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Study by ESR and Optical Spectroscopy of Transition-metal Ions in Zeolites and of Their Complexes with Adsorbed Molecules

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Studies by ESR and optical spectroscopy of zeolites containing transition-metal ions are reviewed. The locations of transition-element ions introduced into zeolites of various types by cation exchange and identified by these techniques are generalised. It is shown that these methods give useful information on the accessibility of the ions by adsorbed molecules and on the electronic structure of the complexes formed by the interaction betweeen adsorbed molecules and transition-metal ions. The properties of these complexes are discussed. 122 references.

CONTENTS

I. Introduction 209
II. Ions of the metals from the first transition period 210
III. Ions of the metals from the second and third transition periods 216
IV. Conclusions 217

I. INTRODUCTION

Cation-exchange forms of zeolites are being used increasingly as catalysts, adsorbents, etc., and many papers on these materials have been published recently. ESR and optical (u.v.) spectroscopy methods have been used to identify the state of the cations in the zeolites, especially in the case of zeolites containing transition-metal ions. Very detailed information has been obtained by these methods: not only the valency and co-ordination states, and the localisation sites of the ions, but also the complexes formed by the interaction of the ions with various adsorbed molecules have been identified.

Mikheikin and coworkers[1] have reviewed the application of spectral methods of investigation to zeolites containing transition-metal ions, and the results obtained, but many new papers have appeared since that review was published. The more recent results have resolved the inconsistencies in some of the earlier work. A new review of the subject therefore seemed desirable.

The present review includes the whole of the work which has come to our notice since the publication of Mikheikin's review[1]. Most of the papers which we shall quote describe studies of ions from the first transition period (Ti–Cu), but we shall also discuss the more recent (and not very extensive) work on ions of metals from the second and third transition periods. With a few exceptions, dictated by the need for clarity in the discussion, we have avoided reference to work mentioned in Ref.1. The discussion is arranged in order of increasing atomic number of the transition elements incorporated in the zeolite, and the nomenclature used by Breck to denote the different localisation sites has been adopted[2].

II. IONS OF THE METALS FROM THE FIRST TRANSITION PERIOD

1. Titanium

The electronic configuration of the ground state of the atom is $(A)(3d)^2(4s)^2$, where (A) is the complete electronic structure of the argon atom. Titanium-containing type Y zeolites have been prepared and studied by ESR.[3] Ion exchange was carried out in an aqueous solution of $TiCl_3$, and it was assumed that after exchange the Ti^{3+} ions are located in the large zeolite holes[3].

Adsorption of oxygen and sulphur dioxide on these samples (after dehydration at 500 °C) produces ESR signals with the parameters $g_1 = 2.0196$, $g_2 = 2.0089$, $g_3 = 2.0031$, and $g_1 = 2.001$, $g_2 = 2.003$, $g_3 = 2.004$, assigned to the O_2^- and SO_2^- anion-radicals respectively. Adsorption of N_2O, followed by heating at 200 °C, gives an ESR signal with the parameters $g_1 = 2.017$ and $g_2 = 2.001$, tentatively assigned to the O^- anion-radicals. Since the adsorption centres are accessible to O_2, SO_2, and N_2O molecules they probably consist of Ti^{3+} ions localised in S_{II}, $S_{II'}$, or possibly S_{III} sites.

2. Vanadium

The electronic structure of the ground state of the atom is $(A)(3d)^3(4s)^2$. Vanadium has been introduced into zeolites only in the form of the vanadyl ion VO^{2+}. The localisation and mobility of vanadyl ions in type X and Y zeolites as a function of the degree of dehydration of the zeolite has been studied in detail by ESR at 77–300 K.[4]

Fully hydrated type Y zeolites at 20 °C give ESR spectra with the parameters $g_\parallel = 1.944$, $g_\perp = 1.978$, and $A_\parallel = 175 \times 10^{-4}$ cm^{-1}, $A_\perp = 70 \times 10^{-4}$ cm^{-1} (I), whereas at 77 K the spectral parameters are $g_\parallel = 1.938$, $g_\perp = 1.986$, $A_\parallel = 178 \times 10^{-4}$ cm^{-1}, $A_\perp = 70 \times 10^{-4}$ cm^{-1} (II). Reversibility of these spectral changes was demonstrated by dehydration at 350 °C followed by rehydration. In this case the dehydrated samples give an ESR signal with the parameters $g_\parallel = 1.917$, $g_\perp = 1.989$, $A_\parallel = 190 \times 10^{-4}$ cm^{-1}, $A_\perp = 79 \times 10^{-4}$ cm^{-1} (III), whose intensity increases with the dehydration temperature. Dehydration at temperatures above 350 °C gave irreversible changes in the intensity of the ESR signals, suggesting changes in the zeolite structure.

Both at −196 and at 20 °C the ESR spectra of fully hydrated type X zeolites gave a signal with the parameters $g_\parallel = 1.943$, $g_\perp = 1.983$, $A_\parallel = 170 \times 10^{-4}$ cm^{-1}, $A_\perp = 60 \times 10^{-4}$ cm^{-1} (IV), whereas after dehydration of the sample at 350 °C the parameters of the signal became $g_\perp = 1.989$, $g_\parallel = 1.918$, $A_\parallel = 178 \times 10^{-4}$ cm^{-1}, $A_\perp = 66 \times 10^{-4}$ cm^{-1} (V).

Spectra (I) and (IV) are similar to those of vanadyl ions in aqueous solution, and have been assigned[4] to VO^{2+} ions in large zeolite holes. Spectra (III) and (V) are believed to arise from VO^{2+} ions also localised in large holes but co-ordinated to OH^- or oxygen ions from the zeolite lattice. All these complexes have distorted octahedral surroundings with C_{4h} symmetry.

A study[5] of type Y zeolites containing vanadyl ions has shown that the VO^{2+} ions are stabilised mainly in S_{III} (and some S_{II}) sites by dehydration at temperatures up to 350 °C. Interactions between neighbouring vanadyl ions can be detected at exchange levels higher than 20%.

3. Chromium

The electronic configuration of the ground state of the atom is $(A)(3d)^5(4s)^1$. The commonest oxidation states of the chromium ions in solution under ordinary conditions are Cr^{3+} and Cr^{6+}. Because of the difficulty of introducing complexes with a charge greater than three into the zeolites all the work so far reported (with a few exceptions[6–8]) has been on zeolites prepared by exchange with trivalent chromium compounds.

Leaving aside the work on the localisation sites and on the properties of Cr^{3+} in zeolites, which has already been reviewed[1], we shall examine only the most recent work. The following zeolites have been studied[9,10] by ESR: CrNaA (8% exchange), CrNax (9.3% exchange), and CrNaY (13.6% exchange). The complex ions $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_6^{3+}$ were shown to be present, after exchange, in the S_{IA} and S_{II} sites of the type A and X zeolites and in the large holes of the type Y zeolites. We should note that in type A zeolites the symbol S_{IA} denotes the cation stabilisation sites in the hexagonal windows of oxygen ions giving access to the cubo-octahedra[2] whereas in type X and Y zeolites the same sites are denoted S_{II} or $S_{II'}$ (depending on the side of the window plane in which the cation is stabilised). Treatment of the zeolite in a stream of dry air at 350 °C causes oxidation of the Cr^{3+} ions to the Cr^{6+} and Cr^{5+} states, though the proportion of quinquevalent cations is always small. Between 80% (type A) and 30% (type X) of the originally present Cr^{3+} ions is oxidised. The parameters of the ESR spectra of the Cr^{5+} ion in oxidised chromium-containing A, X, and Y zeolites are consistent with the formation of chromyl ions (CrO^{3+}) in an octahedral configuration. The perpendicular component of the ESR spectra showed a hyperfine structure assigned[9,10] to the aluminium atoms of the zeolite skeleton. However, the proposed model includes four oxygen ions from the lattice as equatorial ligands, which it is difficult to reconcile with the suggestion that the cations are localised preferentially in S_{II} (or S_{IA}) sites to give a C_{3v} (or D_{3h}) symmetry. We should also note that the oxidation of chromium ions to Cr^{5+} and Cr^{6+} must involve some breakdown of the zeolite crystal lattice[1].

