) [17].

Table 5.

Molecular size	N_0	[N+·].spins g^{-1}	[N+·]/N_0
Anthracene, 6 A	$5.05 \cdot 10^{20}$	$4.17 \cdot 10^{19}$	1:12
Perylene, 7.7 A	$4.37 \cdot 10^{19}$	$4.34 \cdot 10^{19}$	1:1
Coronene, 10.4 A	$1.63 \cdot 10^{19}$	$6.8 \cdot 10^{17}$	1:11.4

This conclusion conflicts with probably all the previous experimental data obtained for zeolites. It is unlikely that the difference of almost two orders of magnitude between the concentrations of the perylene and coronene radical-cations (Table 5) is caused solely by the difference between the sizes of these species, if adsorption on the outer surface alone is postulated. This is particularly true, since Dollish and Hall [7] assume that the size of the windows in the large type Y zeolite cavities is 8–9 Å and not 7.5 Å as in Neikam's study [17]. It is apparently not permissible to reach such far-reaching conclusions solely on the basis of small differences between the dimensions of the perylene molecule (7.7 Å) and the inlet windows of the zeolite (7.5 Å). As will be seen below, in cases where the difference between the dimensions is large (in the adsorption of perylene on H-mordenite), the formation of radical-cations is not observed.

III. THE OXIDISING AND REDUCING PROPERTIES OF MORDENITES

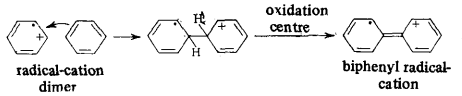
1. The Characteristics of the Formation of Radical-ions on Mordenites

Analysis of studies on the oxidising and reducing properties of zeolites of types X and Y has shown that the adsorption of hydrocarbons with a high ionisation potential (approximately 9.0 eV) on zeolites of this type under normal conditions does not lead to the formation of the corresponding radical-cations. Naturally, we are not considering studies in which the formation of radical-ions was observed after additional treatments of the zeolite–adsorbate system, say, after ultraviolet irradiation. The formation of benzene, toluene, and *p*-xylene radical-cations has been observed [17] after adsorption on the CeY zeolite. However, no data concerning the nature of the ESR spectra (with the exception of the concentration of the radicals formed) are quoted in this report. Other workers [10,14] have also merely stated that weak and poorly resolved ESR spectra appear in the adsorption of benzene and its methyl derivatives on certain cationic forms of zeolites of types X and Y. The interpretation of these spectra is extremely difficult. After the publication of the first communications [18,19] about the ESR spectra of the radical-cations of benzene and its methyl derivatives, observed when they are adsorbed on a synthetic mordenite, there was a sharp growth of interest in the study of the oxidising and reducing properties of zeolites of this type. The point is that only on mordenites under normal conditions is the adsorption of hydrocarbons with a high ionisation potential (benzene, toluene, and xylene) accompanied by the appearance of intense ESR spectra with a well resolved HFS, which make it possible to identify the radical-cations formed on adsorption.

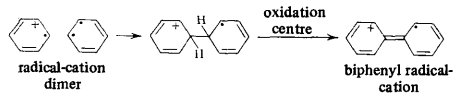
The study by Corio and Shih [18] is probably to be regarded as the first investigation in which an attempt was made to interpret the ESR spectra appearing after the adsorption of benzene and its methyl derivatives on the hydrogen-form of mordenite. The preliminary treatment of H-mordenite consisted in heating for 1 h at 500°C in an atmosphere of oxygen with subsequent evacuation for about 3 h at the same temperature. Liquid hydrocarbons were adsorbed at room temperature and solid hydrocarbons were fused and mixed with the zeolite. The ESR spectra were recorded at room temperature. Immediately after the adsorption of benzene on H-mordenite, the ESR spectrum consists of at least 7 HFS components and its overall width is approximately 30 G. The splitting between the components in the central part of the spectrum is approximately 2.2 G immediately after adsorption, increasing to approximately 3.8 G when 1 h has elapsed since the adsorption of benzene. Corio and Shih [18] assume that a radical-cation dimer, in which the unpaired electron is delocalised over the two benzene rings arranged in the form of a sandwich, is formed immediately after the adsorption of benzene. The subsequent time variation of the ESR spectra is due to the rapid establishment of equilibrium between the dimeric and monomeric forms of the radical-cations.

