Translated from *Uspekhi Khimii* **61** 1687–1719 (1992) U.D.C. 541.128.3+543.422.27

Solid state reactions as a method of introducing transition metal cations into high-silica zeolites

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ABSTRACT. **Solid state reactions can be used to introduce one or more multivalent transition metal cations into high-silica zeolites. Most such cations cannot be introduced into these matrices by other methods. The influence of various factors on the processes of stabilisation of the cationic species in the zeolite channels is analysed. Pentasil-based systems with distinct, isolated centres form unique subjects for studying the relationship between the catalytic properties of the transition metal cation and the local structure of the centre. Highly active and stable catalysts for the complete oxidation of alkanes and for the decomposition of nitrogen oxides can be obtained by solid-state modification of the pentasils.**

The bibliography comprises 65 references.

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I. Introduction

The introduction of different ions into zeolites is one of the methods of modifying their adsorption and catalytic properties and there is therefore great interest in this topic. For wide-pore zeolites, e.g. those of the faujasite type, exchange from the liquid phase (usually from aqueous solution) is a universal method for introducing any ion into the cationic sites. The results obtained by using ion exchange for such zeolites have been reviewed.[1,2]

However, ionic exchange from the liquid phase has very limited potentialities for zeolites of the pentasil type because the channels are too small for diffusion of multiply charged ions in their solvation shells. For this type of zeolite only singly charged, and some doubly charged, ions can be introduced by exchange methods but most transition metal ions, which are precisely those of greatest interest from the point of view of oxidation-reduction catalytic properties, cannot be introduced into the channels by this means. Modified high-silica (HS) zeolites particularly have unique potentialities for the catalytic processes to be analysed at the atomic-molecular level because it is possible to produce in them a distinct set of isolated centres whose topography and structure are determined by the type of zeolite lattice and whose spatial environment is determined by the structure of the channels.

HS-zeolites have a framework that is thermally highly stable and this enables us to use topochemical methods of introducing cations by means of solid state reactions with various transition metal compounds. The present review is devoted to an analysis of this particular line of research, which only started to be developed in the last decade.

Our aim was to summarise the data on the introduction of transition metal ions into HS-zeolites by means of solid state reactions and to discuss the nature of the oxidation-reduction centres formed and the catalytic processes involving them. The subject matter is to a large extent a review of our own work because we have a great interest in the topic under discussion and have carried out systematic research in this field since 1984.

II. Procedure for carrying out exchange in the solid state and methods for studying the products

The typical procedure for exchange in the solid state is very simple, involving heating a mechanical mixture of the zeolite with a transition metal oxide (or salt) in a stream of inert gas, under vacuum, or in air. Soluble compounds can be deposited on the outer surface of the zeolite more uniformly by the "dry" impregnation method and this makes the subsequent solid state reaction more rapid.

The temperature at which the solid-state exchange reaction reaches an appreciable rate depends on the type of cation and anion. Under sufficiently drastic conditions the degree of exchange reaches the maximum possible for a given zeolite and the excess of the transition metal compound remains in the mixture as a separate phase.

A number of methods can be used to study solid-state exchange reactions with the NH_4- or H-forms of zeolites: i.r. spectroscopy, RFES [probably X-ray photoelectron spectroscopy (Ed. of Translation)], thermogravimetric analysis, and analysis of the gaseous products liberated (HCl in the case of metal chlorides, H_2O for oxides). However EPR is extremely sensitive and informative for transition metal cations. For cations such as Cu^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, V^{4+}, Cr^{5+}, and Mo^{5+} EPR data not only enable the process of dispersion of the ions in the zeolite matrix to be recorded but also provide a safe estimate of the coordination environment of isolated cations and the changes in it on reaction with various molecules.

In the early 1970's some interesting results were obtained which showed that solid state reactions between a zeolite and alkali metal salts can be accompanied by ion exchange. For example, Rabo and co-workers[3–5] observed replacement of the residual protons by Na^+ cations when mixtures of the zeolites NaY, CaY, BeY, and LaY with NaCl are heated (at 575–675 K). HCl was evolved during the reaction and the catalytic activity of the zeolites in reactions catalysed by acidic groups decreased sharply. After CaY and LaY had been heated with NaCl their i.r. spectra showed a reduction in the intensities of the bands due to acidic OH groups. A solid state reaction with NaCl has been used to remove the residual acidic groups in a Y zeolite.[3–5]

In the preparation of specimens for EPR studies, evolution of HCl and stabilisation of ions in the cationic centres of zeolites of types A, X, and Y occurred as a result of solid state reactions of the H-forms of these zeolites with zinc, cobalt, nickel, and chromium chlorides.[6]

This line of research, related to the modification of the acid-base properties of zeolites by alkali metal and alkaline-earth metal salts, has recently been extended to HS-zeolites (mordenite, H-ZSM-5). Detailed studies in this area have been made by a group under the direction of Professor Karge (see Ref. 7 for a summary of their results). In the present review we shall not be concerned with the modification of the acid-base properties of zeolites by alkali metals but shall concentrate on systems with transition metal cations.

Table 1. Specimens studied by Kucherov and Slinkin.[11]

Zeolite	Si_2O_2/Al_2O_3	Exchange of Na^+ by H^+, %	Zeolite	Si_2O_2/Al_2O_3	Exchange of Na^+ by H^+, %
NaM	10	0	pentasil-140	140	95
HNaM	10	50	pentasil-280	280	95
HM	10	95	amorphous alumino-silicate ($S = 360\ m^2\ g^{-1}$)	14	—
HNa-ZSM-5*	69	40			
H-ZSM-5	69	95			

*Obtained by baking out the organic cations from a specimen with 40% deficiency of Na^+.

III. Introduction of transition metal ions into the cationic sites in HS-zeolites by means of solid state reactions

The first papers in which the migration of transition metal ions through zeolite crystals was discussed were Ref. 6 and also Refs. 8–10, in which reduction–reoxidation processes in the ion-exchange zeolites of CuY, CuM, and AgY were investigated. With CuY specimens reduced in hydrogen two types of Cu^0 crystals are formed:[8] inside large cavities in the zeolite and on the outer surface. Reoxidation of small Cu^0 crystals takes place easily and is accompanied by the reappearance of Cu^{2+} in the cationic sites of the zeolite. When CuM specimens are reduced no Cu^{2+} ions are left in the mordenite channels but Cu^0 particles ~200 Å in diameter are formed on the outer surface.[9] However, reoxidation of the specimens does not lead to the formation of CuO crystals on the outer surface but to migration of Cu^{2+} ions which are then trapped in the mordenite channels. Thus in the H-forms of the zeolite there can be diffusion from the outer surface to the cationic sites in an oxidising atmosphere. Similar effects were observed by Beyer, et al.[10] who found that the reoxidation of AgY can be regarded as a solid state reaction between the H-form of the zeolite and an Ag/Ag_2O phase situated on the outer surface of the crystals.

The papers quoted above naturally provided an impetus to detailed studies of solid state reactions in HS-zeolite–transition metal oxide (or salt) mechanical mixtures. Research was carried out first on copper-containing systems because Cu^{2+} ions (unlike most transition metal ions) can be introduced into HS-zeolite by ion exchange. The detailed studies of ion-exchange specimens carried out recently form an excellent basis for a comparative analysis.

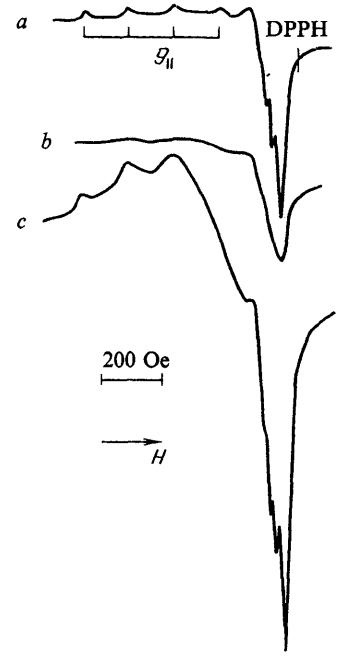


Figure 1. EPR spectra (at 20 °C) of an [HM + BCC] mixture heated in air:[11] *a*, 550 °C, 1 h, specimen evacuated at 20 °C; *b*, air admitted; *c*, 700 °C, 1 h + 800 °C, 1 h, specimen evacuated t 20 °C. [DPPH = diphenylpicrylhydrazine.]

1. Topochemical reactions of copper compounds with mordenite and pentasils

The introduction of Cu^{2+} cations using solid state reactions at 400–800 °C between copper compounds [CuO, basic copper carbonate (BCC), copper metal, $CuCl_2$, CuF_2, $Cu_3(PO_4)_2$, Cu_2S] and various mordenite and pentasil specimens has been investigated thoroughly[11,12] (Table 1).

The EPR spectra of Cu^{2+} ions in an [HM + BCC] mixture heated at various temperatures are shown in Fig. 1. Access of air at 20 °C leads to reversible broadening of the hyperfine-structure (HFS) lines in the spectra and the disappearance of the splitting in the perpendicular component (Fig. 1*b*). On oxidative heating of the [HM + Cu^0] mixture a complex pattern of EPR signals is observed. The only difference is that after heating for an hour at 550 °C the EPR signal is ~5 times weaker than the spectrum in Fig. 1*a* (the HFS agrees completely). However, raising the temperature to 700 °C leads to a considerable increase in the intensity of the signal and after heating at 800 °C for an hour the signal for the [HM + Cu^0] mixture (Fig. 1*c*) agrees with that for the [HM + BCC] mixture in both shape and intensity.

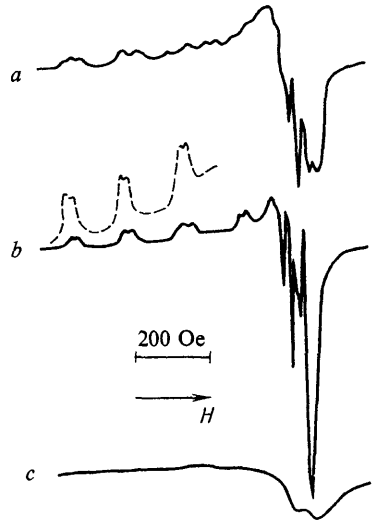


Figure 2. EPR spectra (at 20 °C) of an [H-ZSM-5 + Cu^0] mixture heated in air:[11] *a*, 550 °C, 1 h, specimen evacuated at 20 °C; *b*, 800 °C, 1 h, specimen evacuated at 20 °C; *c*, air admitted.

There are qualitatively no differences between the processes accompanying the oxidative heating of the mixtures of zeolites with BCC, CuO, and Cu^0. In all three cases the reaction of course involves copper(II) oxide which, at the temperatures used, is formed rapidly from both BCC and Cu^0. However, the degree of dispersion of the CuO has a marked effect on the rate of the reactions. In the most heterogeneous system, where Cu^0 powder with a particle size measured in tens of microns is used, the rate of formation of isolated ions, which give the EPR signal, is substantially lower. However it is of fundamental importance that, when the various mixtures are heated under sufficiently drastic conditions, the intensity of the EPR signal from the dispersed Cu^{2+} ions reaches the maximum possible for the given zeolite specimen.

EPR signals from Cu^{2+} do not appear when an [NaM + BCC] mixture is heated at 550–800 °C in air, i.e. there is no exchange of Na^+ by Cu^{2+}; protonic centres are necessary for the stabilisation of Cu^{2+} ions.

The EPR signals produced when an [H-ZSM-5 + Cu^0] mixture is heated in air are shown in Fig. 2. The HFS of the EPR signal (Fig. 2*b*) shows no change and the intensity does not increase when the heating time at 800 °C is increased to 4 h. Admitting O_2 to the specimen at 20 °C causes pronounced reversible broadening of the Cu^{2+} lines in the EPR spectrum (Fig. 2*c*).

The EPR signals obtained when HNa-ZSM-5 is heated with CuO have different parameters (Table 2) and the maximum intensity of the EPR signal from Cu^{2+} is appreciably smaller in this case than for H-ZSM-5. Clearly the Na^+ cations present in the zeolite block those centres that are capable of binding Cu^{2+} cations in H-ZSM-5.