Vogt and coworkers[11,12] studied CrNaY zeolites with different chromium content by optical spectroscopy, and showed that on dehydration the chromium ions are localised initially in S_{II} sites (at 200 °C), then in $S_{I'}$ or $S_{II'}$ sites (400 °C) and lastly (at least partly) in S_I sites (500–600 °C). The occupation of S_I sites is inferred from the appearance of absorption bands at 14 300 and 18 800 cm^{-1}. This red shift from the spectrum of the hexa-aquo complexes (16 400 and 23 600 cm^{-1}) is explained by postulating that the lattice oxygen is a weaker ligand than the oxygen in a water molecule. Similar conclusions were obtained from X-ray diffraction studies.

Vacuum heat treatment at 450 °C suppressed the ESR signal from the Cr^{3+} hexa-aquo complex ions[11,12], indicating a transition from octahedral co-ordination of the chromium ions to a tetrahedral co-ordination distorted along a trigonal axis[1]. This conclusion was confirmed by measurements of magnetic susceptibility as a function of temperature. It was pointed out that heat treatment in a stream of dry air at 450 °C causes breakdown of the zeolites as a result of the oxidation of the Cr^{3+} ions to Cr^{5+} and Cr^{6+}. Breakdown is produced also by dehydration of the chromium-containing zeolites when the degree of exchange is more than 40%. Breakdown of the crystal structure of chromium-containing zeolites under oxidising conditions was first suggested in Ref. 13.

Thus the work published since the last review[1] is mainly a confirmation of previous results. The only novel feature is the discovery of Cr^{3+} ions in S_I positions in samples dehydrated at 500–600 °C.[9,10]

We shall now review the work on the adsorption of some molecules on chromium-containing zeolites. Formation of cation radicals has been observed during adsorption of naphthalene, anthracene, and perylene on CrNaY samples heat treated in a stream of air at 150–400 °C,[14] and ascribed to interactions of the Cr^{6+} ions with adsorbed molecules in the large zeolite holes. However, as we have already pointed out, the chromium-containing zeolites tend to break down under these conditions, and it is no longer legitimate to assume the presence of large holes.

The adsorption of nitric oxide and nitrogen dioxide on chromium containing type Y zeolite and mordenite is discussed in Ref.15. If the zeolites are oxidised at 500 °C the adsorption of NO and NO_2 produces ESR signals only from molecules loosely bound to the surface, whose characteristic ESR spectra are well known. However, if the same molecules are adsorbed on zeolites which have been reduced in hydrogen after the oxidising treatment a new ESR signal appears ($g_\perp = 2.000$, $g_\parallel = 1.917$ for both molecules and both types of zeolite): this is ascribed to the formation of complexes with the d^5 electronic structure (Cr^+NO^+ and $Cr^+NO_2^+$ for the NO and NO_2 molecules respectively). These complexes are formed by the interaction between the adsorbed molecules and the Cr^{2+} ions produced by the reducing treatment. We should once again point out that although the zeolites used in this work[15] had been reduced in hydrogen they had been previously subjected to an oxidising treatment, which must have destroyed the crystal structure and produced an amorphous alumina–silica. This probably explains why identical complexes were obtained with faujasite and mordenite.

Studies of zeolites containing Cr^{2+} ions introduced directly from solutions have also been reported[6–8]. Kellerman and coworkers[6] studied the adsorption of oxygen on Cr(II)NaA zeolite dehydrated at 300 °C, and concluded that the Cr^{2+} ions (stabilised mainly in S_{IA} sites) produce weak oxygen complexes at room temperature, with optical spectra characterised by absorption bands at 4000, 10 000, 14 200, 18 000, 20 600, and 26 200 cm^{-1}. Further work[7] showed that trigonally co-ordinated Cr^{2+} ions can form weak complexes with N_2O, CO_2, and C_2H_4 molecules also at room temperature. In this case the Cr^{2+} ions adopt a distorted tetrahedral co-ordination. At 150 °C the adsorption of O_2 and N_2O is dissociative, with formation of Cr^{4+} ions by oxidation of Cr^{2+}. The Cr^{4+} ions have an approximately tetrahedral co-ordination consisting of three oxygen atoms from the zeolite skeleton and one from the adsorbate. This latter oxygen atom can react with CO at 300 °C, thus re-establishing the initial valency and co-ordination state of the chromium ions.

A detailed study of type Y zeolites containing Cr^{2+} ions (prepared by exchange with a solution of $CrCl_2.4H_2O$) has been reported from our laboratory[8]. Dehydration of these zeolites at temperatures up to 500 °C was not accompanied by breakdown of the crystal structure for degrees of exchange up to 70%. The following results were obtained with samples in which the degree of exchange was 14%. The optical spectrum of the zeolite dried in a vacuum at room temperature had an absorption band at 13 500 cm^{-1}, characteristic of octahedrally co-ordinated Cr^{2+} complexes. Dehydration at 500 °C causes this band to split into two (12 200 and 16 200 cm^{-1}) as a result of a change in symmetry of the co-ordination sphere and of the formation of co-ordinationally unsaturated Cr^{2+} ions. Dehydration also causes replacement of the water ligands by oxygen from the zeolite skeleton, as shown by the shift of the charge-transfer absorption peak from 38 000 to 30 000 cm^{-1}. Adsorption of water or ammonia re-establishes the octahedral co-ordination of the Cr^{2+} ion. The formation of weak ethylene complexes at room temperature was also reported. The accessibility of the Cr^{2+} ions in dehydrated zeolites to various adsorbed molecules suggests that these ions are stabilised in S_{II} or $S_{II'}$ sites.

We also showed[8] that the redox properties of the Cr^{2+} ions in dehydrated zeolites are different from those of the same ions in solutions or on the surface of SiO_2. The co-ordinationally unsaturated Cr^{2+} ions in dehydrated zeolites are more stable in an oxygen atmosphere, and their valency is not changed by adsorption of oxygen at room temperature. The only effect of oxygen adsorption is the formation of weak complexes between O_2 molecules and Cr^{2+} ions, characterised by maxima in the optical spectrum at 12 000, 16 600, 18 300, 21 200, 28 000, and 31 000 cm^{-1}.

4. Manganese

The electronic structure of the ground state of the atom is $(A)(3d)^5(4s)^2$. Only bivalent manganese ions have been introduced into zeolites by ion exchange. Since the intensity of the d–d absorption bands of the Mn^{2+} ions is low, optical methods of investigation have not been widely used. On the other hand, manganese-containing zeolites have been studied in depth by ESR because the ESR signals from Mn^{2+} ions can be observed over a wide range of temperature and concentration.