Other workers also concluded that the radical-cation dimers of benzene are formed when it is adsorbed on H-mordenite [19]. In this investigation the ammonium-form of mordenite was subjected to a preliminary heat treatment for 18 h in air at 520°C. The authors [19] reached the following conclusion on the basis of the time variation of

the ESR spectra appearing after the adsorption of a 1.8 M benzene solution in carbon tetrachloride on H-mordenite and a comparison of these spectra with the spectrum obtained after the adsorption of a 0.1 M solution of biphenyl in n-hexane. The ESR spectrum observed immediately after the adsorption of pure benzene results from a superposition of the spectra of the benzene radical-cation dimer and the biphenyl radical-cation. At room temperature the spectrum of the dimer disappears after approximately 24 h and that of the biphenyl radical-cation (HFS constants of 6.74, 3.37, 0.52 G) remains. The adsorption of toluene and *o*-xylene under analogous conditions leads to the appearance of ESR spectra characteristic of the corresponding biphenyl radical-cations (the 4,4'-dimethylbiphenyl radical-cation for toluene and the 3,4,3',4'-tetramethylbiphenyl radical-cation for *o*-xylene). The formation of toluene and *o*-xylene radical-cation dimers was not observed. Kurita et al.[19] postulate two mechanisms for the formation of biphenyl radical-cations when the benzene cation and neutral molecule react on an oxidation centre of H-mordenite. The ionic mechanism is as follows:



In methylbenzenes, the interaction may be between the carbon atom with the maximum positive charge in the cation and the carbon atom with the maximum negative charge in the neutral molecule. The second, radical mechanism is



In methylbenzenes, the interaction via the radical mechanism can occur between the carbon atom having the maximum spin density in the cation and the carbon atom having the maximum free valence in the neutral molecule. However, calculations by the simple Hückel method of the charge, spin density, and free valence in the cations and neutral molecules of toluene and *o*-xylene did not enable the authors[19] to make a choice between the radical and ionic mechanisms.

A more detailed analysis of the temperature variation (in the range 77–300 K) of the ESR spectra of tetramethylethylene and cyclopentene adsorbed on H-mordenite has been described by Corio and Shih[20]. The methods used in the preliminary treatment of the zeolite and in the adsorption of the hydrocarbons were the same as in their earlier study[18]. They showed that the activation energy for the rotation of cyclopentene on the surface of H-mordenite is 1.4 ± 0.2 kcal mole^{-1}. Such a low activation energy indicates virtually free rotation of the adsorbed cyclopentene molecule.

In the studies quoted above[18-20], the formation of radical-cations in the adsorption of various hydrocarbons (mainly aromatic hydrocarbons) on H-mordenite was postulated. However, the study of the ESR spectra of C_3–C_5 olefins adsorbed on H-mordenite led Leith[21] to a different conclusion. He showed that the adsorption of propene at room temperature on H-mordenite evacuated for 12 h at 450°C and then treated in oxygen at the same temperature leads to the appearance of an ESR spectrum consisting of 19 HFS components with a splitting of 8.1 G. Analogous spectra were observed also in the adsorption of but-1-ene and pent-1-ene. Fig. 6 presents the experimental spectrum of the adsorbed propene and its theoretical interpretation (a superposition of a triplet with the HFS constant a_1 = 33.6 G, a quintet with a_2 = 16.8 G, and a triplet with a_3 = 8.1 G). This spectrum does not correspond to the propene radical-cation, the formation of which would have been extremely difficult in any case owing to the high (9.73 eV) ionisation potential of propene. Leith[21] suggests that the observed ESR spectrum is due to the formation of the allyl radical

$$CH_3{-}CH{=}\dot{C}H{=}CH{-}CH_2{-}CH_3.$$

The triplet with a_1 = 33.6 G was assigned to the splitting of the energy levels of the unpaired electron at the β-proton and a proton in the methyl group. The quintet with a_2 = 16.8 G was assumed to be due to the interaction with two α-protons, the β-proton, and another proton of the methyl group. Finally, the triplet with a_3 = 8.1 G was attributed to the interaction with the central proton of the allyl group and the remaining proton in the methyl group. Bearing in mind the identity of the ESR spectra from adsorbed propene, but-1-ene, and pent-1-ene, it is suggested that the olefin is dimerised after adsorption with subsequent abstraction of a hydrogen atom and the formation of the allyl radical.