Table 2. Parameters of the EPR spectra due to Cu^{2+}.[11]

Specimen	Heated at (°C)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$, Oe	$A_{\perp}$, Oe
HM+CuO	550	2.325	2.055	144	19
HNa-ZSM-5+CuO	550 and 800	2.37	2.075	135	—
H-ZSM-5+CuO	550	2.33	2,07	142	17,5
		2.27	2,045	175	29
H-ZSM-5+CuO	800	2.31	2.06	153	
		2.29	2.05	156	23
H-ZSM-5+CuF_2 or $Cu_3(PO_4)_2$	500 and 700	2.31		153	
		2.29		156	
		2.37		120	
		2.38		120	

The reaction of CuO with pentasil specimens with various modules gives EPR spectra with almost the same shape but a different maximum intensity. The intensity of the Cu^{2+} EPR signal is linearly dependent on the aluminium content of the zeolite, providing clear confirmation that the Cu^{2+} is located at the sites of the cationic vacancies formed by the Al^{3+} in the framework.

Heating a mixture of H-ZSM-5 with anhydrous $CuCl_2$ under vacuum at 400 °C for 30 min gives the Cu^{2+} EPR spectrum shown in Fig. 3*a*. Heating the mixture at 550 °C for an hour causes a considerable increase in the signal intensity and heating in air at 800 °C for an hour gives the signal shown in Fig. 3*b*. Heating mixtures of H-ZSM-5 with CuF_2 and $Cu_3(PO_4)_2$ under vacuum at 550–800 °C also gives EPR signals from isolated Cu^{2+} ions. Admitting air leads to reversible broadening of the EPR lines. X-Ray analysis shows that there is no disruption of the zeolite framework when H-ZSM-5 is heated with CuF_2 at 800 °C for 2 h. The parameters of the EPR spectra of Cu^{2+} ions in specimens studied by us previously[11,12] are given in Table 2.

Analysis of the results obtained greatly facilitates detailed comparisons with the data for copper-containing zeolites prepared from the same specimens by ion exchange and studied thoroughly previously,[13,14] and also with data for CuH-ZSM-5.[15,16] When markedly heterogeneous mechanical mixtures of the H-forms of mordenite and pentasil with CuO are heated there is evidently considerable dispersion and migration of some of the Cu^{2+} ions into the zeolite channels. The ions in mordenite and pentasil are located at the same cationic sites as are found in the corresponding

specimens obtained by ion exchange. Thus the EPR signal produced when HM is heated with BCC under fairly mild conditions (Fig. 1*a*) is almost the same as the spectrum of an ion-exchange specimen of CuHM with a small degree of exchange [1 Cu^{2+} ion for each 3 unit cells (u.c.)], where almost all the copper introduced occurs as isolated ions with square pyramidal coordination. The broadening of the components of the Cu^{2+} ion EPR spectrum due to dipole-dipole interaction with O_2 molecules present in the first coordination sphere indicates 100% dispersion of the Cu^{2+} cations in the zeolite channels. When the thermal treatment of HM with CuO is made more severe the EPR spectrum increases in intensity and its shape changes, indicating an interaction between the Cu^{2+} ions. The spectrum shown in Fig. 1*c* is characteristic of weak association of interacting Cu^{2+} ions and is identical in shape and intensity to the spectrum of an exchange specimen of CuHM containing two Cu^{2+} ions to one unit cell. Thus the pattern of changes in the EPR signals accompanying the solid state reaction of HM with CuO is identical to that observed on increasing the concentration of exchanged Cu^{2+} cations in HM. Hence as the migration of Cu^{2+} ions in HM increases they occur first as isolated cations and then as they increase in number in the channels weak associates are formed and a maximum possible concentration is reached (notwithstanding the large excess of CuO on the outer surface).

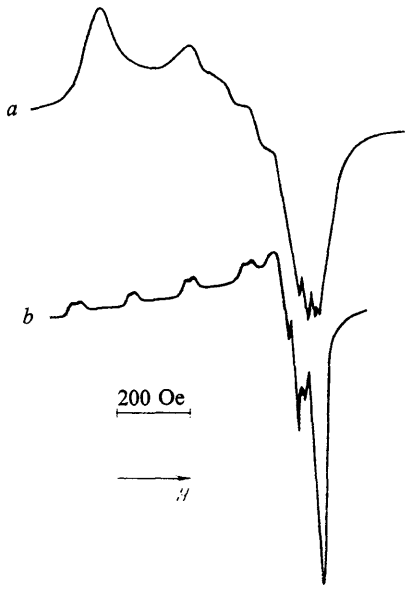


Figure 3. EPR spectra (at 20 °C) of a mixture of H-ZSM-5 with $CuCl_2$ heated under vacuum:[12] *a*, 400 °C, 30 min; *b*, 800 °C, 1 h.

In order to compare the amounts of Cu^{2+} introduced into mordenite by different methods, the oxidative heating of a mixture of BCC with an ion-exchange specimen of CuHM with the maximum degree of exchange was investigated.[12] No increase in the intensity of the Cu^{2+} EPR signal was obtained by heating at 700–800 °C. Hence for mordenite the maximum number of Cu^{2+} cations is not significantly dependent on the method of introduction but is determined by the number of accessible sites in which they can be located. This number is only half of the total cation capacity.

For pentasil-type zeolites the Cu^{2+} introduced by exchange in aqueous solution can be ~20% of the amount of aluminium in the framework and after heating at 500 °C all the copper occurs as two types of isolated, coordinately unsaturated cations with square pyramidal ($g_{||}$ = 2.31, $A_{||}$ = 155 Oe) and square planar ($g_{||}$ = 2.27, $A_{||}$ = 175 Oe) coordination. On increasing the ignition temperature to 800 °C two types of location are retained (square pyramids with a degree of distortion towards square planar). The EPR spectra obtained by heating mechanical mixtures (Fig. 2, *a* and *b*) agree completely with the spectra of the Cu^{2+} cations in the exchange specimen CuH-ZSM-5 which has been heated at 550 °C and 800 °C respectively. The effect of O_2 on the HFS of the EPR spectra is equally pronounced for both the exchange specimen and the heated mechanical mixtures.

Thus for pentasil also, the diffusion of Cu^{2+} ions from the outer surface leads to their being trapped in the cationic sites that are characteristic of the exchange specimens. In spite of the large excess of CuO on the outer surface of the pentasil the number of Cu^{2+} ions dispersed singly reaches a constant value and formation of associates does not take place. The maximum degree of occupation of the cationic vacancies in H-ZSM-5 by Cu^{2+} ions diffusing from the surface has been estimated as 30–40% of the total capacity.[12] When a mixture of the ion-exchange specimen CuH-ZSM-5 (20% exchange) with BCC is heated oxidatively at 700–800 °C the intensity of the EPR signal from isolated Cu^{2+} ions increases by a factor of ~1.5; this also indicates an increase in the degree of exchange to 30%. Thus, for pentasil solid state reactions lead to a somewhat greater degree of exchange than does ion exchange in aqueous solution.

It should be emphasised that the ion-exchange specimens and the specimens prepared by heating mechanical mixtures with CuO are identical as regards adsorption of various substances from the gaseous phase. All the changes in the coordination of the isolated Cu^{2+} ions are absolutely identical for the two types of specimen. This applies both to adsorption of strong ligands (NH_3, pyridine C_3H_6 [17,18]) and to the effects produced by the physical adsorption of hexane and xenon.[19,20]

2. Changes in the ligand environment of Cu^{2+} on adsorption of various molecules in H-ZSM-5

The number of states in which the Cu^{2+} cations occur in the zeolite ZSM-5 depends on the thermal treatment conditions and the Cu^{2+} cation concentration in the zeolite. Anderson and Kevan[15] introduced Cu^{2+} cations by ion exchange into the zeolite NaH-ZSM-5 which is obtained by decomposition of NaTPA-ZSM-5 under vacuum at 600 °C. After the exchange the zeolite contained approximately one Cu^{2+} cation per 10^3 tetrahedra. Dehydration of this zeolite at 400 °C gave an EPR signal from Cu^{2+} ions present in only one state ($g_{||}$ = 2.310, $g_{\perp}$ = 2.052, $A_{||}$ = 172 × 10^{-4} cm^{-1}). The concentration of Cu^{2+} cations in this zeolite was 1 cation per 10 u.c. According to Sendoda and Ono[16] there are ~6 Cu^{2+} cations in 10 u.c. of the zeolite and the EPR spectrum of a specimen which has been dehydrated under vacuum at 400 °C contains three signals corresponding to three Cu^{2+} cation states ($g_{||}^1$ = 2.31, $A_{||}^1$ = 164 × 10^{-4} cm^{-1}; $g_{||}^2$ = 2.30, $A_{||}^2$ = 163 × 10^{-4} cm^{-1}; $g_{||}^3$ = 2.27, $A_{||}^3$ = 176 × 10^{-4} cm^{-1}). When dehydration under vacuum is carried out at 550 °C one of the states of the Cu^{2+} ions disappears and the two remaining states have almost the same EPR parameters

($g_{\|}^1$ = 2.31, $A_{\|}^1$ = 170 × 10^{-4} cm^{-1}; $g_{\|}^2$ = 2.30, $A_{\|}^2$ = 175 × 10^{-4} cm^{-1}). In other studies[11–14,19,20] the amount of Cu^{2+} in H-ZSM-5 reached ~1 cation to 1 u.c., with the zeolite containing two types of Cu^{2+} cation (see Table 2), and the specimens obtained by exchange and by a solid state reaction were identical.

There is an important aspect of the behaviour of Cu^{2+} ions in the zeolite H-ZSM-5 during vacuum conditioning. The intensity of the EPR signal decreases significantly after conditioning of the specimen under vacuum at various temperatures for 3 h.[16] However this effect is not observed if the specimen undergoes oxidative thermal treatment immediately before evacuation.[11–14] It is not impossible that the reduction in intensity is due to the presence of small quantities of adsorbed organic impurities in the specimen. Judging from their results, Sendoda and Ono[16] made no observation of oxidative treatment of the specimen before the vacuum conditioning.

Adsorption of NH_3 at 20 °C does not lead to a significant change in $A_{\|}$ [17,18] and, in contrast to other reports,[15,16] splitting due to interaction with the nuclear spin of the atoms in the coordinated NH_3 molecules was not observed in the $g_{\perp}$ region. This may be due to steric hindrance in the reaction of the NH_3 molecules with the Cu^{2+} cations trapped in the ZSM-5;[16] the steric hindrance probably increases as the concentration of Cu^{2+} cations in the zeolite increases.[15] The two types of Cu^{2+} cation react differently with NH_3.[16,17] The reaction of the Cu^{2+} in the zeolite ZSM-5 with pyridine is more hindered than that with NH_3.[16] In accordance with this the parameter of the EPR spectrum of the Cu^{2+} cations change even less[17,18] and no HFS component due to interaction with the nuclear spin of the nitrogen atom is observed in the $g_{\perp}$ region.

There is a vigorous reaction between $(CH_3)_2O$ molecules and the Cu^{2+} cations in ZSM-5.[17,18] Both types of Cu^{2+} cations are evidently involved in this reaction with formation of two types of complex which probably contain different numbers of $(CH_3)_2O$ molecules in the coordination sphere.[15] Several adsorption complexes with different numbers of molecules are also produced in the reaction of CH_3OH with Cu^{2+} in the zeolite ZSM-5. It is found that the type of change in $g_{\|}$ and $A_{\|}$ in the reaction of Cu^{2+} cations with $(CH_3)_2O$ and CH_3OH molecules ($g_{\|}$ increases and $A_{\|}$ decreases compared to the values for the Cu^{2+} cations in the initial specimen) is similar to the changes in these parameters on hydration of the Cu^{2+} cation;[15] this confirms that the complex-formation reaction takes place with escape of the complexes into a straight channel or to the point of intersection of the channels.

Substantial additions to the information on the stereochemistry of paramagnetic Cu^{2+} complexes in H-ZSM-5 were obtained by using pulsed spin-echo spectroscopy as well as EPR.[15,16]

Anderson and Kevan[15] consider that in the initial hydrated specimen the Cu^{2+} is octahedrally coordinated by 6 water molecules and this complex is located at the intersection of the channels. Evacuation at 20 °C is found to be sufficient for the removal of three molecules of water while activation at 400 °C leads to complete removal of H_2O and formation of Cu^{2+} species with restricted accessibility from the large channel in the zeolite, i.e. situated in a five-membered ring. Adsorption of polar molecules (H_2O, NH_3, pyridine, alcohols) causes rapid migration of Cu^{2+} to positions in the large channels and the formation of Cu^{2+} complexes coordinated to two CH_3OH molecules, three C_2H_5OH or pyridine molecules, or four ammonia molecules. The reaction of Cu^{2+} with the non-polar molecules ethylene and benzene is considerably worse.