The ESR work published up to 1972 is described in detail in Ref.1. That work established the existence of Mn^{2+} ions in zeolites in different co-ordination states, but it left unresolved a number of inconsistencies in the treatment of the experimental results.

More recent work on manganese-containing zeolites was reported by Tikhomirova and coworkers[16–20] and by Taranukha and coworkers[21–24]. The samples examined contained, in addition to manganese ions, the cations Li, K, Cs, Mg, Ca, Co, Sr, Ba, La, or Y. The Mn^{2+} ions, introduced to an extent of 0.05–2 ions per elementary cell, were used as paramagnetic probes.

Tikhomirova and coworkers[16–20] studied manganese-containing zeolites of types Y and A. The ESR spectra were measured at Q band (35 GHz). The localisation sites of the Mn^{2+} ions were identified from the change in g-factor and from the splitting between the central components of the hyperfine structure, and also from the width of the first and the sixth component, which allowed the different spectra to be clearly distinguished. Measurements on manganese-containing sodalite and erionite (in which hexagonal prisms are absent) gave, for the first time, pure ESR spectra which could be assigned with full confidence.

By analysing the spectra of samples before and after dehydration these workers concluded that in type Y zeolite ion migration occurs in the direction large hole → $S_{II}(S_{II'})(O_h)$ → $S_{II}(S_{II'})(T_d)$ → $S_{I'}$ → S_I, and in the opposite direction during hydration[20]. The adsorption of ammonia, pyridine, and some other molecules also causes Mn^{2+} ions to migrate along the zeolite skeleton.

It was also noted that the changes in the ESR spectra accompanying dehydration and the adsorption of various molecules are very sensitive to the nature of the second cation present in the zeolite. Thus, in the dehydration of CaY and CdY zeolites these cations effectively block the S_I sites and impede the penetration of manganese ions. In the MgY zeolite a significant fraction of the Mn^{2+} ions can find its way into S_I sites, and in ZnY all the S_I sites are occupied

by manganese ions. These results are explained[20] by postulating a heat of dehydration of the Mn^{2+} ions greater than that of Ca^{2+} and Cd^{2+} ions but smaller than that of Mg^{2+} and Zn^{2+} ions. Since the S_I sites are accessible only to ions which have lost the whole of their co-ordinated water they should be occupied, in the first instance, by the ions with the lowest heat of hydration, as is found in practice.

The existence in type Y zeolites of Mn^{2+} ions in octahedral, distorted octahedral, tetrahedral, and lower symmetry configurations has been confirmed by ESR and by optical and luminescence spectroscopy[21-24].

5. Iron

The electronic structure of the ground state of the atom is $(A)(3d)^6(4s)^2$. Relatively few studies of iron-containing zeolites by ESR have been reported, and none by optical spectroscopy. The first publication[25] on this topic described a study by ESR and magnetic susceptibility measurements, showing that dehydration of the ammonium form of a type Y zeolite (10^{-2} at.% Fe) produces ferromagnetic structures with $g_{eff} = 2.4 \pm 0.1$ and $\Delta H = 1600$ Oe. It was assumed[25] that the diameter of the ferromagnetic particles is less than 20 Å, and their composition is $Al_{3-x}Fe_xO_4$ (where $x \leq 3$).

Other work[26,27] on iron in zeolites has relied on ESR and luminescence methods. The Na and NH_4 forms of zeolite Y and mordenite (0.1 wt.% Fe) were studied in this way. The initial zeolites contained isolated Fe^{3+} ions in tetrahedral co-ordination, as shown by the ESR spectra ($g_{eff} = 4.3$) and the luminescence spectra. As the zeolites are dehydrated at temperatures up to 600 °C the ESR signal is gradually suppressed, and the ESR spectra of the dehydrated ammonium forms of both zeolite types develop a broad signal with $g_{eff} \cong 2.3$ which is ascribed to the formation of ferromagnetic particles. In the Na forms a weak signal from ferromagnetic particles is observed only from the type Y zeolite dehydrated at temperatures above 500 °C. This behaviour is explained[26,27] in terms of the deficit of Na^+ ions in the type Y zeolite ($Na^+ : Al^{3+} = 0.97$).

The ESR method has been used also to study FeNaY zeolites containing Fe^{3+} ions introduced from a solution of $FeCl_2$ (27% exchange)[28]. The ESR spectrum immediately after exchange was almost indistinguishable from that of the initial NaY zeolite, and consisted of a single broad line. Dehydration led to the appearance of a signal with $g \cong 4.31$, whose intensity increased with the dehydration temperature. This signal was assigned[28] to Fe^{3+} ions in a co-ordination "substantially" different from octahedral". By using the molecular probe method it was concluded that the Fe^{3+} ions are localised in $S_{I'}$ ($S_{II'}$) sites.

Ref. 29 describes a study of iron-containing type Y zeolites prepared by exchange with an iron thiocyanate solution. The ESR spectra obtained after exchange include a signal from Fe^{3+} ions in a distorted octahedral configuration with $g \cong 3.75$. Heat treatment of the samples in a stream of He at 550 °C lowered the width of the signal by a factor of 2 without affecting the g-factor, which the authors ascribe to changes in both the relative position and the immediate surroundings of the Fe^{3+} ions. Heating the samples in a hydrogen–nitrogen mixture at 350 °C (the temperature of incipient reduction of the iron) produces a signal with $g = 2.04$ ($T_{meas} = -196$ °C) which is assigned to Fe^{2+} ions. Reduction in the same atmosphere at 550 °C causes the formation of metallic iron and the appearance of ferromagnetism. By comparing the ESR results with those of nuclear gamma-resonance (NGR) (i.e. Mössbauer) spectroscopy the authors conclude that in this gas mixture the transition from Fe^{3+} to Fe^0 takes place through the Fe^{2+} state in the range 350–550 °C. They also showed that the crystal structure of the iron-containing zeolites is distorted in the reduced samples.

The interactions of adsorbed NO and NO_2 molecules with bivalent iron ions in NaY zeolites and in mordenite have been studied[30] by ESR and i.r. spectroscopy. Two types of nitrosyl $Fe(I)NO^+$ complexes, differing in the effective spin number ($S = 3/2$ and $S = 1/2$), were detected. The high-spin complexes are formed by the adsorption of nitric oxide at pressures of several Torr, and are characterised by the parameters $g_\perp = 4.07$ and $g_\parallel = 2.003$. When samples containing high-spin complexes are treated in a vacuum at 25–100 °C this ESR signal is gradually replaced by a new signal with $g_1 = 2.015$, $g_2 = 2.055$, $g_3 = 2.089$, produced by the low-spin complexes. The complexes are formed by the interaction of the NO molecules with Fe^{3+} ions, involving the transfer of the unpaired electron from the molecule to the cation. The adsorption of NO_2 molecules on these zeolites leads to oxidation of the Fe^{2+} ions to Fe^{3+} ions (in a distorted tetrahedral co-ordination). The ESR spectra contain, in addition to the signal from these ions, a characteristic triplet with $g = 2.005$ and $A = 56$ Oe, assigned to NO_2 molecules vibrating in the zeolite holes. Since the samples used in that work[30] had been reduced in hydrogen the possibility of a breakdown in their crystal structure[29] must be borne in mind.