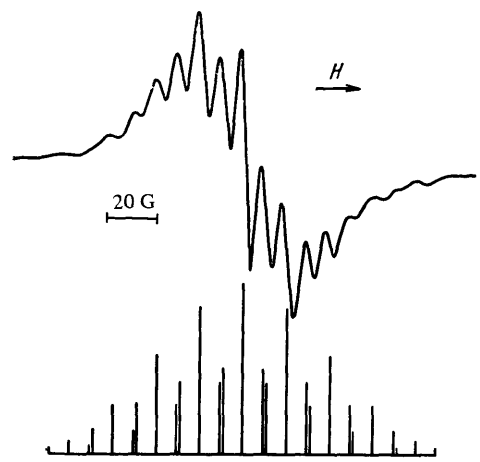


Figure 6. The ESR spectrum of propene adsorbed on H-mordenite and its theoretical interpretation[21].

2. The Influence of Heat Treatment and the Role of Chemisorbed Oxygen

The important role of oxygen in the formation of radical-ions following the adsorption of hydrocarbons on amorphous and crystalline aluminosilicates has been demonstrated in a series of studies. The problem has been investigated in relation to mordenites[22,23], a detailed study[22] having been made of the influence of the vacuum heat treatment of H-mordenite as well as the influence of H_2 and O_2 on the yield of benzene radical-cations. H-mordenite was first heated in air for 16 h at 500°C and then rehydrated for several days in a moist atmosphere. The standard heat treatment consisted in evacuation for 16 h at the given temperature in the range 100–800°C.

The treatment in hydrogen included the following stages: contact with H_2 at a pressure of 1 atm for 15 min at the standard heat treatment temperature and evacuation of H_2; repeated contact with H_2 under the same conditions with its subsequent evacuation for 3 h and cooling of the specimen *in vacuo*. Fig. 7 illustrates the influence of the temperature of the standard heat treatment of H-mordenite on the yield of benzene radical-cations (when 0.5 ml of benzene is adsorbed on 1 g of the zeolite) and on the specific surface of the zeolite determined by the BET method at 77 K from the adsorption of N_2. The weak maximum near 400°C can be attributed to the inaccuracy of the determination of the concentration of the radical-cations (errors of ±10%). However, it appears that the experimental error is not the real cause, since the changes in the concentrations of radical-cations on specimens evacuated at 300° and 500°C and treated in hydrogen are significantly different (Table 6). This finding probably indicates the formation of two different types of oxidation centres in specimens treated at 300° and 500°C respectively.

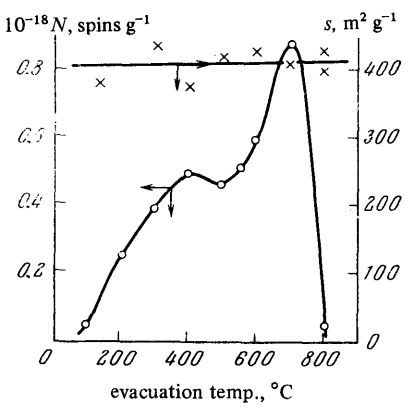


Figure 7. The influence of the heat treatment of H-mordenite on the concentration of benzene radical-cations (N) and the specific surface of the zeolite (s, determined by the BET method) [22].

The maximum number of benzene radical-cations is reached in the adsorption of 0.1 ml of benzene per gram of H-mordenite. The total adsorption capacity with respect to benzene at 25–28°C corresponds to approximately 0.09 ml per gram of zeolite. Consequently the maximum yield of the radical-cations is observed only when the mordenite channels are fully saturated by benzene. It must be emphasised that under these conditions approximately only 0.1% of the adsorbed molecules are oxidised to the radical-cations.

The data in Table 6 illustrate the influence of O_2 on the concentration of the radical-cations formed. It is evident from a comparison of these results with those presented in Fig. 6 that a particularly marked increase in the concentration of the radical-cations under the influence of O_2 is observed on the specimen evacuated at 800°C. The authors [22] showed that the ratio of the maximum number of radical-cations (2.1×10^{18} spins g^{-1}) and the number of O_2 molecules chemisorbed after treatment in hydrogen is 1 : 1.2. The treatment in hydrogen probably removes the most strongly chemisorbed oxygen remaining in the zeolite after the standard treatment. The evacuation of the O_2 adsorbed at room temperature and a pressure of 745 mmHg before the admission of benzene reduces the yield of radicals by approximately only 30% compared with the yield in the presence of O_2. Consequently chemisorbed by not physically sorbed oxygen plays an important role in the formation of the radical-cations. It is suggested that the chemisorption of an O_2 molecule on an H-mordenite active centre (or close to it) leads to the formation of a strong electron-accepting centre capable of oxidising benzene to the radical-cation. The yield of the radical-cations is limited by the amount of chemisorbed oxygen.