The absence of modulation by ^{27}Al in spin-echo spectra shows that the Cu^{2+} cations are not located preferentially on the negatively charged AlO_2^- units in the lattice (the Cu–Al distance is not less than 6 Å). The Cu^{2+} concentration in the zeolite may play an important role in the formation of Cu^{2+} ions coordinated in different ways.[15] For example, for a specimen containing 7 times more copper two types of species were detected after evacuation at 20 °C.[16] It was also found that on adsorption of pyridine a Cu^{2+} complex with two, not three, molecules is formed.

The coordination and location of the Cu^{2+} are affected not only by a low copper concentration in the zeolite but also by the presence of sodium.[11–14] Na^+ ions in the zeolite occupy most of the sites securely, blocking them from coordination with Cu^{2+}. This can only be avoided by using the initial H- or NH_4-forms of ZSM-5.

This was confirmed by Sendoda and Ono[16] who compared the ability of Cu^{2+} in H-ZSM-5, Na-ZSM-5, K-ZSM-5, and Ca-ZSM-5 to form complexes with methanol and ethanol. This ability was found to depend on the presence of the second cation and it is suggested that complexes with 4 molecules of the alcohol are formed in H-ZSM-5 but with only 3 molecules of the alcohol in the other specimens. Furthermore the EPR spectroscopic parameters quoted for Cu^{2+} in pure H-ZSM-5 are similar to our values[11–14] ($g_{\|}$ = 2.27, $A_{\|}$ = 180 Oe; $g_{\perp}$ = 2.05) and are markedly different from those for Cu^{2+} in a zeolite containing Na^+ (see Table 2).

3. Physical adsorption of n-hexane and xenon

In studies of the interaction of isolated Cu^{2+} cations with various molecules in the channels in ZSM-5 it was found that not only unsaturated and polar molecules affect the coordination of the Cu^{2+} but the adsorption of n-hexane is also accompanied by measureable changes in the EPR spectra. We have made a detailed analysis of the effects produced by the physical adsorption of alkanes (n-hexane) and inert gases (Ar, Xe) in the channels in CuH-ZSM-5.[19,20] The EPR signal from the initial CuH-ZSM-5 which has been heated at 800 °C is a superposition of two spectra from isolated Cu^{2+} ions: $g_{\|}^1$ = 2.30, $A_{\|}^1$ = 159 Oe, and $g_{\|}^2$ = 2.31, $A_{\|}^2$ = 156 Oe. The perpendicular components were not completely resolved but the analysis gave the values $g_{\perp}^1$ = 2.05, $A_{\perp}^1$ = 23.5 Oe, and $g_{\perp}^2$ = 2.06, $A_{\perp}^2$ = 22.5 Oe. These values show that the specimen contains two distinct types of isolated Cu^{2+} cations located in square pyramids with appreciable distortion towards square planar.

Adsorption of argon (~150 mm Hg) on to the CuH-ZSM-5 specimen at 20 °C did not produce measureable changes in the Cu^{2+} EPR spectrum. However, sorption of xenon (200 mm Hg) was accompanied by an appreciable and reversible effect on one of the two sets of EPR lines.

Sorption of n-hexane (at 20 °C and saturated vapour pressure) was also accompanied by changes in the HFS of one of the Cu^{2+} EPR signals. A slow increase in temperature to 200 °C with continuous evacuation (to 10^{-6} mm Hg) was accompanied by slow changes in the Cu^{2+} EPR spectrum and after evacuating at 200 °C for 30 min the EPR spectrum reverted almost completely to the original spectrum.

Thus appreciable changes in the EPR parameters on adsorption were found for only one of the two types of Cu^{2+} cation ($\Delta g_{\|}$ = 0.03–0.04, $\Delta g_{\perp}$ = 0.01, $\Delta A_{\|}$ = 9–12 Oe, $\Delta A_{\perp}$ ~ 3 Oe). Hence the Cu^{2+} cations located in two distinct sites which differ very little in their type of coordination show a significant difference in their ability to interact with adsorbed molecules of xenon or hexane. For one type of ion the changes in the coordination are negligibly small but for the other type sorption causes an appreciable reduction in the distortion of the square pyramidal coordination of the Cu^{2+}.

Changes in the symmetry of the Cu^{2+} ion due to formation of a coordinate or covalent bond are common for most compounds (unsaturated and polar molecules). However it is difficult to imagine the formation of bonds between Cu^{2+} ions and a non-polar saturated molecule (hexane) and even more so with an inert gas atom (xenon). It is known that the sorption of hexane in H-ZSM-5 at 20 °C can be described as filling of the channels with the liquid hydrocarbon. The sorption does not take place at specific centres but the whole volume of the channels is filled with the condensed phase. In our opinion[19,20] the results obtained indicate some geometrical displacement of the Cu^{2+} ions to one of the types of cationic site due to a dispersion interaction with the adsorbate molecules (or atoms) occupying the channels in the zeolite.

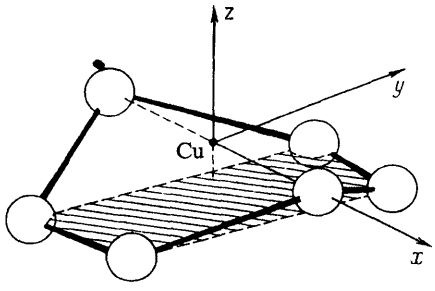


Figure 4. $[Cu^{2+}(O_b^{q-})_6]^{Q}$ **cluster model for an isolated** Cu^{2+} **ion in a structural unit in H-ZSM-5,[17] as determined by X-ray diffraction.[21]**

4. Quantum-chemical analysis of the interaction of molecules with isolated Cu^{2+} cations in H-ZSM-5

There is only one instance where the position of a transition metal cation (Ni^{2+}) in the zeolite H-ZSM-5 has been determined by X-ray diffraction.[21] The ions were found to be located in two sites: (1) in a straight channel close to the wall, and (2) inside a $T_{14}O_{20}$ unit composed of five-membered rings. The cation in the straight channel is bonded to only 3 oxygen atoms in the network but it must have oxygen ligands outside the network. The second site is less accessible and the cation in this site has 6 network ligands. The geometry of this site is shown in Fig. 4. Aspects of the location of the copper cation have been analysed using quantum-chemical calculations.[17,18] The components of the g tensor g_{qq} calculated by the standard method using the Stown approximation agree well with the components of the experimental spectrum. The almost equal components g_{11} and g_{22} are close to the value $g_{\perp} = 2.05$ and the theoretical value g_{33} agrees satisfactorily with the experimental $g_{||}$. However, the most interesting result is that small displacements of the Cu^{2+} ion in the chelate site under discussion can cause marked changes in the parameters of the g factor. Even a negligibly small displacement of the ion ($\Delta z = 0.01$ Å) will lead to appreciable changes in the components g_{qq} (especially g_{33}). There is also a marked dependence of the calculated parameters of the EPR spectrum on changes in the donor-acceptor properties of the ligand environment of the Cu^{2+} when $\Delta z = 0$.

Quantum-chemical calculations of the components of the g tensor[17,18] were also used to assess the interaction of Cu^{2+} in this centre (see Fig. 4) with ammonia. The EPR parameters of complexes with 1 or 2 NH_3 molecules situated on the z axis above and below the Cu^{2+} ion with typical $Cu^{2+}-NH_3$ distances can easily be calculated. However, the differences between the calculated and observed parameters are very large. For complexes with one NH_3 molecule above the cluster $g_{11} = 2.003$, $g_{22} = 2.383$, and $g_{33} = 2.493$, and for those with two NH_3 molecules $g_{11} = 2.003$, $g_{22} = 2.057$, and $g_{33} = 2.090$. Hence either the interaction with ammonia takes place with removal of the Cu^{2+} from such a site or the NH_3 molecule is located sufficiently far away from the cluster under consideration.

Thus it is possible for some of the Cu^{2+} ions in H-ZSM-5 to be located in positions where the EPR parameters are very sensitive to both small geometrical displacements of the ion and small changes in the donor-acceptor properties of the ligand environment. The results of the quantum-chemical calculation confirm that it is possible for the weak effects of physical adsorption of xenon or hexane to cause measurable changes in the Cu^{2+} EPR parameters, as mentioned above.

5. Aspects of the reaction of H-ZSM-5 with various copper compounds

Results published by us[11,12] show that protonic centres in HS-zeolites can be regarded as powerful energy traps for migrating ions. From this point of view the topochemical reaction under discussion can be described as the reaction of CuO with an acid (the protonic centres) and formation of a sort of "salt" of a weak base and a strong acid. The reaction of CuO with H-ZSM-5 at 550–800 °C under vacuum (10^{-6} mm Hg) takes place exactly the same as in air, i.e. the absence of O_2 from the gaseous phase has no effect on the migration and location of Cu^{2+} ions in H-ZSM-5.

It was noted above that H-ZSM-5 can react in the solid state with various compounds. High-temperature reactions of H-ZSM-5 under vacuum with $Cu_3(PO_4)_2$, $CuCl_2$, and CuF_2, like the reaction with CuO, give EPR signals from isolated Cu^{2+} ions (see Figs. 3 and 4). However, the marked differences in the HFS of the EPR spectra in these cases clearly demonstrate the effect of the anion which will act as a ligand, for the isolated Cu^{2+} cations trapped in the zeolite, which is outside the framework (see Table 2).

The appreciable migration of Cu^{2+} at 400 °C in a mixture of $CuCl_2$ with H-ZSM-5 is due to the low stability of the $CuCl_2$ lattice (m.p. 596 °C). Differences occur in the types of coordination of Cu^{2+}, due to the presence of different anionic fragments. For example, in the heated systems (H-ZSM-5 + CuF_2) and [H-ZSM-5 + $Cu_3(PO_4)_2$] at least 4 types of coordination can be distinguished. Two of these are entirely the same as the types found for (CuO + H-ZSM-5) but the other two correspond to a crystal field with octahedral symmetry. It therefore appears that a significant proportion of the isolated Cu^{2+} cations in the zeolite channels interact with the strong ligands F^- and PO_4^{3-} which are outside the framework.

Studies of the reaction of H-ZSM-5 with a copper(I) compound such as Cu_2S [12] show that isolated Cu^+ ions can also migrate to cationic sites in the zeolite after the mixture has been heated under vacuum and their subsequent oxidation produces isolated Cu^{2+} ions.

Thus, using copper-containing high-silica zeolites as an example,[11,12] it has been shown that, due to the thermal stability of the framework of the HS-zeolite and the characteristics of the protonic centres present in them, it is possible to introduce cations by solid state reactions. Not only physicochemical studies but also catalytic data, which will be discussed in a later section, confirm that the specimens obtained are identical to ion-exchange specimens.

In addition to the research on copper-containing HS-zeolites a whole series of papers has been published in which the potentialities of solid state reactions are analysed using a number of other transition metals as examples.

6. Reactions of mordenite and pentasils with chromium compounds

Solid state reactions of mordenite and pentasils (see Table 1) with chromium oxides at 500–820 °C have been studied thoroughly.[22–26]

Heating mechanical mixtures of the H-forms of zeolites with CrO_3 and Cr_2O_3 gives EPR signals of isolated Cr^{5+} ions. When different mixtures are heated under sufficiently drastic conditions the intensities of these signals reach a limit which is determined by the concentration of acidic centres in the zeolite. Heating mixtures containing NaM to 820 °C does not give EPR signals representing isolated ions.

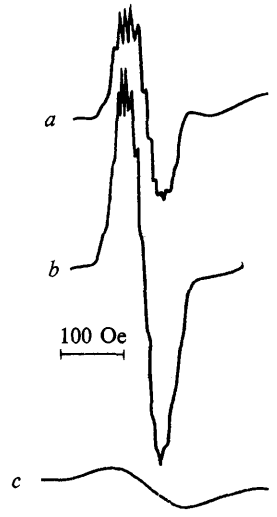


Figure 5. EPR spectra (at 20 °C) of Cr^{5+} ions introduced into H-ZSM-5 by a reaction with CrO_3:[23] *a*, specimen heated in air at 550 °C for 1 h and evacuated at 20 °C for 5 min; *b*, specimen heated at 800 °C for 1 h and evacuated at 20 °C for 5 min; *c*, air admitted to specimen (*b*).

The EPR spectra produced by heating a mechanical mixture of H-ZSM-5 with CrO_3 in air and under vacuum are shown in Fig. 5. Cooling the specimen to –196 °C under vacuum increases the intensity of the signal (Fig. 5*b*) without changing its form (ΔH = 50 Oe, g_0 = 1.98). Admitting air at 20 °C causes a marked, but reversible, broadening of the signal (Fig. 5*c*).