An extensive investigation by Krzyzanowski[31-36] of Fe-containing type Y zeolites revealed that the Fe^{2+} ions are easily oxidised to Fe^{3+} in oxygen. Though the main theme of that work was the formation of radicals during the adsorption of unsaturated hydrocarbons and benzene on cerium-containing zeolites, FeY zeolites were shown to have very similar properties in respect to radical formation. Kinetic measurements by the ESR method led to a mechanism of radical formation involving the transfer of an electron from the oxygenated adsorbed species to the organic molecule. In the case of FeY zeolites these species are diamagnetic, and their structure is thought to be O_x^{2-}, where $x = 2$ and (or) 1.

Paramagnetic forms of adsorbed oxygen have been observed on reduced iron-containing FeNaHY zeolites: O_2^- anion radicals and oxygen-containing particles stable up to 500 °C whose structure has not been established[37]. Even small amounts of iron (≤0.07 wt.%) added to NaHY and LiY zeolites have been shown to induce the formation of these oxygen radicals following oxygen adsorption, the Fe^{2+} ions acting as electron donors.

6. Cobalt

The electronic structure of the ground state of the atom is $(A)(3d)^7(4s)^2$. Whereas very few papers on cobalt-containing zeolites had been published when the previous review[1] was written, in recent years these systems have attracted much attention. Klier[38,39] has extended his early work[1] on CoNaA zeolites, and has shown that in the hydrated zeolites the Co^{2+} ions are located in large holes as the $[Co(H_2O)_6]^{2+}$ hexa-aquo complexes, giving an absorption band at 19000 cm^{-1} in the optical spectrum. Dehydration of the zeolites causes localisation of the Co^{2+} ions at the centres of triangles of oxygen ions forming the windows of cubo-octahedra (S_{IA} sites). The adsorption of cyclopropane, olefin, and acetylene molecules causes complex formation between these molecules and the Co^{2+} ions: the complexes have a distorted

tetrahedral co-ordination consisting of three oxygen ions from the zeolite skeleton and one adsorbed molecule. The adsorption of ammonia and water molecules is accompanied by complex formation followed by a change in co-ordination in the sequence triangle → tetrahedron → octahedron, depending on the amount of adsorbate present.

An ESR study of CoNaA zeolites is reported in Refs. 40 and 41. The dehydrated zeolites at 4.2 K give a signal with $g_{\parallel} = 2.003$ and $g_{\perp} = 5.7$, consistent with localisation of the Co^{2+} ions in a trigonal co-ordination (S_{IA} sites). The hydrated zeolites give a signal with $g_{\parallel} \cong 2.2$ and $g_{\perp} \cong 5.1$, assigned to hexa-aquo cobalt complexes in large zeolite holes. We should note that data on the localisation of Co^{2+} ions in dehydrated type A zeolites obtained by ESR and optical spectroscopy methods agree with X-ray structural studies[42] of these zeolites, according to which the Co^{2+} ions are localised near the centres of the entry windows of the cubo-octahedra, with a slight shift (0.16 Å) from the plane of the window towards the centre of the hole.

There is general agreement[43–48] that the cobalt ions in hydrated X and Y zeolites are present as $Co(H_2O)_6^{2+}$ complexes in the large holes. Upon dehydration of the CoX zeolites the Co^{2+} ions acquire a tetrahedral co-ordination, and become stabilised in S_{II}, $S_{II'}$, or $S_{I'}$ sites[43–46], whereas in CoY zeolites the ions are either tetrahedrally co-ordinated[45–47] or octahedrally co-ordinated (in S_I sites)[48] and inaccessible to adsorbed H_2O and NH_3 molecules at room temperature[45,46].

A detailed comparative study of the properties of A, X, and Y zeolites containing Co^{2+} ions, carried out by reflectance u.v. spectroscopy and ESR, is described in Ref. 49. Under specified conditions the ESR spectra of Co^{2+} ions in the zeolites could be observed at 77 K and above. It was shown that A, X, and Y zeolites differ in their ability to stabilise the Co^{2+} ions, depending on the dehydration conditions, and this was ascribed to the difference in polarisability of the zeolite lattice for different Si/Al ratios. Thus, differences can be detected even in the hydrated zeolites: in type A zeolites the $Co(H_2O)_6^{2+}$ complexes interact with the zeolite lattice, whereas in X and Y zeolites they are relatively free. Tetrahedrally co-ordinated Co^{2+} ions are formed in type Y zeolites under dehydration conditions more rigorous than in types A and X.

Dehydration of zeolite A under mild conditions (110 °C, 12 h, helium stream) leads to stabilisation of the Co^{2+} ions in six-sided windows (S_{II} sites) to give tetrahedral $Co(Ox)_3 . H_2O$ complexes. As the dehydration temperature is raised to 600 °C the ions migrate to $S_{I'}$ or $S_{II'}$ sites, forming $Co(Ox)_3OH^-$ or $Co(OX)_3O^{2-}$ complexes, where Ox is an oxygen atom from the zeolite skeleton and OH^- and O^{2-} are residual fragments of H_2O molecules. On the other hand dehydration of X and Y zeolites at 600 °C leads to the formation of both tetrahedral $Co(Ox)_3O^{2-}$ complexes (in $S_{I'}$ or $S_{II'}$ sites) and of octahedral $Co(Ox)_6$ complexes (in S_I sites). We note that the reported[49] stabilisation of Co^{2+} ions with a tetrahedral co-ordination in strongly dehydrated type A zeolites is inconsistent with reports[38–42] that Co^{2+} is stabilised in a trigonal co-ordination after drastic dehydration. This discrepancy may be due in some measure to differences in the sample activation conditions: Heilbron and Vickerman[49] dehydrated their materials in a stream of helium, whereas most other workers have used vacuum dehydration. Differences in the heating rate of the samples may also have had some effect.

Measurements of the optical spectra of Co-containing A, X, and Y zeolites are reported also in Ref. 50. It is concluded that the Co^{2+} ions in dehydrated CoNaA zeolite have a trigonal co-ordination, whereas in CoNaX and CoNaY samples these ions adopt both tetrahedral and octahedral co-ordinations.

The adsorption of various molecules on dehydrated A, X, and Y zeolites containing Co has attracted much attention. We have already mentioned a study[39] of the adsorption of olefins and acetylene on CoNaA zeolite. The adsorption of alkane and alkene hydrocarbons (ethylene, propene, but-1-ene, and pent-1-ene) has been studied, by optical spectroscopy, also in CoNaX zeolites, which are catalytically active towards olefin oxidation[44]. The optical spectra were found to be unaffected by alkane hydrocarbons, whereas the adsorption of alkenes distorts the co-ordination sphere of the tetrahedral Co^{2+} complexes.

The adsorption of various nitrogen-containing molecules has been studied by two groups of workers[45,51–55]. Adsorption of ammonia leads to the formation of octahedral complexes. Adsorption of methyl isocyanide on CoCaY zeolite at room temperature[51,52] produces the five-co-ordinated $Co(CH_3NC)_5^{2+}$ complexes, which are converted (in the presence of an excess of methyl isocyanide) into the six-co-ordinated $Co(CH_3NC)_6^{2+}$ complexes, with ESR spectral parameters $g_{\parallel} = 2.003$, $g_{\perp} = 2.172$ and $g_{\parallel} = 2.008$, $g_{\perp} = 2.087$ respectively. Adsorption causes the Co^{2+} ions to migrate into large zeolite holes, where the complexes are formed.