Table 6. The influence of treatment in hydrogen and of the oxygen pressure on the concentration of radical-cations formed.

Evacuation temperature, °C	Treatment in hydrogen	O_2 pressure, mmHg	Concentration of radical-ions, 10^{-17} spins g^{-1}
550	no	2.7	21.0
550	no	9.5	17.5
550	no	11.0	20.4
800	no	6.0	6.19
300	yes	0	1.18
500	yes	0	<0.01

It was shown on the basis of the estimates quoted in the report of Sagert et al. [22] that only one mordenite unit cell in 100 contains a strong oxidation centre. The exact nature of these centres is unknown, but their formation is probably associated with mordenite crystal lattice defects. These centres are located in the principal mordenite channels. This conclusion is confirmed, on the onehand, by adsorption measurements and, on the other, by experiments with perylene. In the adsorption of perylene, which has a significantly lower ionisation potential and a larger molecular size than benzene, the authors [22] failed to observe the formation of radical-cations. According to other data [24], approximately 20% of the overall adsorbed species are located on the outer surface of mordenite. Thus the absence of perylene radical-cations shows that the oxidation centres are located within the mordenite structure and not on its outer surface.

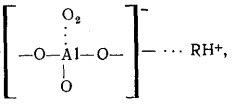
More definite conclusions about the nature of the oxidation centres of mordenite responsible for the formation of benzene radical-cations were reached by Tokunaga et al. [23], who also investigated the influence of the preliminary heat treatment and the adsorption of O_2 and SO_2 on the yield of the radical-cations of benzene in its adsorption from the gas phase on NH_4Na-mordenite with a degree of exchange of 32%. It was shown that the benzene radical-cations are formed only after the evacuation of the zeolite at temperatures of the order of 500°C and that their concentration increases almost by an order magnitude with increase of the vacuum heat treatment temperature to 700°C. The parameters of the ESR spectrum and its time variation are analogous to those described by Kurita et al. [19] and correspond to the formation of benzene radical-cation dimers, which are converted after a time into biphenyl radicals. The yield of benzene radical-cations increases by a factor of approximately 5 as a result of the subsequent adsorption of O_2 at room temperature after the removal of benzene from the gas phase. The increase of the concentration of

radicals has also been observed when O_2 was adsorbed before the adsorption of benzene, the magnitude of the effect depending in this case on the temperature of the preliminary adsorption of O_2: with increase of temperature from room temperature to 400°C, the concentration of benzene radical-cations increased by a factor of approximately 15. The adsorption of SO_2^- has the same effect on the yield of benzene radical-cations as the adsorption of oxygen.

Perhaps the most interesting result of this investigation [23] is the observation of the ESR signal of the SO_2^- radical-anion as a result of the adsorption of SO_2 on mordenite after the preliminary adsorption of benzene. A significant increase of the intensity of the benzene radical-cation signal was observed simultaneously with the appearance of the SO_2^- ESR spectrum.

The authors [23] suggest that the oxidation centre of mordenite includes a tricoordinate aluminium ion, the electron-accepting properties of which are enhanced under the influence of O_2 or SO_2 owing to the inductive effect. The negative charge is distributed between the aluminium ion involved in the one-electron transfer and the nearest adsorbed O_2 molecule. Such charge distribution for SO_2 leads to the formation of the SO_2^- radical-anion.

The above mechanism does not of course differ significantly from the mechanism involving the adsorption complex



proposed [1] to account for the influence of O_2 on the formation of radical-cations in the adsorption of hydrocarbons on amorphous aluminosilicates. However, this complex can be formed on any aluminosilicate and is not a characteristic feature of mordenites. Nevertheless, as already mentioned above, the radical-cations of benzene and other molecules with high ionisation potentials are formed under normal conditions only on mordenites. We shall consider this process in greater detail below. In conclusion of the analysis of the study of Tokunaga et al. [23], we shall mention here that the ESR spectrum of the SO_2^- radical-anion observed by them is very remarkable. In discussing earlier investigations [2,12], we already noted the fact that, in the ESR study of the radical-cations formed in the adsorption of hydrocarbons on zeolites, it was impossible to detect the unpaired electron captured by the solid. The possible causes of this phenomenon were also briefly discussed, one of them being associated with the delocalisation of the captured electron over the entire bond system of the solid. One cannot rule out the possibility that the appearance of SO_2^- radical-anions observed by Tokunaga et al. [23] is in fact due to the localisation of the captured electron at the sulphur atom.