For the initial mixture of H-ZSM-5 with 1.2 mass% Cr_2O_3 the EPR spectrum at 80 °C is a broad symmetrical line (ΔH = 460 Oe) characteristic of bulk antiferromagnetic α-Cr_2O_3. Heating this mixture in air leads to a considerable reduction in the intensity of this signal from the Cr_2O_3 phase and the appearance of a sharp line observed at 20 °C which is identical to the spectrum shown in Fig. 5*b*.

Thus copper is not exceptional and similar processes involving the migration and redistribution of ions in the solid state can occur for other transition metals.

Results published by us[22–25] indicate unequivocally that Cr^{5+} ions are trapped in the H-forms of mordenite and pentasils. In the pentasils the ions occur as isolated, coordinately unsaturated cations which are accessible to molecules from the gas phase. When air is admitted a dipole-dipole interaction with O_2 molecules leads to a marked, reversible broadening of the HFS lines in the spectrum (Fig. 5*c*).

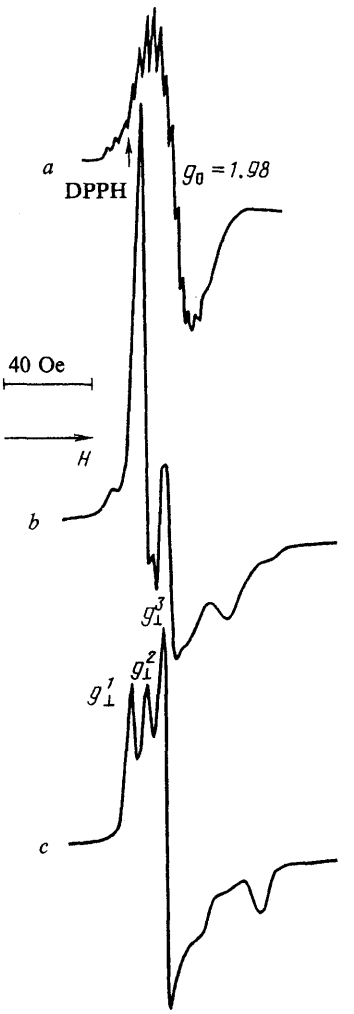


Figure 6. EPR spectra (at 20 °C) of Cr^{5+} ions introduced into H-pentasil-280:[24] *a*, specimen evacuated at 20 °C for 5 min; *b*, after admitting NH_3; *c*, after admitting pyridine; [$g_\perp^1$ = 2.00; $g_\perp^2$ = 1.99; $g_\perp^3$ = 1.98; $g_\parallel^1$ = 1.95; g^2 = 1.93; $g_\parallel^3$ = 1.91].

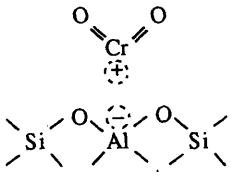
An important aspect of the Cr/HS-zeolite system needs emphasising: the chromium ions in the cationic sites are stabilised in the chromium(V) state when the reaction is carried out in an oxidising medium using both chromium(VI) (CrO_3) and

chromium(III) (Cr_2O_3) compounds. Thus stabilisation of the chromium cations in the matrices of HS-zeolites makes the valence state Cr^V stable.

It is difficult to imagine that, in the HS-zeolites, highly charged pentavalent ions are trapped as cations with no ligands outside the framework and we have therefore suggested[23,24] that the ions stabilised in the cationic sites of the pentasil are not isolated Cr^{5+} ions but isolated CrO_2^+ species balancing the single charge on the framework. The maximum concentration of the CrO_2^+ species depends on the concentration of acidic centres in the specimen.[23,24]

The extra hyperfine structure (EHFS) in the Cr^V EPR spectra (see Fig. 5) provides direct evidence for interaction of the ionic species with an Al^{3+} ion in the framework, creating a cationic vacancy.[23,24] EHFS was also observed for Cr/H-Y.[27,28] In reactions of specimens with NH_3 and pyridine the EHFS disappears and two or three anisotropic signals from Cr^V are superimposed (Fig. 6), i.e. the interaction with these strong ligands leads to a considerable change in the coordination sphere of the cations.[23,24]

The splitting by an aluminium atom situated nearby in itself again confirms the cationic location of Cr^V in the zeolite. However our interpretation of the spectrum with HFS[23,24] was not definitive because, from a formal point of view, an EPR signal with ~15 components obtained in the *X*-band may not be interpreted in terms of splitting by one ^{27}Al nucleus but by two or three aluminium atoms side by side. Although such close alignment of the aluminium atoms in the framework of the ZSM-5 zeolite is improbable, this interpretation of the spectrum (see Fig. 5) is still possible. The problem has been solved by Hemidy, et al.:[29,30] the EPR spectrum of the same Cr^V/ZSM-5 specimen is recorded in the *Q*-band (λ = 8 mm) for comparison (Fig. 7*a*). Using recording in the *Q*-band the anisotropic nature of the spectrum becomes considerably more marked. The groups of lines can be divided into parallel and perpendicular components (6 lines) with slightly different splittings. It is clear from this spectrum that in this system there is an interaction of an isolated Cr^{5+} cation with one Al^{3+} ion in the framework, creating a cationic vacancy. The small magnitudes of the splittings (6–7.5 Oe) indicate that the Al^{3+} is situated in the second coordination sphere of the Cr^{5+} cation and the following mutual arrangement, which allows an interaction between the unpaired electron and the ^{27}Al nuclear spin, is proposed:



The dependence of the distribution of chromium cations in different valence states in a ZSM-5 type zeolite (Si/Al = 20) on the chromium concentration and the conditions of the oxidation-reduction treatment has been studied in detail using chromium concentrations from 0.8 to 3.5 mass%.[25,26] It was shown that at different stages of the thermal treatment of impregnated Cr–TsVM specimens containing 0.8 and 1.8 mass% Cr the Cr^{5+} cations can have different coordination environments. After impregnation and drying in air at 140 °C the major part of the chromium in the specimens occurs as chromates. However even heating at this temperature is sufficient for some of the Cr^{5+} cations to be stabilised within the zeolite channels as hydrated octahedral complexes. When the thermal treatment in air is more drastic the concentration of isolated, coordinately unsaturated Cr^{5+} cations in the zeolite channels increases and aluminium atoms are found in their coordination sphere. The concentration of this type of cation is determined by the concentration of chromium introduced at the impregnation stage.

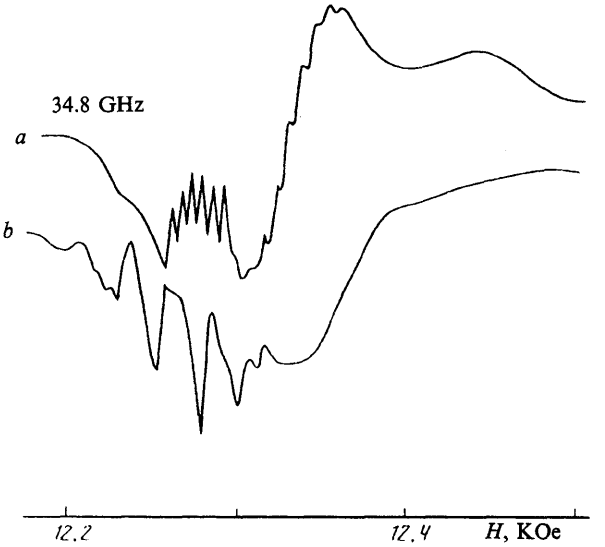


Figure 7. EPR spectra recorded in the *Q* band at 20 °C due to Cr^{5+} cations[28] in: *a*, H-ZSM-5; *b*, H-[Ga]ZSM-5.

A further increase in the concentration of chromium in the chromium–zeolite system leads to new features in its distribution. For example, for specimens containing 2.5 and 3.5 mass.% Cr no EPR spectra due to Cr^{5+} cations were observed either after drying (at 140 °C) or after heating in air at 500 °C for 10 min. This indicates that fairly large crystals of a chromium-containing phase are formed on the outer surface of the zeolite and diffusion of chromium cations from this phase and their stabilisation in the zeolite channels as Cr^{5+} take place slowly. However, heating for an hour is sufficient for this concentration to become high. On passing through the Néel point (314 K), in addition to the signal due to Cr^{5+} cations, an intense broad EPR signal due to formation of large antiferromagnetic crystals of α-Cr_2O_3 on the outer surface of the zeolite is produced. For the specimen containing 3.5 mass% Cr the proportion of Cr^{5+} cations formed is only 20% of the total number of chromium cations in the specimen because a considerable amount of the chromium is stabilised as Cr^{3+} cations in the α-Cr_2O_3 crystals. In other words, these results[25,26] show that the Cr^{5+} cations in an H-ZSM-5 type zeolite may be trapped in several types of centre with different symmetries and with some of the ligands in the first coordination sphere not belonging to the zeolite framework. The results also indicate that, in spite of the considerable variation in the total chromium content and the treatment conditions, it is not possible to introduce more than $(9-10) \times 10^{19}$ Cr^{5+} cations per 1 g of zeolite, i.e. ~0.8 mass% Cr and corresponding to a Cr/Al ratio of ~0.2.

Using a 2.5% Cr–TsVM specimen an investigation was also made of the consistency of the distribution of the different forms of chromium on repetition of the oxidation-reduction treatment at 500 °C.[25,26] It was found that the distribution of the components obtained on preparation of the specimen is very stable and repeating the oxidation-reduction treatment 20 times does not lead to any irreversible changes in the distribution of Cr^{5+} and Cr^{3+} cations in the channels and on the outer surface of the zeolite. An analysis of the EPR spectra due to Cr^{3+} confirms that heating the specimens in hydrogen at 500 °C has no effect on that part of the chromium occurring in the Cr–TsVM in the form of α-Cr_2O_3 crystals. However the Cr^{5+} cations are reduced very easily and quantitatively, most probably to form Cr^{2+} ions.

The results in Refs. 23–26, where the chromium is introduced into H-[Al]ZSM-5, can be compared with more recent research[31] where aspects of the stabilisation of chromium in H-[Cr]ZSM-5, a chromium-silicate with the pentasil structure which contains no aluminium, are discussed. In this matrix, which has the same lattice geometry, some of the Cr^{3+} ions enter the zeolite framework in the synthesis. After the specimens have been heated in air the major part of the chromium introduced is aggregated into an inert Cr_2O_3 phase on the surface of the zeolite but a small proportion of the chromium ions are firmly stabilised by the zeolite as isolated Cr^{5+} ions with a low coordination. However, these ions, which remain grafted to the framework of the H-[Cr]ZSM-5, have properties which differ markedly from those of the CrO_2^+ cationic species that are the counter-ions of the framework aluminium in H-[Al]ZSM-5.

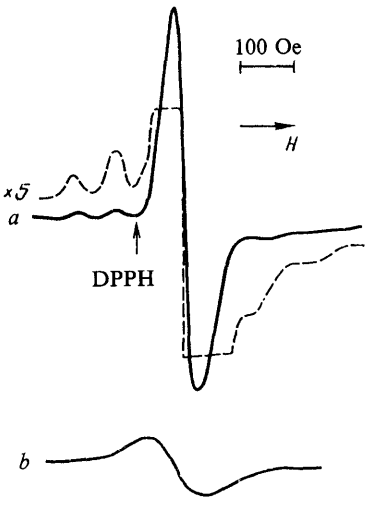


Figure 8. EPR spectra of Mo^{5+} ions introduced into H-ZSM-5 by a reaction with $MoCl_5$ at 450 °C under vacuum:[23] *a*, under vacuum; *b*, in air.

7. Introduction of Mo^{5+} cations into HS-zeolites

Studies have been made of the solid state reactions of mordenite and pentasils with molybdenum compounds.[24,25] The processes of migration of ions into HS-zeolites (see Table 1) when mechanical mixtures with MoO_3 and $MoCl_5$ are heated in air or under vacuum at 150–820 °C have been discussed. Heating mechanical mixtures of the H-forms of zeolites with $MoCl_5$ gives EPR signals from isolated Mo^{5+} ions (Fig. 8). As in the case of Cu^{2+} and Cr^{5+}, when the heating is under sufficiently drastic conditions the intensities of these signals reach a limit which is determined by the concentration of the acidic centres. No isolated molybdenum ions are produced in reactions with NaM up to 820 °C.