Lunsford and coworkers[53–55] found that the Co^{2+} complexes formed in the large holes of CoNaY zeolites by the adsorption of amines interact with oxygen to give O_2^- anion radicals in the co-ordination sphere of the cobalt ion: $[Co(III)L_xO_2^-]^{2+}$, where $L_x = NH_3$, CH_3NH_2, and $C_3H_7NH_2$. In the case of NH_3 and CH_3NH_2 storage of the zeolites at 20 °C for 10–15 h produces also the binuclear complexes $[L_xCoO_2^-CoL_x]^{5+}$. The ESR spectral parameters of both types of oxygen adduct are similar to those of the analogous complexes in solution.

Some of the most recent publications describe studies by u.v. and ESR spectroscopy of the localisation sites of Co^{2+} ions in natural zeolites (montmorrillonite[56] and clinoptilolite[57]). The conclusion was that, as in type X and Y zeolites, dehydration leads to the formation of tetrahedrally co-ordinated Co^{2+} ions. In clinoptilolite trigonal co-ordination of the ions is also possible.

7. Nickel

The electronic structure of the ground state of the atom is $(A)(3d)^8(4s)^2$. All the studies of zeolites containing nickel(II) so far reported have been by optical spectroscopy. The earliest work[58–60] was on the state of the Ni^{2+} ions in type A zeolites (see Ref. 1). Further developments of that investigation are reported in Refs. 61–63. The observed[61,62] migration of Ni^{2+} ions from large holes into S_{IA} sites upon dehydration of the type A zeolites is consistent with the conclusions from earlier work[58–60].

Studies of X and Y zeolites[61–63] have shown that Ni^{2+} ions present in the large holes as hexa-aquo complexes after exchange will gradually migrate, during dehydration, into S_{II} sites (up to 200 °C), then into $S_{II'}$ and $S_{I'}$ sites, and lastly into S_I sites (at 500 °C), where they are stabilised in a distorted octahedral co-ordination (with adsorption bands at ~10 000, 16 000, and ~22 000 cm^{-1}). These conclusions on the stabilisation of Ni^{2+} ions in S_{IA} sites (A zeolites) and in S_I sites (X and Y zeolites) are consistent with results obtained by X-ray diffraction analysis[64,65].

The diffuse reflectance spectra of type Y zeolites have revealed[66,67] in addition to isolated ions, aggregates of Ni^{2+} ions. The degree of aggregation of the ions was shown to

be very sensitive to the exchange conditions. In the absence of hydrolysis of the salt used for ion exchange different types of isolated Ni^{2+} ions are detected, localised in different sites, depending on the concentration of the ions and on the heat treatment conditions of the zeolite. If the ion-exchange salt is partially hydrolysed the nickel ions are incorporated in the zeolite as polynuclear hydroxo complexes, yielding aggregates of nickel ions when the samples are heated. The bridging oxygen of these aggregates (Ni–O–Ni) does not belong to the zeolite skeleton. The aggregates of nickel ions give a charge-transfer absorption band at a lower frequency than the isolated ions.

In addition to the work on nickel-containing A, X, and Y zeolites, one paper has been published on NiL zeolite[68]. In this work the nickel ions were found to take up two co-ordination states as the dehydration temperature was raised. In the first of these states the nickel is bound to the zeolite skeleton through the residual water molecules, whereas in the second state (observed for dehydration temperatures above 300 °C) the Ni^{2+} ions are co-ordinated directly to the skeleton. As the temperature is raised above 100 °C the Ni^{2+} ions become gradually more accessible to water and ammonia molecules adsorbed from the gas phase.

The adsorption on NiA, NiX, and NiY zeolites dehydrated at temperatures up to 500 °C of strongly polar molecules such as water (at room temperature) and pyridine (at 200 °C) causes inverse migration of the Ni^{2+} ions from S_I (or S_{IA}) sites into large holes[61,62]. In the case of pyridine the planar complexes $[Ni(Py)_4]^{2+}$ are formed, with absorption bands at ~10 000, 16 000, ~20 000, and ~25 000 cm^{-1}. Adsorption of NH_3 on zeolites dehydrated at temperatures up to 200 °C leads to the formation of ammine complexes of the Ni^{2+} ions. On the other hand no complex formation is observed on zeolites dehydrated at higher temperatures[63]. This is explained by pointing out that the Ni^{2+} ions in S_I and S_{IA} sites (unlike those in $S_{I'}$ and $S_{II'}$ sites) are not accessible to ammonia molecules.

The adsorption of acetylene on type Y zeolite containing dehydrated or partially dehydrated Ni^{2+} ions causes reduction to the Ni^0 or Ni^+ state[69], and the Ni^+ ions react with acetylene to give $[Ni(C_2H_2)_n]^+$ complexes, where $n = 2, 3$. Complex formation between Ni^+ ions and acetylene or ethylene molecules was observed also on partially reduced X and Y zeolites[61]. By combining X-ray diffraction results with measurements of magnetic susceptibility the authors[61] were able to assign the Ni^+ ions which interact with alkene molecules to S_{II} (or $S_{II'}$) stabilisation sites.

The formation of Ni^+ ions has been observed also after reduction in H_2 or Co at 200–400 °C of nickel-containing NaA, NaX, NaY, NH_4A, NH_4X, NH_4Y, and CaNaY zeolites[70–73]. The concentration of Ni^+ ions was found to depend on the crystal structure type of the zeolite. In NiCaNaY zeolites[71,72] two types of Ni^+ ions were detected, with different stabilisation sites and characterised by ESR spectra with $g_\perp = 2.09$, $g_\parallel^1 = 2.48$, and $g_\parallel^2 = 2.80$. Adsorption of O_2 produced an ESR spectrum from the O_2^- anion radical ($g_1 = 2.045$, $g_2 = 2.008$, $g_3 = 2.0015$), whereas in an NO atmosphere the Ni^+ ions were oxidised to the bivalent state. The interaction of Ni^+ ions with CO produces the $Ni(CO)_2^+$ and $Ni(CO)_3^+$ complexes[72,73].

The adsorption of NO on nickel-containing zeolites is discussed in Refs.74–76. The interaction between NO molecules and Ni^{2+} is shown to lead to the formation of a charge-transfer complex in which the nickel ions initially occupy S_I positions but are subsequently transferred to $S_{I'}$ positions. The adsorption of NO and NO_2 is discussed also in Ref.15: as in the chromium-containing samples, mentioned above, the $[Ni^+NO^+]$ and $[Ni^+NO_2^+]$ complexes, which have identical ESR spectra, were detected ($g_\perp = 2.169$ and $g_\parallel = 2.33$).

8. Copper

The electronic structure of the ground state of the atom is $(A)(3d)^9(4s)^2$. Copper is particularly convenient for ESR and optical spectroscopy studies, and therefore many publications on copper-containing zeolites have appeared since the last review[1]. The more recent work has largely resolved the inconsistencies noted in the earlier review[1].

Refs.77 and 78 discuss copper-containing type A zeolites. Hydration of CuNaA and CuLiA zeolites was found to produce tetrahedral complexes of Cu^{2+} ions with one water molecule and three oxygen anions from the zeolite lattice as ligands, located near the hexagonal windows (S_{IA} sites). It was also found that hydration of Ca^{2+}- and Mg^{2+}- substituted type A zeolites causes migration of the Cu^{2+} ions into the large holes, where hexa-aquo complexes can be accommodated. A study[79] of the effect of copper content on the ESR spectra of type A zeolites has shown that electronic exchange interaction between the copper ions sets in when the copper content reaches one ion for every seven elementary cells, and this leads to the appearance of a new signal (in addition to the signal from isolated ions): a somewhat distorted singlet ~120 Oe wide.