3. The Oxidising Properties of Mordenites from Which Metal Cations and Aluminium Have Been Eliminated

Few studies on the influence of the elimination of metal cations and aluminium from mordenites on their oxidising and reducing properties are described in the literature. It has been shown [25] that the sharp increase of the ESR signal intensity following the adsorption of anthracene on specimens freed from metal cations is observed for degrees of exchange in excess of 50% (Table 7, Nos. 1–6). The size of the adsorbed molecule is significant in adsorption on mordenites. The dimensions of the small and large elliptical channels in mordenite are 3.8–4.7 Å and 5.8–7.0 Å respectively. The narrow channels (~4 Å) are inaccessible to anthracene molecules. During the metal cation-elimination process, Na^+ ions are removed from the large channels, which increase the effective diameter of the latter [26] and thus the rise of signal intensity may be caused both by the increase in the number of oxidation centres and by the greater accessibility of the bulk of the zeolite to anthracene molecules.

Table 7. Dependence of the number of anthracene radical-ions (N) on the degree of elimination of metal cations and aluminium from mordenite.

No. of specimen	Type of zeolite	SiO_2/Al_2O_3	Degree of exchange of Na^+ for H^+, %	$10^{-17}N$, spins g^{-1}
1	NaM	10.14	—	no signal
2	»	10.14	15.0	ditto
3	»	10.14	25.0	very weak signal
4	»	10.14	50.0	2.2
5	»	10.14	80.0	7.2
6	HM	10.14	99.4	7.6
7	»	13.3	99.4	10
8	»	16.8	99.4	10
9	»	20.6	99.4	15
10	»	48.0	99.4	4.4
11	»	55.0	99.4	6.7
12	»	73.0	99.4	7.6

The dealumination of an HM specimen is accompanied by an increase in the ESR signal intensity, which reaches a maximum for the preparation with the ratio SiO_2/Al_2O_3 = 20.6. The maximum in catalytic activity observed in a series of investigations for mordenite with this SiO_2/Al_2O_3 ratio [27,28] may be associated with the optimum oxidising properties of this catalyst.

Analysis of the results shows that oxidation centres arise mainly when metal cations are removed from NaM, while dealumination of an HM specimen is accompanied by only a twofold increase of the concentration of these centres.

A detailed study of the oxidising properties of mordenite in relation to the formation of benzene, naphthalene, and anthracene radical-cations has been made [29]. Fig. 8*a* presents the ESR spectrum arising immediately after the adsorption of benzene on an HM zeolite heated in air at 300°C.

The nature of the ESR spectra arising in the adsorption of benzene on an HM zeolite and the influence of O_2 on their appearance, investigated in the above study, confirm the earlier literature data [18,19,22,23]. The HFS constant, equal to 2.3 G, corresponds to the formation of the biphenyl radical. This is confirmed by the presence of 11 HFS components in the adsorption of benzene, i.e. the unpaired electron interacts with 10 equivalent protons. The hypothesis [18] of the formation of a "sandwich" of two benzene molecules appears unlikely, bearing in mind the geometry of the large mordenite channels. Furthermore, in such a model it is not clear which central mordenite lattice cation should be involved in the formation of this "sandwich". The initial activation of the benzene molecule by interaction with an electron-accepting centre and the formation of a charge-transfer complex followed by rapid oxidative dehydrogenation and the formation of a biphenyl radical-cation therefore appear more likely.

Experiments with adsorption of C_6H_5D and 1,4-$C_6H_4D_2$ have shown that there is no preferential abstraction of a D atom in the formation of the biphenyl radical-cation. In fact, if mainly the D atoms were abstracted in the oxidative dehydrogenation, the resulting ESR spectrum would have been identical with that arising in the adsorption of C_6H_6. Examination of Figs. 8 and 9 shows that this is not the case. The spreading of the HFS and the narrowing of the ESR spectrum observed in the adsorption of deuterated benzenes are characteristic of radical-cations in which some of the hydrogen atoms have been replaced by deuterium atoms [30].