Heating mechanical mixtures of the zeolites with MoO_3 or ammonium paramolybdate in air or under vacuum does not give an EPR signal due to Mo^V nor does subsequent reduction in hydrogen give appreciable quantities of Mo^{5+}.[24,25] The reason given for the failure to introduce molybdenum cations by this means is that MoO_3 forms large polymeric fragments even in the vapour phase and does not give cationic species,[24,25] i.e. Mo^{6+} ions do not penetrate into the zeolite channels at all on heating in air.

The reaction of various zeolite specimens with $MoCl_5$ under vacuum is different. Fragments of this volatile compound (b.p. 268 °C) migrate extremely easily both on HS-zeolites and on an amorphous aluminosilicate. The EPR spectrum observed at 20 °C (Fig. 8*a* and *b*) is characteristic of isolated Mo^{5+} ions and the weak HFS lines (6 components with a splitting of ~80 Oe) are due to splitting at the ^{95}Mo and ^{97}Mo nuclei which have a nuclear spin of 5/2 (~24%). The cations are considerably more strongly bound to the zeolites than to the amorphous aluminosilicate. This is shown by experiments in which the specimens are heated at temperatures considerably above the volatilisation temperature of $MoCl_5$. On the amorphous carrier the concentration of cations starts to decrease noticeably at 450 °C and they are removed from the surface quantitatively by heating at 550 °C for 30 min. On zeolites the same thermal treatment does not remove more than one-third of the Mo^{5+} cations. Thus the cationic sites in HS-zeolites are powerful energy traps for Mo^{5+} ions (or rather $MoCl_4^+$ specimes which diffuse easily into the zeolite channels in the reaction with $MoCl_5$).

8. Aspects of the introduction of vanadyl cations into HS-zeolites

Reactions of HS-zeolites with V_2O_5 and the properties of the systems obtained have been studied.[24,25,32–34] Topochemical migration into the cationic sites in the zeolites was shown to be characteristic also of vanadium ions. The reaction of H-ZSM-5 with V_2O_5 at 550–800 °C gives a typical EPR signal from isolated V^{4+} cations ($g_{\|} = 1.93$, $g_{\perp} = 2.00$, $A_{\|} = 198$ Oe, $A_{\perp} = 85$ Oe).[32] Admitting O_2 to the specimen at 20 °C leads to a marked, but reversible, broadening of the lines in the spectrum. As with the other transition metals studied, the maximum concentration of isolated vanadyl ions depends on the concentration of acidic centres in the zeolite.

An important and unusual aspect of the stabilisation of vanadyl cations is their extraordinary stability in both reducing and oxidising media: almost the same EPR signal from V^{4+} ions in H-ZSM-5 is obtained when the specimens are heated at 800 °C in H_2 and in O_2.[24,25]

As the vanadyl ion, with the configuration $3d^1$, is electronically analogous to the Cr^V ion, we may expect EHFS in the EPR spectra for the vanadyl cations in V-H-ZSM-5, as for systems containing chromium.[23,25] EHFS was in fact found in the spectra by a careful EPR study of this system in the temperature range from –196 to 300 °C.[33] The HFS lines in the spectrum of isolated V^{IV} ions (Fig. 9*a*) undergo additional splitting due to EHFS coupling (Fig. 9*b* and *c*). The resolution of the EHFS components ($\Delta H \approx 7$ Oe) is considerably dependent on the temperature at which the spectrum is

recorded. At −196 °C EHFS is almost absent and at 20 °C the poor resolution makes it impossible to determine the number of components. As the temperature is increased the EHFS lines become narrower and signals with a fairly well resolved EHFS can be obtained at 200−300 °C (see Fig. 9*b* and *c*).

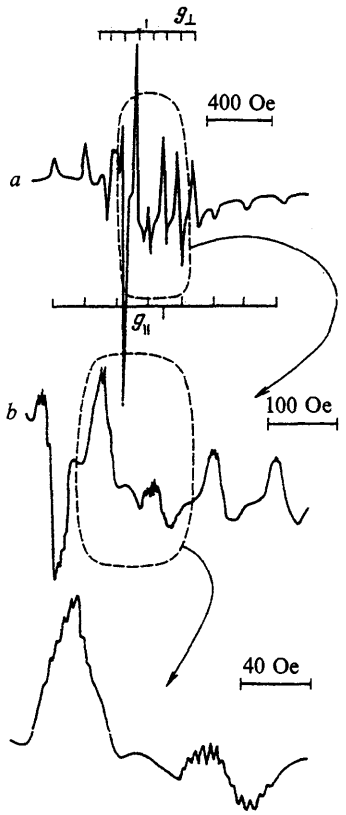
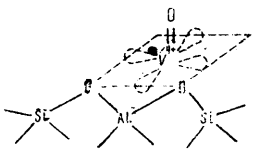


Figure 9. EPR spectra of isolated vanadyl cations ($^{51}V^{IV}$, $3d_1$, I = 7/2) introduced into H-ZSM-5:[33] *a*, complete spectrum recorded at 20 °C; *b* and *c*, parts of spectrum (*a*) recorded at 200 °C.

The detection of EHFS at a ^{27}Al nucleus in the V^{IV} EPR spectra (see Fig. 9) provides unambiguous evidence for an electronic interaction between the vanadyl cation and an Al^{3+} ion in the framework of the zeolite. The mutual disposition of the two ions will pave the way for an interaction between their outer electron shells and this will place limitations on the spatial arrangement of the vanadyl ions in the H-ZSM-5 channel. By taking into consideration the small magnitude of the EHFS splitting, which indicates that the Al^{3+} ion is in the second coordination sphere of the V^{IV}, and also that the unpaired electron is in the d_{xy} orbital of the V^{IV}, the following arrangement of the ions has been proposed:[33]



Solid state reactions of the H- and Ca-forms of ZSM-5 with V_2O_5 have also been shown to give paramagnetic vanadium species that are amenable to reactions with H_2O and O_2.[34] The number of V^{4+} ions formed is less for the Ca-form than for pure H-ZSM-5, the Ca-form having a smaller concentration of protonic acidic centres. The use of spin-echo spectroscopy as well as EPR[34] enabled the mutual arrangement of the vanadium and aluminium ions to be deduced from echo data at 4 K. The distance from the V^{4+} to the nucleus of the framework aluminium was found to be not more than 5 Å. The effect of the conditions under which the zeolite is heated with V_2O_5 was also investigated[34] and the possible reduction of V^{4+} with hydrogen was proposed. This conclusion was based on very small changes in the parameters of the EPR spectrum from paramagnetic vanadium and also changes in the colour of the specimens from yellow to grey. However these arguments are not very convincing in view of the fact that mixtures containing 4 mass% V_2O_5 were used in this work. This is a large excess compared to the amount required to fill all the cationic vacancies in the zeolite channels, i.e. some of the V_2O_5 will remain on the outer surface of the zeolite in the form of a phase, the changes in which will account for the observed effects.

In order to investigate thoroughly the distributiom of V^{IV} cations in the structure of the zeolite H-ZSM-5 and to analyse the properties of the vanadyl cations introduced by the solid state reaction, the changes in the parameters of the EPR spectra due to V^{4+} occurring on adsorption of various molecules (NH_3, pyridine, 2,4,6-trimethylpyridine *p*-xylene, nitrobenzene) were studied.[32] The adsorption of these molecules (with the exception of 2,4,6-trimethylpyridine) leads to splitting of the initial EPR spectrum into two, indicating that there are two types of VO^{2+} cation in the zeolite structure. Since adsorption of the sterically hindered 2,4,6-trimethylpyridine molecules has no effect on the parameters of the spectrum it is clear that the two types of cation are located inside the zeolite structure and not on the outer surface. It was shown previously that the zeolite CuH-ZSM-5 contains two types of Cu^{2+} cation, one of which is probably located in a channel and the other in a five-membered ring adjacent to a channel, with square pyramidal coordination. We have suggested[32] that a similar situation may apply to the trapping of VO^{2+} in H-ZSM-5. When a weak ligand such as *p*-xylene is adsorbed there is almost no change in the parameters of the EPR spectrum due to V^{4+} but there is some narrowing of the components and disappearance of the EHFS due to interaction of VO^{2+} with the framework Al^{3+}. By analogy with the effects of weak ligands on Cu^{2+} cations in H-ZSM-5 [20,21] there may be a small displacement of the VO^{2+} cations in the chelate site due to the effect of occupation of the channels in H-ZSM-5 by the *p*-xylene molecules.[32] The *p*-xylene molecules react not only with the cationic centres but also with the oxidation-reduction centres, giving an intense EPR signal from cation-radicals in the region of g = 2.004. Thus the introduction of VO^{2+} cations into the zeolite does not suppress the one-electron transfer centres in the zeolite.

The adsorption of pyridine, NH_3, and nitrobenzene is accompanied by considerable changes in the EPR spectral parameters due to the entry of these strong ligands into the coordination sphere of the VO^{2+}. An analysis of the spectra suggests that, on adsorption of pyridine and NH_3, delocalisation of the unpaired electron from the d_{xy} orbital to the ligand orbitals takes place, leading to increased covalency of the bonds. On the other hand, on adsorption of nitrobenzene the electron delocalisation is reduced and the V=O bonds become more polar.

As was mentioned above, the valence state of a VO^{2+} cation trapped in the zeolite H-ZSM-5 is extremely stable under high-temperature oxidation-reduction conditions: there is no oxidation of this cation to V^{5+} even on heating in a stream of air at 800 °C. This feature has been discussed using ideas put forward in a paper by us[32] where it was shown that the value of $B = \Delta g_{\|}/\Delta g_{\perp}$ characterises the strength of the V=O bond. For example, for V^{4+} cations deposited on Al_2O_3 and SiO_2 B has the values 2.1 and 2.4 respectively but after further reduction it decreases to 1.1 for the V^{4+}/Al_2O_3 system, i.e. the V=O bond becomes weaker, but it increases to 3.1 for the V^{4+}/SiO_2 system, i.e. the V=O bond becomes stronger. However in these instances the B values are small, i.e. on these carriers the V=O bond is not very strong and the V^{4+} cations will undergo oxidation-reduction changes. For VO^{2+} cations stabilised on H-ZSM-5 the B values calculated[32] vary from 8 to 15 and hence in these instances the V=O bond is considerably stronger than for deposition of vanadium cations on Al_2O_3 and SiO_2. However the physical reasons for this are not clear. The question as to which features of the structure of H-ZSM-5 and the location of the VO^{2+} cations guarantee such a high vanadyl bond strength remains undecided.

The solid state reaction of V_2O_5 with the zeolite NaY in air at 420–480 °C has been studied using a combination of methods (X-ray analysis, EPR, ^{29}Si and ^{129}Xe NMR, electron microscopy).[36] When the vanadium concentration is appreciable [R = V/(Al + Si) = 0.2] the lattice of the Y zeolite breaks down and the structure collapses. However, when R = 0.005 or 0.05 the zeolite structure is retained although the V_2O_5 phase disappears during the reaction. Some of the entrances to the zeolite cavities are blocked by a compound which contains V^{4+} ions. It is suggested that the reation of V_2O_5 with Na^+ may lead to formation of a vanadium bronze of the $NaV_5^{V}V^{IV}O_{15}$ type but there is no direct confirmation of this. However it is significant that in this case also,[36] where the zeolite NaY was used, there is an intense solid state reaction between the zeolite and V_2O_5 at fairly low temperatures.

9. Introduction of manganese cations into ZSM-5 zeolites

A number of methods (EPR, RFES†, adsorption of Ar, thermal desorption of NH_3, catalytic testing) have been used to study thoroughly the possible introduction of Mn^{2+} ions into H-ZSM-5 and Na-ZSM-5, both by ion exchange and by solid state reactions with MnO, $MnCl_2$, and $MnSO_4$.[37–39] It was shown that during a solid state reaction with H-ZSM-5 at 430–650 °C the manganese salts or MnO disappear from the surface of the zeolite and manganese ions are uniformly distributed throughout the zeolite crystals. The introduction of the ions is accompanied by a reduction in the number of strong Brønsted acid centres. There is no reaction with the Na-form of the zeolite. Hence, as with the other ions discussed above, stabilisation of the manganese is due to the presence of free protonic centres. However, note that the replacement of the strong acidic centres in H-ZSM-5 reaches a limit of only ~50%.[37,38] Using $MnCl_2$ an exchange reaction takes place to an appreciable extent even on heating at 300 °C for 1 h.[38] Under identical conditions the degree of exchange decreases in the order: $MnCl_2 > Mn_3O_4 > MnSO_4$.[39] Some of the manganese cations are stabilised in the zeolite as manganese(II), which is very stable and undergoes no changes on oxidation-reduction treatment in a stream of oxygen or hydrogen. The properties of the isolated Mn^{2+} cations do not depend on the method of introduction into the zeolite (ion exchange or solid state reactions). However the specimens may also contain manganese in other oxidation states which will complicate the analysis of their properties.