The localisation sites of Cu^{2+} ions in type X zeolites are discussed in Refs.80–84. Kenzi and coworkers[80] examined, by ESR, samples of CuNaX containing 1.9 Cu^{2+} ions per elementary cell, and found that the copper ions migrate during dehydration and become stabilised in S_{III}, S_{II} (or $S_{II'}$), and $S_{I'}$ sites at 70–200 °C, whereas at 400 °C they penetrate into S_I sites. Localisation of Cu^{2+} ions in S_I sites during dehydration is reported also in Ref.81, but these results should be accepted with caution because the samples were exposed to an atmosphere of butene at 200 °C, followed by oxygen at the same temperature, before the measurements. In an extension of this work[82] the authors point out that Cu^{2+} ions become strongly bound to the zeolite skeleton even for dehydration temperatures as low as 80–100 °C. ESR measurements at 77 K revealed three distinct signals, corresponding to stabilisation of the copper ions at different locations in the skeleton (S_{III}, S_{II}. and $S_{II'}$). After dehydration at 120–200 °C a substantial fraction of the copper ions is localised in $S_{II'}$ sites, and raising the dehydration temperature to 400 °C causes migration of the ions to S_I sites. However, as the authors themselves point out[82], additional evidence is needed to confirm these conclusions.

Vansant[83] does not discuss the stabilisation sites of Cu^{2+} ions specifically, but he points out that in dehydrated zeolites these ions are co-ordinated by three lattice oxygens, suggesting localisation in $S_{II}(S_{II'})$ or $S_{I'}$ sites. Lastly, Peigneur and coworkers[84] also mention S_{II} and $S_{II'}$ sites as possible localisation positions in the zeolite X skeleton.

Most of the work on copper ions has been done with type Y zeolites. Changes in ESR spectra similar to those described in Ref.1 have been observed[85] after dehydration of CuNaY zeolites, though in this case there was no decrease in the intensity of the ESR signal after dehydration at 400 °C. This difference is apparently due to the oxidising treatment (O_2, 400 °C) to which the sample were subjected after dehydration. Turkevich and coworkers[86] reported, in addition to the signals described in the previous review[1], a symmetrical signal with $g \cong 2.17$ whose intensity increased with the degree of exchange. They ascribed this signal to cluster

formation without defining the cluster structure. Cluster formation is reported also by Mörke and coworkers[87], who studied the state of copper ions in CuNaY zeolites (9–64% exchanged) dehydrated at 200–600 °C. A substantial fraction of the copper ions was found to be localised in S_I, $S_{I'}$, and $S_{II'}$ sites, and it was noted that cluster formation is favoured not only by an increase in the degree of exchange but also by an increase in the dehydration temperature. Reports of the localisation of copper ions in S_{III} and S_{II} sites of hydrated zeolites were confirmed by Soria and coworkers[88], and the localisation in $S_{I'}$ and $S_{II'}$ sites after dehydration of the zeolites at 400–600 °C was confirmed by X-ray structural analysis[89]. The stabilisation of copper ions in S_I sites was further confirmed by Jacobs and coworkers[90], who pointed out that the ease with which the copper ions are reduced depends on the localisation sites of the ions.

Cu^{2+} ions stabilised in S_I, $S_{I'}$, and $S_{II'}$ sites can form ion pairs of various types at high degrees of exchange[91–94]. The stabilisation of copper ions in S_I and $S_{I'}$ sites has been shown[94] to be influenced by the heating rate of the zeolite during dehydration. Thus, for a heating rate of 1.7 K min^{-1} the Cu^{2+} ions can be localised in hexagonal prisms, but an increase in the heating rate to 25 K min^{-1} prevents the ions from entering those sites. This effect can explain the slight discrepancies which still exist between the conclusions of different workers on the ability of copper ions to be stabilised in S_I sites of type Y zeolites.

Investigations by optical spectroscopy[95,96] also suggested the possibility of forming copper ion pairs at high degrees of exchange. Again, S_{III} sites were found to be the preferred stabilisation point of Cu^{2+} ions in the hydrated zeolites. Dehydration at gradually increasing temperatures initially causes migration to S_{II} and $S_{II'}$ sites (100–300 °C), followed by migration to S_I and $S_{I'}$ sites (300–600 °C).

Extensive studies[66,67,97–103] of the effect of exchange, dehydration, and redox conditions on the state of copper ions in type Y zeolites have been carried out by ESR, i.r., and optical spectroscopy methods. The stabilisation sites of isolated copper ions identified by this work agree, on the whole, with conclusions from earlier work. The suggested formation of "strong" or "weak" associations of copper ions, differing in the intensity of the spin–exchange interaction, is interesting. The "weak" associations are assumed to have characteristics similar to those of isolated copper ions localised in S_{III} and S_{II} sites, whereas the "strong" associations differ very substantially from isolated ions: they are formed by heat treatment under oxidising conditions of the clusters arising from the hydrolysis of the copper ions in the zeolite holes during exchange at pH 8–9. The "strong" associations are thought to be bridging structures of the M–O–M type, including non-lattice oxygen.

Many recent publications discuss the adsorption of ammonia, pyridine, and other nitrogen-containing molecules on copper-substituted zeolites. The interest in this type of investigation appears to stem from the specificity of the resulting complexes, which makes it very easy to identify them by ESR and optical spectroscopy.

The ESR method has been used[104] to study the adsorption of ammonia and pyridine on CuNaY zeolite, and the formation of the square coplanar complexes $[Cu(NH_3)_4]^{2+}$ and $[Cu(Py)_4]^{2+}$ has been demonstrated (ESR spectral parameters $g_\parallel = 2.25$, $g_\perp = 2.04$, $A_\parallel = 175$ Oe, and $g_\perp = 2.03$, $g_\parallel = 2.24$, $A_\parallel = 185$ Oe respectively). Vacuum heat treatment at 100 °C did not affect the spectrum of a sample on which pyridine had been adsorbed, whereas inversion of the g-factors occurred in the sample on which ammonia had been adsorbed ($g_\perp = 2.26$, $g_\parallel = 2.03$). The inversion was produced by removal of the ammonia molecules and by the resulting change in the symmetry of the co-ordination sphere to that of a tetrahedron compressed along the trigonal axis. It was also found that in the case of samples containing adsorbed pyridine a change in measurement temperature from room temperature to −196 °C does not affect the ESR spectra. Hence the authors suggest[104] that the $[Cu(Py)_4]^{2+}$ complexes are formed within the sodalite cells, which "freezes" the motions of the complex and makes the spectral parameters independent of the measurement temperature.

Further developments in this work have also been reported. It was shown[83] that the behaviour of Cu^{2+} ions towards the adsorption of pyridine and ammonia is substantially the same in types Y and X zeolites, and also[86] that the specific adsorption of pyridine (unlike that of ammonia, which interacts with copper ions even at room temperature) is limited to temperatures above 120 °C. This difference is most probably due to the inability of pyridine molecules to penetrate into the sodalite cells except at high temperatures.