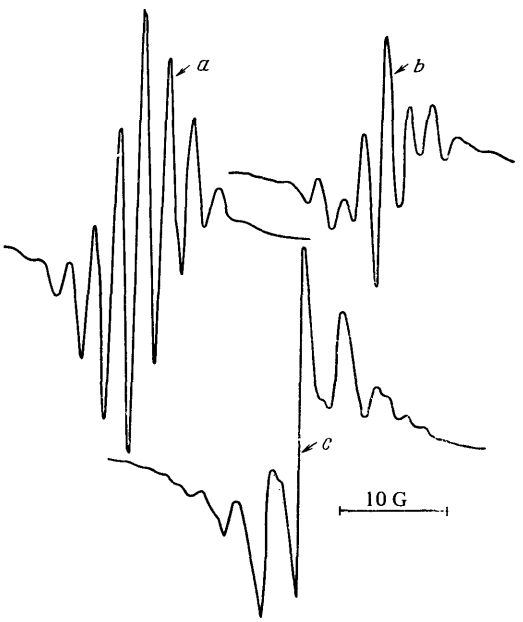


Figure 8. The ESR spectrum of the radical-cations of benzene adsorbed on H-mordenite heated in air at 300°C: *a*) immediately after adsorption; *b*) after 1.5 h; *c*) after 24 h [*a*) and *b*) identical amplification; *c*) amplification greater than in cases *a* and *b*] [29].

A characteristic feature of the ESR spectra of adsorbed C_6H_6 is their rapid time variation (Fig. 8), particularly on heating the zeolite. This is associated with the subsequent occurrence of processes leading to the formation of polyphenylene radicals, giving rise to a singlet ESR line. In contrast to C_6H_6, the adsorption of naphthalene and anthracene on an HM zeolite is accompanied by the appearance of much more stable radical-cations, the ESR signals of which (Fig. 10) hardly vary at room temperature over a long period (1 month in the case of anthracene). The different stabilities of the benzene, anthracene and naphthalene radical-cations can probably be explained by the greater reactivity of the biphenyl radicals, leading to the formation of polyphenylenes.

In all the studies on the ESR spectra of molecules with cojugated bonds adsorbed on type X and Y zeolites made hitherto, the adsorbents were subjected to a rigorous preliminary heat treatment (at about 500°C), since it was assumed that centres capable of the formation of radical-cations arise only under these conditions. Fig. 11 illustrates the changes in the concentration of the anthracene, naphthalene, and benzene radical-cations as a function of the temperature of the heat treatment of the HM zeolite in air [29]. Evidently the lower the ionisation potential of the hydrocarbon, the lower the temperature of the heat treatment after which the ESR spectrum of the radical-cation appears. An intense signal of the anthracene radical-cations appears at a heat-treatment temperature as low as ~150°C, although this temperature is too low even for the elimination of the entire molecular water from the mordenite channels. Thus, powerful oxidation centres appear in H-mordenite even at low dehydration temperatures.

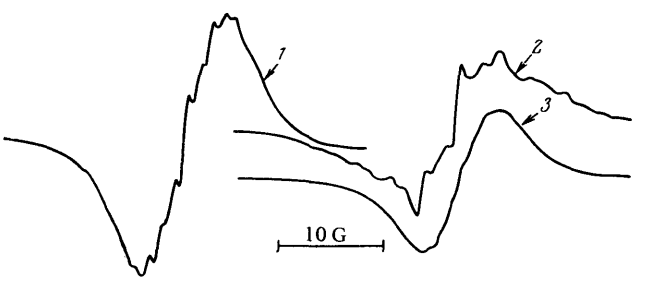


Figure 9. The ESR spectra of deuterated benzenes adsorbed on H-mordenite heated in air at 450°C: 1) immediately after adsorption of C_6H_5D; 2) 24 h after adsorption of C_6H_5D; 3) immediately after adsorption of 1,4-$C_6H_4D_2$ (identical amplification) [29].

One should note that an increase of dehydration temperature entails an increase not only in the number of oxidation centres but probably also in their activity. A dehydration temperature of 150°C is sufficient for the formation of centres capable of oxidising anthracene to the radical-cation, but is insufficient for the appearance of centres on which benzene radical-cations are formed.

The different activities of the oxidation centres suggest that the molecules of aromatic hydrocarbon differing in their ionisation potentials will interact with these centres, forming charge-transfer complexes with different bond strengths. It might therefore have been expected that the anthracene molecule, which has the lowest ionisation potential compared with naphthalene and benzene, would be linked to the electron-accepting centre most strongly and anthracene molecules should therefore displace the radical-cations formed in the adsorption of benzene and naphthalene. It has indeed been found that, when a zeolite with adsorbed naphthalene radical-cations (Fig. 10*a*) is exposed to anthracene in carbon tetrachloride solutions, the spectrum of the naphthalene radical-cations vanishes after 15 min and that of the anthracene radical-cations appears (Fig. 10*b*). It is remarkable that the rate of the displacement process is fairly high, despite the difficulty of the migration of relatively large molecules in the narrow mordenite channels.