There is another feature of the Mn^{2+}–H-ZSM-5 system: only hydrated specimens give a typical EPR signal in the X-region with HFS due to isolated Mn^{2+} ions (6 components, g = 2.00); in the absence of H_2O molecules the signal is markedly broader.[37–39] This phenomenon has been analysed in detail for Mn^{2+} ions in Y zeolites.[40,41]

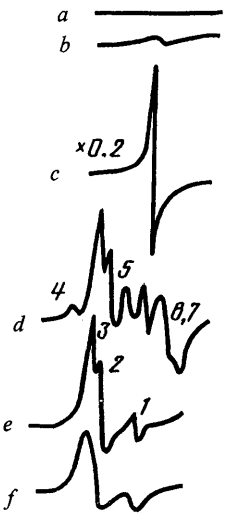


Figure 10. Changes in the EPR spectrum occurring when a mixture of $FeCl_3$ with H-ZSM-5 is heated:[42] *a*, specimen 1; *b* and *c*, specimen 2; *d*, specimen 3 evacuated for 2 min; *e*, specimen 4 evacuated for 2 min; *f*, adsorption of O_2 (100 torr) by specimen 4. Spectra (*c*) and (*d*) were measured at −196 °C. g values: *1*, 4.27; *2*, 5.65; *3*, 6.25; *4*, 9.1; *5*, 4.95; *6*, 3.7; *7*, 3.4

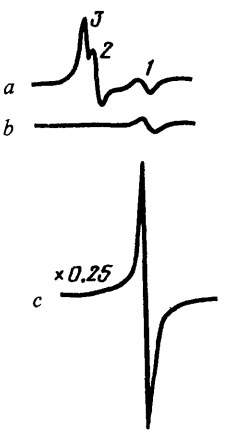


Figure 11. Effect of adsorption of NH_3 on the EPR signal from specimen 4:[42] *a*, initial signal at 20 °C; *b*, after adsorption at 20 °C; *c*, specimen (*b*) at −196 °C. g values; *1*, 4.27; *2*, 5.65; *3*, 6.25.

†Probably X-ray photoelectron spectroscopy (Ed. of Translation).

10. Reactions of H-ZSM-5 with iron compounds

Reactions between iron compounds and H-ZSM-5 have been studied thoroughly by the EPR method.[42,43] The location, coordination and properties of Fe^{3+} in this zeolite were investigated and comparisons made with a Y type zeolite, and also with a ferrisilicate analogue of the ZSM-5 zeolite (H-[Fe]ZSM-5) containing Fe^{3+} in the framework tetrahedra.

The initial mixtures of H-ZSM-5 with iron oxides give EPR spectra having only a very broad line with $g \simeq 2.0$. No new EPR signals due to Fe^{3+} are obtained by heating the mixtures to 800 °C under vacuum or in air. Heating specimens prepared by exchange with $(NH_4)_4Fe(CN)_6$ does not give any lines due to Fe^{3+}. However, the situation is different when $FeCl_3$ is used.[42,43]

The EPR spectrum of the initial mechanical mixture of H-ZSM-5 with $FeCl_3$ (specimen 1)[43] is shown in Fig. 10*a*. Heating this specimen under vacuum at 300 °C for 2 h (specimen 2) leads to the formation of the signal shown in Fig. 10*b*. Cooling specimen 2 to −196 °C produces an anomalous increase in the intensity of the EPR line with $g = 4.27$ [by a factor of more than 100: $I = (2-3) \times 10^{19}$ spins g^{-1}]. There are no changes in this signal when specimen 2 is heated under vacuum at 300−400 °C for a longer time.

The subsequent heating of specimen 2 in air at 300 °C for 30 min (specimen 3) leads to a decrease in the intensity of the line with $g = 4.27$ and a considerably more complicated EPR spectrum (Fig. 10*d*). When the sample is heated at 550 °C (specimen 4) the intensities of the two low-field lines ($g = 5.65$ and 6.25) continue to increase, the intensity of the line with $g = 4.27$ decreases considerably, and the lines with g factors equal to 9.1, 4.95, 3.7, and 3.4 disappear (Fig. 10*e*). No further changes in the spectrum result from increasing the time of oxidation of specimen 4 at 550 °C to 4 h or raising the temperature of oxidation (to 750 °C, 30 min). Measuring the EPR spectra of specimen 4 at −196 °C increases the intensities of all the lines in the spectrum (Fig. 10*d*) by a factor of only 2.5−3, i.e. there are no anomalous changes in intensity on cooling as were observed for the line with $g = 4.27$ for specimen 2 (see Fig. 10*b* and *c*). Admitting dry oxygen to specimen 4 at 20 °C causes a significant reversible broadening of the low-field lines in the spectrum (Fig. 10*f*). Adsorption of NH_3 or pyridine on specimen 4 at 20 °C leads to complete disappearance of the lines with g equal to 5.65 and 6.25 (Fig. 11*a* and *b*) and after adsorption the intensity of the line with $g = 4.27$ starts to show an anomalous dependence on temperature (Fig. 11*b* and *c*). On the adsorption of H_2O on specimen 4 the intensities of the lines with g equal to 5.65 and 6.25 decrease by a factor of approximately 3 and there is a similar increase in the intensity of the low-temperature line with $g = 4.27$.

Thus these results[42,43] show that solid state reactions do not give isolated Fe^{3+} ions in all cases. Nevertheless this method can be used to introduce Fe^{3+} into H-ZSM-5 but the part played by the anionic fragment is a controlling factor.

The data on the reaction of iron oxides with H-ZSM-5 are inconsistent: we found[42,43] that reactions with FeO and Fe_3O_4 do not proceed at an appreciable rate up to 800 °C but in other work[37] a reaction with Fe_2O_3 led to the introduction into the zeolite of Fe^{3+} ions giving an EPR signal with $g = 4.27$ and readily amenable to reduction. These peculiarities may be due to the different stabilities of the lattices of the iron oxides. When $FeCl_3$, whose lattice is considerably less stable (m.p. 309 °C), is used[42,43] the migration and redistribution of Fe^{3+} is observed at 250−300 °C. The appearance of the EPR signal with $g = 4.27$ (Fig. 10*b* and *c*) unambiguously indicates the occurrence of isolated Fe^{3+} ions in a strong crystal field of low symmetry. In the case of iron[42,43] the ion stabilised is not likely to be Fe^{3+} but the singly charged species $FeCl_2^+$ and FeO^+ which balance the single charge on the framework. The changes in the EPR spectrum on oxidative heating of specimen 2 (Fig. 10*b*−*e*) are precisely due to a gradual change from $FeCl_2^+$ type cationic species to FeO^+. The disappearance of the anomalous signal with $g = 4.27$ and the appearance in its place of lines with g equal to 6.25 and 5.65 can be interpreted in terms of a further reduction in the symmetry of the Fe^{3+} crystal field.

The reversible broadening of the lines in the EPR spectrum occurring when oxygen is admitted (see Fig. 10*f*), which is due to a dipole-dipole interaction with the O_2 molecules, indicates that the Fe^{3+} ions giving the EPR signals with $g = 6.25$ and 5.65 are accessible to molecules in the gas phase. The changes in the spectra due to Fe^{3+} occurring when strong ligands such as NH_3 and pyridine are adsorbed on specimen 4 (see Fig. 11) confirm the suggestions made above. The interaction of coordinately unsaturated Fe^{3+} ions with these ligands will lead to an increase in the crystal-field symmetry of the Fe^{3+} and a shift of the EPR lines towards lower g values, as has been observed.[42,43]

A comparison of the optical spectra shows[43] that the lines in the u.v. region (250 and 320 nm) are due to the presence in the specimen of Fe^{3+} ions with low coordination. Adsorption of NH_3 raises the coordination of the Fe^{3+} and leads to disappearance of these bands.

Reduction of specimen 4 by the adsorbed NH_3 does not take place up to 300 °C.[42,43] More drastic thermal treatment (550 °C, 30 min) is accompanied by the complete disappearance of Fe^{3+} and the appearance of iron metal species which give a ferromagnetic resonance (FR) spectrum. The broad FR line is characteristic of fairly large Fe^0 particles which may be located on the outer surface of the zeolite crystals.

Reoxidation of the reduced iron-containing H-ZSM-5 is accompanied by the complete disappearance of the FR line due to Fe^0, but it does not lead to full restoration of the EPR spectrum due to isolated Fe^{3+} ions.[43] The concentration of such ions is 3−5 times lower than the original even after reoxidation at 750 °C for an hour. There are two possible reasons for this irreversible decrease in their concentration due to the reduction-oxidation treatment: (1) the number of centres in which the Fe^{3+} ions are located is reduced, and (2) there is no reduction in the number of centres in the channels but migration of the oxide species occurring on the outer surface of the zeolite crystals takes place with great difficulty (as with mechanical mixtures of H-ZSM-5 with iron oxides). An experiment involving the reintroduction of $FeCl_3$ into this specimen[43] shows that the second suggestion is correct. The migration of mobile $FeCl_2^+$ species leads to refilling of all the vacant cationic sites in the zeolite and the concentration of isolated Fe^{3+} ions reaches the original value.

The changes in the EPR spectra due to the Fe^{3+} in H-ZSM-5 occurring on reaction with weak ligands such as H_2O and *p*-xylene[42,43] indicate that there is considerable coordination unsaturation of the Fe^{3+} in the specimens. Furthermore effects due to the weak interaction of coordinately unsaturated Fe^{3+} cations with xenon and n-hexane physically adsorbed in the channels in H-ZSM-5 have been observed.[20] The sorption of xenon or hexane at 20 °C causes appreciable broadening of the lines with $g^2 = 5.8$ and $g^3 = 6.3$ in the EPR spectrum due to Fe^{3+} ions.[20] In addition, the sorption of n-hexane results in an anomalous variation of intensity with temperature for the lines with $g^1 = 4.3$; the original evacuated specimen does not show this anomaly. This effect may indicate some reduction in the disortion of the environment for some of the Fe^{3+} cations, caused by displacement of the cation due to a dispersion interaction with the hexane molecules occupying the

channel. The broadening of the low-field lines at 20 °C[20] may also indicate some changes in the conditions of the spin-lattice interaction due to changes in the symmetry of the environment. Such an effect is significant only for Fe^3 ions located in a very strong crystal field with low symmetry.

The set of properties of the Fe^{3+} cations in H-ZSM-5 described above enable them to be distinguished quite clearly from the isolated Fe^{3+} ions introduced isomorphously into the H-ZSM-5 framework on synthesis. Although the isolated tetrahedral Fe^{3+} ions in the zeolite lattice give very similar low-field EPR spectra, they are quite insensitive to interactions with various molecules (even including strong ligands) and differ in being very difficult to reduce.

11. Introduction of Ni^{2+} ions into H-ZSM-5

Solid state reactions of H-ZSM-5 with NiO, $NiCl_2$, $NiSO_4$, and $Ni(CH_3COO)_2$ have been investigated.[38,39] When $NiCl_2$ is used heating in a stream of dry oxygen at 500 °C for 6 h leads to complete replacement of the strongly acidic OH groups in the zeolite (on the basis that an Ni^{2+} cation replaces 2 acidic protons). Subsequent reduction of the specimen with hydrogen at 450 °C or exchange with NH_4NO_3 leads to the complete reduction of the initial concentration of the acidic centres. When nickel sulphate is used the reaction with H-ZSM-5 is less effective and there is no reaction at all with nickel acetate and NiO. Thus for nickel ions also, the anionic fragments have an important role in the solid state reactions.