An ESR study of the adsorption of ammonia on CuNaY zeolite as a function of the amount of ammonia adsorbed is described in Ref. 98. Four types of complex were shown to be formed, differing in the number of ammonia molecules (five, three, and two) and in their disposition in the co-ordination sphere.

Optical spectroscopy has shown[66] that the adsorption of NH_3 on dehydrated zeolites leads to the formation of di- and tri-ammines (absorption maximum at ~15 200 cm^{-1}), with a very small number of tetra-ammines (shoulder at 17 000 cm^{-1}). Adsorption of pyridine produces di- and tetra-pyridine copper complexes (15 400 and 17 200 cm^{-1}), whereas the adsorption of large quantities of ammonia[105] produces mainly tetra-ammines (16 500 cm^{-1}). Partial desorption of the ammonia leads to the formation of complexes to which the structure $(O)_3$–Cu–NH_3 has been assigned.

Thus, whereas in the case of pyridine adsorption the structural information given by optical spectroscopy is consistent with the ESR results, pointing to the formation of $[Cu(Py)_4]^{2+}$ complexes, there is some disagreement between the two methods in determining the structure of the copper ammine complexes. The ESR measurements indicate preferential formation of the $[Cu(NH_3)_4]^{2+}$ complex [for example, Lunsford and coworkers[94] failed to detect any other ESR signals, even at very low levels of adsorption ($N_{NH_3}/N_{Cu^{2+}} \ll 1$)], whereas the optical spectra suggest that these complexes are formed only when the zeolites are saturated with ammonia.

Vansant and Lunsford[91] studied the adsorption of ammonia, methylamine, and ethylamine molecules on CuNaY zeolite. Ammonia adsorption was found to give rise to complexes containing four ammonia molecules and having the D_{4h} square coplanar symmetry, whereas only one adsorbate molecule entered into the co-ordination sphere of the copper ion after adsorption of the amines. It is interesting to note that two types of complex between copper ions and amines were detected in the sodium form of the zeolite, whereas in the calcium form only one complex was found. The difference in structure between the two types of complex in CuNaY probably involves differences in the stabilisation sites of the copper ions ($S_{II'}$ or $S_{I'}$).

Interesting results were obtained in an extensive investigation by optical spectroscopy of the adsorption of ammonia, pyridine, and ethylenediamine molecules from aqueous solutions on CuNaY zeolite[46,96,106]. The following copper ion complexes were detected: $[Cu(NH_3)(H_2O)_5]^{2+}$, $[Cu(NH_3)_2 \cdot (H_2O)_4]^{2+}$, $[Cu(NH_3)_6]^{2+}$, $[Cu(Py)_4]^{2+}$, and $[Cu(en)_3]^{2+}$. On the other hand, after adsorption of ethylenediamine from the gas phase[84] the complexes $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$

have been detected by ESR and u.v. spectroscopy. [Cu.$(en)_3]^{2+}$ complexes were formed only after lengthy exposure of the sample to ethylenediamine.

The adsorption of molecules not containing nitrogen has not been studied in such detail. Leith and Leach[82] examined, in addition to the adsorption of ammonia and pyridine, also the adsorption of butene, cyclopropane, and 3,3-dimethylbutene, and they showed that the latter molecules interact with Cu^{2+} ions in $S_{II'}$ positions whereas NH_3 and pyridine molecules can interact with Cu^{2+} ions in $S_{I'}$ positions.

A study by ESR and i.r. spectroscopy of the interaction within zeolites between carbon monoxide molecules and copper cations in different states has been reported[99,101]. Isolated copper ions were found not to interact with CO up to 500 °C, whereas the weak magnetic associations of these ions form complexes with CO at low temperatures and oxidise it to CO_2 at temperatures above 300 °C (being reduced to Cu^{2+} by this reaction). These processes are thought to involve non-lattice oxygen. The stronger associations of copper ions, which include a bridging oxygen atom not belonging to the zeolite skeleton, oxidise the CO molecules to CO_2 and to carbonates even at low temperatures.

We should note that the ESR method can be used also to study complex formation between adsorbed molecules and univalent copper ions. The adsorption of nitric oxide on Cu^+–Y zeolites prepared by reduction of zeolites containing copper(II) has been studied in this way[85,107], and the formation of the Cu^+–NO complex has been observed ($g_\parallel = 1.89$, $g_\perp = 2.009$). The results of various studies of the complexes of copper and some other transition metals (Co, Cr, Ni, Fe) with nitrogen-containing molecules are discussed in detail in Refs.108 and 109.

III. IONS OF THE METALS FROM THE SECOND AND THIRD TRANSITION PERIODS

Relatively few papers on studies by ESR and optical spectroscopy of zeolites containing ions from the second and third transition period have been published. As far as the present writers are aware, all of them are concerned with ions from Group VIII of the Periodic Table.

1. Ruthenium

The electronic structure of the ground state of the atom is $(K)(4d)^7(5s)^1$. Ruthenium-containing type Y zeolites have been studied[110] by ESR and optical spectroscopy, and the properties of the ruthenium ions were shown to be very sensitive to the exchange conditions and to the subsequent treatment of the samples. Thus, samples exchanged in an excess of ammonia gave signals from Ru^{3+} complexes differing in the number of ammonia ligands ($g_1^A = 2.57$, $g_2^A = 2.20$, $g_3^A = 1.73$, and $g_1^B = 2.44$, $g_2^B = 2.12$, $g_3^B = 1.82$), whereas after exchange at pH ~7 only one broad band (with $g \approx 2.5$) is observed. Dehydration of the samples reduces some of the ruthenium to the metal with formation of ferromagnetic micro-crystals of an alloy of ruthenium with the iron present as an impurity in the zeolites. The formation of these micro-crystals is indicated by the appearance of a very strong ESR signal at low fields. The size of the micro-crystals depends on the exchange conditions (increasing with pH). In very finely divided crystals the adsorption of hydrogen molecules has a marked effect on the ferromagnetic properties, as shown by the substantial decrease in signal strength.

The preparation of ruthenium zeolites of types A, X, and Y by exchange methods is discussed also in Ref.111.

2. Rhodium

The electronic structure of the ground state of the atom is $(K)(4d)^8(5s)^1$. Rhodium-containing X and Y zeolites (2–80% exchange) have been studied by ESR.[110,112–114]. In type X zeolites exposed to an oxidation (O_2, 500 °C) and a reduction treatment (H_2, 150 °C) in succession, ESR signals from Rh^{2+} ions in a distorted octahedral co-ordination have been observed[110]. The adsorption of various molecules (O_2, NO, Co, NH_3) at room temperature had no effect on the ESR spectrum (i.e. complex formation was not observed). This observation, together with the co-ordination of the Rh^{2+} ions, suggests that these ions are localised in S_I sites.

Unlike the type X zeolites, in which only isolated Rh^{2+} ions are observed, type Y zeolites give rise to paramagnetic centres after an oxidising treatment ($g_\perp = 2.69$, $g_\parallel = 2.18$, $A_1 = 355$ Oe, $A_2 = 110$ Oe). These centres consist of two non-equivalent rhodium ions (called an ion pair[112]). Integral intensity measurement indicates that ~20% of the rhodium ions take part in ion pair formation.

Rhodium pairs have been shown[112–114] to act as adsorption centres for various molecules (H_2O, NH_3, O_2, CO, NO, etc.). Adsorption of water molecules causes the formation of paramagnetic associations in the large holes of the zeolite, containing at least four rhodium atoms. Storing the samples in an ammonia atmosphere at room temperature or at 100 °C also produces changes in the ESR spectra, resulting from the interaction of the rhodium pairs with ammonia.