One of the fundamental problems in the study of the mechanism of the formation of radical-cations on aluminosilicates and zeolites is that of the nature of the

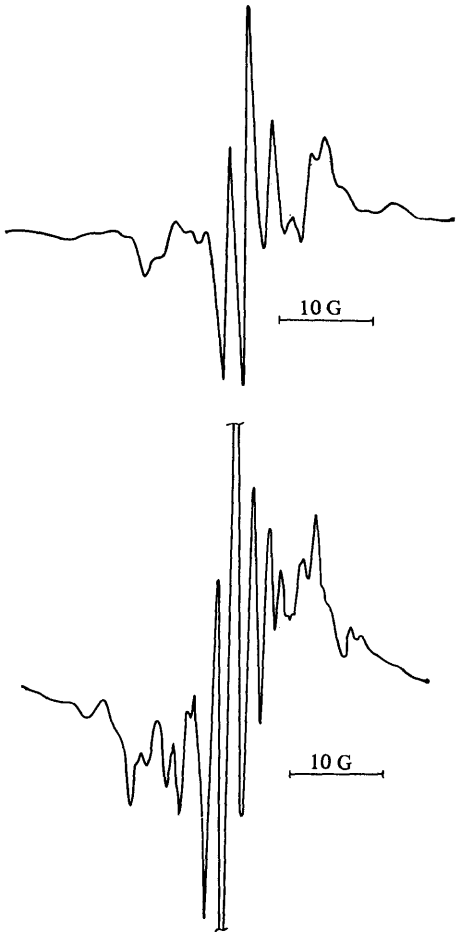
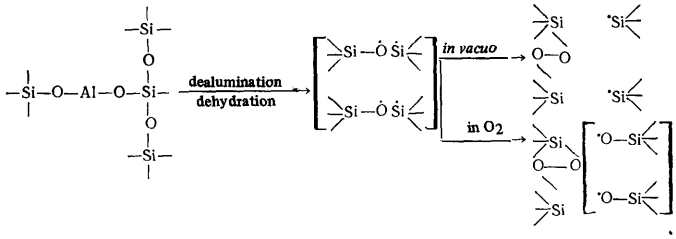


Figure 10. The ESR spectra of the radical-cations of naphthalene (*a*) and anthracene (*b*) adsorbed on H-mordenite[29].

electron-accepting centre and of the role of oxygen. It has been suggested that the electron-accepting centre consists of an Al^{3+} ion. The role of oxygen in the formation of radical-cations, for example in the adsorption of benzene on H-mordenite, reduces to the inductive effect on the Al^{3+} ion, which facilitates the electron transfer[23]. We already noted above that this mechanism does not differ in any significant way from the adsorption complex mechanism proposed[1] to account for the influence of O_2 on the formation of radical-cations in the adsorption of hydrocarbons on amorphous aluminosilicates. It was also emphasised that this mechanism does not explain the appearance of radical-cations in the adsorption of benzenes on H-mordenite, because H-mordenite is the only one of the zeolites investigated hitherto on which benzene radical-cations are formed readily at room temperature without any additional influences on the system, for example ultraviolet irradiation. Consequently the activity of the electron-accepting centres in H-mordenite, at any rate in the formation of benzene radical-cations, should significantly exceed the activity of the electron-accepting centres in other zeolites and amorphous aluminosilicates.

Since treatment of mordenite with oxygen is a necessary condition for the generation of centres responsible for the formation of benzene radical-cations and the mechanisms involving Al^{3+} ions alone does not account for this process, the centres are presumably formed[29] as a result of the interaction of oxygen with silicon. Judging from the intensity of the ESR signal, the number of such centres is small, amounting to approximately one centre for 100 unit cells in anthracene, the number in benzene being smaller by a factor of 2–3.

If it is supposed that dealumination takes place at certain sites in the structure during the formation of mordenite, the subsequent formation of centres can be represented by the following scheme:



(I)

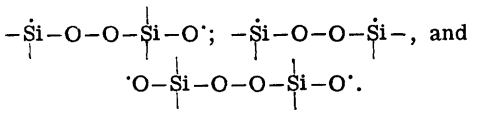
The pairs of radicals $\geq$Si–O$^{\cdot}$ and $\geq$Si$^{\cdot}$ arising in the dehydration process cannot lead to the formation of the Si–O–Si linkage. The point is that there are four different sites in mordenite where Si(Al) atoms are located[31], for which the distance between the nearest Si atoms has been shown by calculations to vary in the range 4.36–5.77 Å. The average Si–O bond length for the same lattice sites varies in the range 1.59–1.63 Å.[31] Consequently the Si–Si distance exceeds by approximately 1 Å twice the Si–O bond length, so that only Si–O–O–Si linkages can formed. On the other hand, the formation of such a peroxy-bridge between two other silicon atoms in the interaction with oxygen is probably impossible owing to steric hindrance.