12. Reactions of H-ZSM-5 with zinc and gallium oxides

The modifying effect of ZnO and Ga_2O_3 on the catalytic properties of H-ZSM-5 has been mentioned in many studies but in the present review we shall concentrate on a group of papers[44–47] in which attempts have been made to observe the physicochemcial changes in [ZnO + H-ZSM-5] and [Ga_2O_3 + H-ZSM-5] mixtures during heating by employing a number of methods (RFES, TPR, thermal desorption of NH_3, i.r. spectroscopy). Thermal treatment leads to migration of Zn^{2+} ions from the outer surface into the zeolite channels and to a decrease in the concentration of Brønsted acid centres.[44] The Zn^{2+} ions in H-ZSM-5 are more easily reduced than is the ZnO phase.[44] Migration into the pores of H-ZSM-5 has also been observed for gallium oxide,[45,47] the gas phase having a decisive role. Using oxidative heating the Ga_2O_3 phase is located on the outer surface of the zeolite crystals and the features of the introduction affect only its degree of dispersion.[47] However treatment in a hydrogen or hydrocarbon atmosphere results in the Ga-phase entering the zeolite channels, the gallium introduced having an oxidation state appreciably less than three.[45,46] Migration of Ga_2O species and their stabilisation in the vicinity of Brønsted acid centres in the zeolite channels has been proposed.[47]

13. Aspects of the introduction of transition metal cations into H-ZSM-5 (and of their properties) resulting from isomorphous replacement of framework Al^{3+} ions by Ga^{3+} or Fe^{3+}

It is known that the properties of the acidic centres in high-silica zeolites can be changed by isomorphous replacement of the framework Si^{4+} ions by other triply charged ions instead of Al^{3+}. Conclusive evidence for the possible synthesis of gallosilicates and ferrosilicates with the ZSM-5 structure has been published and the lower strength of the acidic centres in such structures (H-[Al]ZSM-5 > H-[Ga]ZSM-5 > H-[Fe]ZSM-5) and the changes in the catalytic properties in acid-base reactions resulting from this have been demonstrated. The stabilisation of cations in the same zeolite matrix, but at weaker acidic centres, is naturally of considerable interest. In addition changing from Al^{3+} ions (nuclear spin $I = 5/2$) to Ga^{3+} ($I = 3/2$) will lead to changes in the EHFS of the spectra of Cr^V and V^{IV} due to interaction of the unpaired electron on the cationic species with the nucleus of the framework ion creating the cationic vacancy.

Solid state reactions of H-[Ga]ZSM-5 with CuO, $FeCl_3$, CrO_3, V_2O_5, and $VO(NO_3)_2$ at 300–800 °C have been studied and the results obtained compared with data for the zeolite H-ZSM-5.[27,28] The migration of Cu^{2+} ions in H-[Ga]ZSM-5 is identical to that observed for H-ZSM-5. The results obtained[27,28] indicate conclusively that the concentration and coordination of isolated Cu^{2+} cations in H-ZSM-5 and H-[Ga]ZSM-5 are very similar. Specimens heated at 550 °C contain two distinct types of Cu^{2+} coordination: square planar and square pyradmidal. These two types are retained in specimens heated at 800 °C (the square pyramids showing considerable distortion towards square planar). A comparison of H-ZSM-5 and H-[Ga]ZSM-5 shows only very small differences in the degree of distortion of the environment.

The changes in the EPR spectra due to the interaction of Cu^{2+} with various adsorbates show that the Cu^{2+} cations in H-ZSM-5 and H-[Ga]ZSM-5 are equally accessible to molecules from the gas phase. For example, adsorption of O_2 causes broadening of the lines in the spectrum due to dipole-dipole interactions, and adsorption of ammonia changes the parameters of the spectrum, indicating some reduction in symmetry. In the case of the physical non-localised adsorption of xenon some geometrical displacement of the Cu^{2+} cations due to dispersion forces is observed, as in CuH-ZSM-5.

Thus the replacement of Al^{3+} ions by Ga^{3+} in a zeolite framework with the ZSM-5 structure causes no appreciable changes in the concentration, coordination, and reactivity of the Cu^{2+} ions introduced into the cationic sites in the zeolite by solid state reactions.[27,28]

The same conclusion was reached for iron:[27,28] the processes of solid state introduction of Fe^{3+} into the cationic sites in H-[Ga]ZSM-5 and H-ZSM-5 are identical. The properties of the cations introduced into the two zeolites are almost the same. For the Fe^{3+} ions in H-[Ga]ZSM-5 location in crystal fields with low symmetry is also found. Adsorption of NH_3 increases the symmetry of the Fe^{III} environment (the lines with $g = 5.7$ and 6.3 disappear) and changes the spin-lattice relaxation conditions (the anomalous temperature dependence for the line with $g = 4.3$ appears).

The processes of introducing chromium into H-ZSM-5 and its gallosilicate analogue are similar and interesting features are observed in the EHFS of the EPR spectra due to Cr^{5+}.[27,28] Heating H-[Ga]ZSM-5 with CrO_3 at 420 °C for an hour gives an anisotropic EPR signal from isolated Cr^{5+} ions (two quartets with the parameters $g_\perp = 1.99$, $A_\perp = 28$ Oe, $g_{||} = 1.94$, and $A_{||} = 26.5$ Oe). Heating at 700 °C gives a signal with $g_0 = 1.97$ and $A \sim 24$ Oe. Chemisorption of NH_3 causes an immediate change in the EPR signal with disappearance of the EHFS and the appearance of anisotropic lines; this indicates a considerable change in the coordination of the Cr^{5+} due to attachment of an additional strong ligand. This EPR spectrum is identical to the signal observed in the reaction of Cr^V/H-ZSM-5 with NH_3 (see Fig. 6).

Thus the Cr^{5+} cations have the same coordination in the presence of NH_3 in the channels of H-ZSM-5 and its gallosilicate analogue (two distinct Cr^V positions with different distortions of the coordination symmetry). One of the two types of Cr^{5+} ion is more easily reduced when the specimens with adsorbed NH_3 are heated. The changes in the EHFS of the Cr^V EPR spectra resulting from the change from Al^{3+} to Ga^{3+} in the ZSM-5 framework are shown in

Fig. 7. The signals in the Q-band are more markedly anisotropic (see Fig. 7), making their interpretation easier. The following conclusion is drawn by reference to theory: the EHFS is due to interaction of a CrO_2^+ cation with one framework Al^{3+} ion ($I = 5/2$) and changing to Ga^{3+} (which has $I = 3/2$) reduces the number of EHFS components from 6 to 4. However there is a marked increase in the splitting constant (from 6 to 24 Oe), i.e. the unpaired electron of the CrO_2^+ has a much stronger interaction with a Ga^{3+} nucleus than with an Al^{3+} nucleus. This change cannot be attributed to a difference in the nuclear magnetic moments: whereas for ^{27}Al $\mu_I/\mu_K = +3.64$, for ^{69}Ga $\mu_I/\mu_K = +2.00$ and for ^{71}Ga $\mu_I/\mu_K = +2.55$. The change in the magnitude of the splitting most likely indicates a small change in the geometry of the cation site since the ionic radius of Ga^{3+} (0.62 Å) is appreciably larger than that of Al^{3+} (0.50 Å).

Comparison of the zeolites H-ZSM-5 and H-[Ga]ZSM-5 containing Cr^V or Fe^{III} shows a marked difference in their thermal stabilities: the Ga^{3+} ion is less strongly bound in the lattice than the Al^{3+} ion. In H-ZSM-5 there is no noticeable disruption of the cationic sites at 750–800 °C. In H-[Ga]ZSM-5 this temperature is sufficient for fairly rapid irreversible disappearance of the sites of the isolated Cr^{5+} or Fe^{3+} cations although X-ray diffraction data indicate that the crystallinity of the zeolite is preserved.[27,28] The disappearance of the sites in which cations are trapped is evidently due to Ga^{3+} escaping from the framework. The isolated cations migrate to the outer surface and are aggregated to form oxides. For Fe^{3+} this is confirmed by EPR data.

In addition to the acidic centres in H-[Ga]ZSM-5 being thermally less stable traps for cationic species than the centres in H-ZSM-5, in the gallosilicate the strength of these centres is insufficient for stabilisation of isolated vanadyl cations. In contrast to H-ZSM-5, the reaction of H-[Ga]ZSM-5 with V_2O_5 at 400–800 °C gives hardly any isolated V^{4+} ions.[27,28] Nor are such ions produced by heating H-[Ga]ZSm-5 under vacuum with compounds such as $VO(NO_3)_2$.

In the ferrisilicates H-[Fe]ZSM-5, which have even weaker and thermally less stable acidic centres, it is not possible to stabilise even such transition metal cations as Cu^{2+} and Cr^{5+}. A comparison of the properties of H-ZSM-5 and H-[Fe]ZSm-5 using a highly sensitive EPR method[38,39] showed that isolated Cu^{2+} ions are not stabilised in a ferrisilicate matrix with the ZSM-5 structure.

14. The concurrent introduction of highly charged ions into H-ZSM-5

EPR has been used to investigate the possible introduction of the ions [Cu^{2+} + CrO_2^+], and also [Cu^{2+} + VO^{2+}], into H-ZSM-5 in the solid state and to study the effect of the thermal treatment conditions on these processes.[48,49] In a number of instances it is possible to replace one highly charged ion by another, and also to introduce two different cations simultaneously. It is significant that the different ions are found to have the same location sites and the processes of their location are competitive and depend on the conditions under which the solid state reaction is carried out.

For example, the reaction of H-ZSM-5 with $CuCrO_4$ at 550–800 °C gives a superposition of two EPR spectra due to Cu^{2+} and Cr^{5+} ions. The well resolved HFS of the spectra indicates that the Cu^{2+} and Cr^{5+} ions are isolated and their coordination is the same as when they are introduced individually. It is suggested[48,49] that the copper and chromium ions are distributed statistically in the cationic sites in H-ZSM-5. Estimation of the intensities of the EPR signals indicates that the concentrations of these isolated ions in the specimen are comparable ($Cu^{II}/Cr^V \simeq 2-3$). It is interesting to compare this specimen with the double mixture [(H-ZSM + 1% CrO_3) + 5% CuO] in which the reactions with the oxides were carried out consecutively.[48,49]

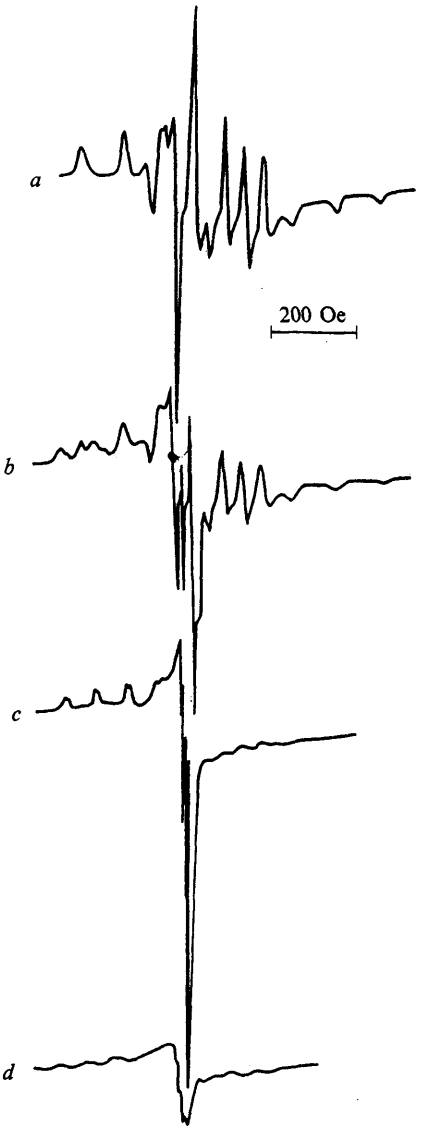


Figure 12. EPR spectra of a [(H-ZSM-5 + V_2O_5) + CuO] mixture under vacuum:[49] *a*, (H-ZSM-5 + CuO) mixture heated in air at 800 °C for 1 h; *b*, the triple mixture heated in air at 500 °C for 1 h; *c*, the same mixture heated in air at 800 °C for 1 h; *d*, after reduction of the specimen in H_2 at 400 °C for 2 h.

Heating H-ZSM-5 with CrO_3 at 800 °C for an hour leads to replacement of the accessible cationic sites in the zeolite by isolated Cr^{5+} ions, giving an intense EPR signal (see Fig. 5*b*). In the subsequent reaction with CuO there are two simultaneous processes:

the intensity of the signal due to Cr^{5+} decreases and that of the signal due to Cu^{2+} increases. It is clear from the changes in the spectra that there is replacement of one ion by the other in the cationic sites, giving a Cu^{II}/Cr^{V} ratio of $\sim 20-30$. It is likely that the equilibrium obtained on heating to a high temperature is dynamic and is dependent on the ratio of the concentrations of the two ions on the outer surface, which in the present case is equal to 5. Reduction of the specimens containing Cu^{2+} and Cr^{5+} ions with hydrogen leads to a rapid disappearance of their EPR signals.