The adsorption of CO, O_2, and NO molecules, unlike the adsorption of strongly polar molecules, leads to the formation of unstable complexes which break down under evacuation even at room temperature. The adsorption of CO molecules was found[113] to produce complexes giving an ESR signal with the parameters $g_\perp = 2.186$, $g_\parallel = 1.992$, and $A_\parallel(Rh) = 18.5$ Oe. By using labelled carbon monoxide (^{13}CO) it was shown that only one CO molecule is present in each complex, and that this molecule is covalently bound to the rhodium.

The adsorption of NO at 77 K causes the formation of nitrosyl complexes whose composition includes two molecules of nitric oxide[114].

The formation of complexes of the peroxy type following oxygen adsorption has been observed ($g_\perp = 1.943$, $g_\parallel = 2.014$). These species (called σ-complexes) were found to be very reactive towards the oxidation of various molecules, including alkenes and hydrogen[110,112].

An ESR study of the properties of rhodium ions in NaY zeolite is described also in Ref.115. In the early stages of the thermal activation of the zeolite in oxygen (at ~100 °C) the tervalent rhodium complexes $[Rh(NH_3)_5Cl]^{2+}$ initially introduced by ion exchange are found to break down, giving the paramagnetic bivalent rhodium complexes $[Rh(NH_3)_5]^{2+}$ whose ESR spectra have the parameters $g_1 = 2.09$, $g_2 = 2.06$, and $g_3 = 1.97$. At higher temperatures (500 °C) Rh^{2+} ions directly attached to the zeolite skeleton are formed. As in our experiments[112,113], these workers observed the formation of complexes with CO and O_2, but their structural interpretation is somewhat different from ours. They assume that oxygen-containing complexes are produced by the oxidation of diamagnetic Rh^+ ions, giving the bridge structure Rh^{2+}–O–O–Rh^{2+}. However, in view of the small distance between the paramagnetic Rh^{2+} ions in this structure, which should lead to substantial interaction between the unpaired electrons, we would expect the ESR spectrum to be more complex than the spectrum actually observed (charateristic of the systems with $S = 1/2$). For these reasons we consider the proposed bridge structure to be improbable.

3. Palladium

The electronic structure of the ground state of the atom is $(K)(4d)^{10}$. All the work on palladium-containing zeolites reported so far has been done on samples prepared by ion exchange between type Y zeolites and solutions of tetra-ammine complexes of bivalent palladium ions.

Naccache and coworkers[116,117] examined by ESR the state of the palladium ions and its dependence on various treatments of the sample (including the adsorption of hydrogen and carbon monoxide molecules). Oxidising treatments were shown to produce a signal in the ESR spectra of the zeolites with the parameters $g = 2.233$, $\Delta H = 16$ Oe, assigned to Pd^{3+} ions in a distorted octahedral or trigonal co-ordination (S_I or $S_{I'}$, S_{II} sites). Adsorption of hydrogen at room temperature on an oxidised sample reduced the Pd^{3+} ions to Pd^{+}, whose ESR signals have the parameters $g_\perp = 2.10$, $g_\parallel = 2.28$ and $g_\perp = 2.11$, $g_\parallel = 2.41$ respectively. It is pointed out that ~8% of the palladium ions give rise to ESR signals. The suggested localisation of the palladium ions in $S_{I'}$ sites is confirmed by X-ray diffraction results[118], which indicate that 10.6 of the 12.5 palladium ions in the elementary cell are located in $S_{I'}$ sites.

The adsorption of CO on these samples causes the appearance of an ESR signal with the parameters $g_1 = 2.192$, $g_2 = 2.061$, and $g_3 = 2.038$. By using carbon monoxide enriched in the ^{13}C isotope the components of the signal for each g-factor were shown to be split into three ($A_1 = 56$ Oe, $A_2 = 56$ Oe, and $A_3 = 60$ Oe). Hence the authors concluded[116,117] that the Pd^{+} ions form complexes with two CO molecules.

An ESR study of the adsorption of NO molecules on PdNaY zeolite is reported in Ref. 119. A signal with $g = 1.95$ was observed on oxidised as well as on reduced samples, leading to the conclusion (confirmed by i.r. spectral measurements) that the complexes formed by the Pd^{2+} ions contain one molecule of NO.

Garbowski and coworkers[120,121] reported a study of PdNaY zeolite by optical spectroscopy. Most of the spectra were complex, and had to be analysed by resolving the absorption lines into their components. The conclusion was that in the initial samples the Pd^{2+} ions were present as $[Pd(NH_3)_4]^{2+}$ complexes in the large zeolite holes, whereas after dehydration at 500 °C in a stream of oxygen the Pd^{2+} ions were converted into the C_{3v} co-ordination[122]. The same workers examined the adsorption of ammonia, pyridine, water, and nitric oxide molecules. From their optical measurements they concluded that the adsorption of water gives two types of complex: tetrahedral, in $S_{I'}$ sites, and square coplanar, in large holes. The adsorption of NO molecules led to the formation of complexes containing one molecule of nitric oxide. A study[121] of the simultaneous adsorption of CO and NO showed that these complexes can be of two types: one type (in $S_{I'}$ sites) does not interact with CO, whereas the other (in $S_{II'}$ sites) can co-ordinate an additional CO molecule to give a complex of composition $Pd(O)_3NOCO$.

IV. CONCLUSIONS

To conclude this review we shall mention an important paper by Sancier and Inami[122], who studied by ESR the reduction in hydrogen at 400 °C of Pd^{2+}NaY and Pd^{2+}CaNaY zeolites containing also iron ions. These workers noted the formation, under these conditions, of reduced forms of iron, whereas no reduction took place in zeolites not containing palladium. The effect is explained by postulating the formation (during the reduction of palladium ions) of atomic hydrogen, which subsequently migrates towards the iron ions and reduces them (the "spill-over" effect).

Our discussion of work by ESR and optical spectroscopy on zeolites containing ions of the transition elements leads to the following general conclusions. Evidently, these methods do not always allow the localisation sites of the ions in the zeolites after dehydration to be identified unambiguously, but they provide reliable data on the accessibility of the ions to adsorbed molecules of various types. The dehydration of zeolites containing ions of the transition elements is usually followed by gradual migration of the ions into S_{II}, $S_{II'}$, $S_{I'}$, and S_I sites. However, the effect is strongly dependent on the dehydration conditions and on the nature of the cation. Thus, the localisation of cations in S_I sites of faujasites is clearly observed only when low heating rates are used.

For these reasons the "centre of gravity" of the research in this area has been shifted from the determination of the localisation sites of ions in zeolites to the study of the electronic structure and of the properties of the complexes formed in the zeolite holes by the interaction of the transition metal ions with adsorbed molecules. In these complexes the ions of the transition elements often form a bond with both the adsorbed molecule and the oxygen ions from the zeolite skeleton, and their co-ordination, localisation site, and even valency can change as a function of the nature of the ligands, the concentration of adsorbed molecules, and the temperature. Another area which has attracted attention in recent years is the identification and study of ions in "unusual" valency states, which can often be stabilised in zeolites by interaction with the alumino-silicate skeleton. ESR and optical spectrosocpy methods offer a high sensitivity and a high information content, and allow these processes to be monitored even when other methods fail.

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