The $\geq$Si$^{\cdot}$ centres are relatively unreactive with respect to the adsorption of hydrocarbons, since the unpaired electron is delocalised in these centres over the Si–O bonds. The adsorption of O_2, leading to the formation of Si–O$^{\cdot}$ radicals, thus creates strong electron-accepting centres, active in the formation of radical-cations.

The mechanism described apparently accounts for the appearance of the intense ESR signals in the adsorption of benzene on hydrated H-mordenite heated at low temperatures (Fig. 11). Heat treatment of H-mordenite at low temperatures (~200°C) in the presence of O_2 already gives rise to structure (I), which is active in the formation of benzene radical-cations. Naturally, apart from these centres, the mordenite contains also the usual electron-accepting centres incorporating Al^{3+} ions, which are responsible for the formation of anthracene and naphthalene radical-cations at still lower heat-treatment temperatures (~150°C).

The possibility of the formation of structure (I) is to some extent confirmed by the results of a study by Low[32], who obtained and investigated active silica gels. By methoxylating aerosil with subsequent pyrolysis and heat treatment, he succeeded in obtaining a silica gel which adsorbed considerable amounts of H_2 and O_2. On the basis of adsorption and infrared spectroscopic studies, he postulated[32] the presence on the adsorbent surface of a

small number of unusual centres, incorporating silicon atoms, linked by a peroxy-chain:



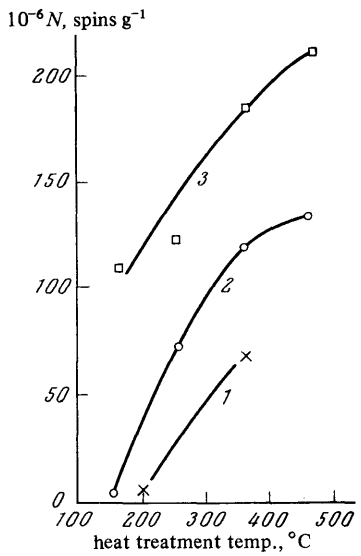


Figure 11. Dependence of the concentration (N) of the radical-cations of benzene (curve *1*), naphthalene (curve *2*), and anthracene (curve *3*) on the temperature of the heat treatment of H-mordenite[29].

Wheareas preliminary methoxylation with subsequent pyrolysis and a fairly severe heat treatment are necessary conditions for the formation of such centres in SiO_2, in mordenite with its unusual crystal structure, centres of this kind can arise under much milder conditions.

IV. CONCLUSION

The studies discussed above have shown that there has been a continuous growth of interest in the study of the oxidising and reducing properties of zeolites. This is due not only to the theoretical importance of the problem but also to its practical aspects, since it has been suggested that the oxidation-reduction centres in aluminosilicate catalysts are involved in the catalytic transformations of hydrocarbons [33].

The characteristic features of the formation of radical-cations on zeolites compared with amorphous aluminosilicates arise from several causes, in particular (1) the specific geometrical structure of zeolites and (2) the presence of more powerful oxidation centres in zeolites. As a result of the latter, radical-cations are formed on zeolites following the adsorption of molecules with high ionisation potentials (benzene and olefins), which is not observed in adsorption on amorphous aluminosilicates.

One of the fundamental problems arising in the study of the oxidation-reduction centres is the elucidation of their nature. The main oxidation centre is believed nowadays to be the tricoordinate Al^{3+} ion (a Lewis centre), but the complete set of data obtained cannot be accounted for solely by the presence of such centres, particularly for H-mordenite. The problem therefore arises whether or not the formation of radical-cations is a specific instance of a general acid–base interaction or whether the oxidation-reduction centres constitute a special group. The elucidation of these problems is of greatest importance for the understanding of the nature of the centres on the surfaces of amorphous and crystalline aluminosilicates and of the mechanism of acid–base catalysis. In this respect, the study of the oxidising and reducing properties of zeolites having a known geometrical structure and susceptible to different types of modification can render invaluable assistance in the solution of the problems formulated above.

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