The studies of the reaction of H-ZSM-5 with V_2O_5 and CuO in different media[48,49] are of great interest because Cu^{2+} is easily reduced in hydrogen at 400 °C but VO^{2+} is stable in both oxidising and reducing media up to 800 °C. The maximum concentration of isolated V^{4+} ions in the cationic sites is obtained by heating H-ZSM-5 with V_2O_5 at 800 °C, as is shown by the EPR signal in Fig. 12*a*. A subsequent reaction with CuO in air leads to a gradual decrease in the intensity of the EPR signal due to V^{4+} and the simultaneous appearance of a signal due to Cu^{2+} which increases in intensity (Fig. 12*b* and *c*). The intensity ratio of the signals shows that more than 90% of the V^{IV} in the cationic sites in H-ZSM-5 is replaced by Cu^{II}. Since both oxides were introduced in excess and are present in similar concentrations on the outer surface it is concluded[48,49] that VO^{2+} is appreciably less strongly bound in the cationic sites in H-ZSM-5 than Cu^{2+}. Presumably, during the reaction with CuO the V^{4+} ions are removed to the outer surface of the crystallites and undergo aggregation, with possible conversion to V^{5+}.

An experiment involving the subsequent reduction of the specimen in hydrogen at 400 °C enabled the location of the ions to be determined more accurately. This temperature is high enough for fairly rapid reduction of Cu^{2+} to Cu^0 yielding the metal on the outer surface but it is too low to ensure diffusion of the V^{4+} ions which takes place at an appreciable rate above 500 °C. If V^{5+} ions were in the immediate vicinity of the cationic sites within the zeolite, we would expect the removal of Cu^{2+} from their sites in the reducing atmosphere to be accompanied by conversion of V^{5+} to V^{4+} and the appearance of the corresponding EPR signal (Fig. 12*a*). However no signal due to vanadyl ions is observed; there is merely a considerable reduction in the intensity of the signal due to Cu^{2+} (Fig. 12*d*). It is only when the temperature is increased to 800 °C, and rapid diffusion of V^{4+} ions occurs again, that they again migrate from the outer surface to the cationic sites and their concentration reaches the same maximum limit as in the initial (H-ZSM-5 + V_2O_5)/800 °C specimen. Repeating the oxidising treatment, in which the formation and migration of Cu^{2+} ions occur, again leads to replacement of almost all the isolated VO^{2+} ions by Cu^{2+}.

The replacement of one transition metal cation by another in H-ZSM-5 was also observed very clearly in the reaction of Fe^{3+}-H-ZSM-5 with CuO.[42,43] After a specimen of FeH-ZSM-5, which contains isolated Fe^{3+} cations, was heated with CuO at 550–750 °C the intensities of the signals due to Fe^{3+} with different coordinations (g = 6.25, 5.65, and 4.27) decreased almost by a factor of 1000 and signals due to Cu^{2+} appeared in their place, i.e. more than 99% of the isolated Fe^{3+} cations were replaced by Cu^{2+}. It is emphasised[42,43] that both the concentration and the coordination of the isolated Cu^{2+} ions are the same as in a CuH-ZSM-5 specimen, i.e the Cu^{2+} ions which replace the Fe^3 are introduced into the same cationic sites as are found in H-ZSM-5.

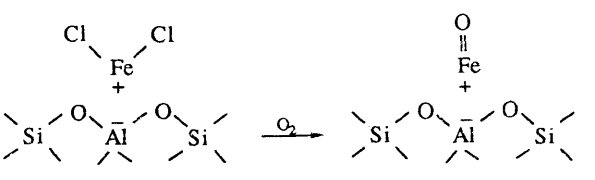
The results obtained demonstrate the complex nature of the processes of migration and redistribution of transition metal ions in HS-zeolites occurring when they are heated to high temperatures. This complexity is due to the differences in the strength of binding of the ions in the cationic site.

IV. The role of the gas phase and the anionic part of the salt in solid state exchange in HS-zeolites

The overwhelming majority of solid state reactions between HS-zeolites and transition metal compounds have been carried out in air in the presence of water vapour and the possible hydrating effect of H_2O molecules cannot be discounted. However the cation migration processes also take place effectively when compounds that are insoluble in water, such as CuO, Cr_2O_3, and V_2O_5, are used. In many instances (V_2O_5, CuO, $CuCl_2$, $FeCl_3$, $MoCl_5$) the reactions take place under high vacuum ($\sim 10^{-5}$ torr), i.e. in the absence of H_2O. Hence the presence of water is not a necessary condition for solid-state ion exchange in HS-zeolites. A similar conclusion was reached regarding solid state processes involving the introduction of alkali metal cations.[7]

A comparison of solid state exchange under vacuum and in air indicates that in the majority of cases (CuO and copper salts, V_2O_5, CrO_3) oxygen has almost no effect on the migration of ions in the zeolite. However in the case of Cr_2O_3 the reaction will not take place under vacuum up to 820 °C but can be carried out in air.[23,24] This peculiarity is probably related to the very high stability of the lattice of the initial oxide (m.p. 2340 °C). It is likely that more labile fragments capable of migrating into the zeolite at 550–800 °C are only formed on the surface of the Cr_2O_3 in the presence of oxygen.

It is clear that the temperature of the reaction can be reduced and the potentialities of the solid-state exchange method extended by using compounds (salts) of a given element which have considerably different labilities. However it must be stressed that the anionic part of the salt, which facilitates the migration, also acts as a ligand for the highly charged cation in the zeolite which is outside the framework, i.e. it changes the symmetry of the crystal field of the cationic centre. In some instances (Cl^-) the ligand can be replaced by heating in air:



but in many cases (PO_4^{3-}, SO_4^{2-}, F^-) the ligand is bonded to the centre very strongly and cannot be removed even by heating the specimens in air at 800 °C.

Clearly, when using transition metal compounds in which the anionic ligand can be replaced by oxygen, the reaction must be carried out under vacuum or in an inert gas. An example of this is the reaction of H-ZSM-5 with $FeCl_3$.[42,43] The reaction with this low-melting salt under vacuum leads, even at 250–300 °C, to stabilisation in the zeolite of isolated $FeCl_2^+$ cationic species. If the specimen is subsequently heated in air the symmetry of the Fe^{3+} environment is reduced, evidently due to conversion to an FeO^+ species.

The effect of a reducing medium (H_2, hydrocarbons) on the state of the cations in HS-zeolites (including those introduced by a solid state reaction) has been studied in many papers. For ions which can be reduced to the metal fairly easily (Cu, Ni, Fe) replacement of the cations within the channels by H^+, migration of the metal atoms, and formation of fairly large metal particles on the outer surface of the zeolite are usually observed. For such metals there is clearly no point in carrying out the solid state exchange in a reducing medium. Reactions with other transition metals in a hydrogen or hydrocarbon atmosphere have hardly been studied but exceptions to this are research involving V^{4+} ions[24,25,32] and gallium ions.[45–47] The solid-state migration of gallium from Ga_2O_3 into the zeolite H-ZSM-5[45–47] takes place only in a reducing medium and the stabilised cations have a charge less than 3+. Vanadyl cations are stable in a reducing medium and they will migrate into the cationic sites in the H-ZSM-5 in a hydrogen atmosphere. For the binary system (Cu + V)/H-ZSM-5, in an oxidising medium the Cu^{2+} ions are bonded to the cationic vacancies much more strongly than the VO^{2+} ions but in hydrogen the Cu^{2+} ions are reduced, Cu^0 drifts to the outer surface, and VO^{2+} cations are stabilised in the sites that have been freed.[48,49]

Thus the possibilities for solid state exchange in HS-zeolites can be extended by varying the transition metal salt and the atmosphere in which the reaction is carried out. However the results obtained indicate a possible substantial redistribution of the modifying components when the atmosphere is altered, e.g. under the conditions of a catalytic reaction.

V. Transition metal cations in an H-ZSM-5 matrix as isolated catalytic centres

In this section a full analysis of all the catalytic data for transition metal/HS-zeolite systems has not been undertaken. Primarily, examples of the oxidation-reduction catalytic properties of HS-zeolites modified by solid state reactions are given and some results obtained for ion-exchange specimens are quoted for comparison.

An important feature of HS-zeolites with the ZSM-5 structure is the stabilisation of isolated cationic species in coordinately unsaturated ligand environments (in fields with low symmetry) and in consequence the high reactivity of such cations with various classes of substances. For example, the H-ZSM-5 matrix provides stabilisation for Cu^{2+} with square planar coordination,[11,12] Fe^{3+} ions in crystal fields with very low symmetries,[42,43] and chromium and vanadium ions in the normally unstable oxidation states Cr^V and V^{IV}.[23–25] Such ions interact not only with the molecules of strong ligands (NH_3, pyridine, H_2O) but also with physically adsorbed molecules of n-hexane and *p*-xylene, and even xenon atoms, which occupy the channels in the zeolite.[20,21,32] In other types of zeolite the cationic centres do not have such a high coordination unsaturation. Furthermore, an important characteristic of the ZSM-5 matrix is that the cationic centres are well separated from each other, i.e. isolated active centres are formed (but only 2–3 distinct types). The coordination of the cations can be altered to a considerable extent by introducing additional anionic ligands.

Thus the cationic centres stabilised by a ZSM-5 matrix provide a unique method for investigating the relationship between the catalytic and physical properties of isolated transition metal ions. In other words, these structures can be regarded as "inorganic analogues of enzymes", in which the isolated active centre is situated in the topologically defined internal space of the zeolite channel. For most transition metals these are oxidation-reduction centres because the ions can easily change their oxidation state. Of course, for ZSM-5 type zeolites, in which the [Si]/[Al] ratio is not less than 16–20, the concentration of isolated centres in 1 g cannot be very large (not more than 1–1.5 mass% of the transition metal compound can be dispersed into the channels and stabilised in the cationic sites created by the framework Al^{3+} ions). However, the abnormally high specific reactivity of the centres suggests that the system is not only of importance theoretically but also has possible practical applications.

Among the oxidation-reduction reactions on modified pentasils the decomposition of NO_x and the burning of hydrocarbons have recently attracted attention.

1. The decomposition of NO and its reduction by hydrocarbons on Cu-H-ZSM-5

The catalytic decomposition of NO on various types of cation-containing zeolites has been studied in a number of papers.[50–58] Cu-containing zeolites display considerable activity and the specific activity of Cu-H-ZSM-5 is unusually high.[50,51] The dependence of the specific activity on the copper content is an S-shaped function. This may indicate the presence of two types of Cu^{2+} ion with considerably different specific activities.[53] The activity of the H-form of ZSM-5 in the stoichiometric decomposition of NO is low.

The situation regarding the reduction of NO by hydrocarbons is more complex: this reaction also takes place on the H-forms of zeolites.[56] However the introduction of copper into H-ZSM-5 has a significant positive effect in lowering the conversion temperature to ~250 °C.[55,57]

The reaction mechanisms and the structure of the active complex were not investigated in detail in the papers quoted above but it was assumed that Cu^+ ions are involved in the catalytic decomposition process. However the effect of SO_x on the decomposition of NO on Cu-H-ZSM-5 has been studied.[58,59] Use of the EXAFS and XANES methods showed that the Cu^{2+} cations in H-ZSM-5 have more ionic character than in CuO.[59] Treatment with SO_x, which causes deactivation of the catalyst, is accompanied by changes in the local structure of the Cu^{2+} and formation of $CuSO_4$-type species.

All the above results were obtained using ion-exchange specimens of Cu-H-ZSM-5 but our recent results indicate that a system with the same catalytic properties, which are of interest for environmental protection, can also be obtained using solid state reactions. This is not surprising because detailed studies of Cu^{2+}/H-ZSM-5 show that there are no differences between the properties of the cations introduced by these two methods.[11–18]

2. Complete oxidation of alkanes

We have studied the burning of low concentrations of CH_4 at 500 °C on H-ZSM-5 containing a number of transition metal ions.[60–64]

In the oxidation of CH_4 and C_2H_6 by oxygen up to 550 °C pure H-ZSM-5 has a negligibly small catalytic activity but the stabilisation of cations in this inert matrix leads to the appearance of activity. This system is very suitable for comparing the specific activities of different ions and also of the same ions with different coordinations.

Coated chromium-containing systems (chromosilicates, chromo-aluminosilicates) are known to be active catalysts for complete oxidation. A study of aspects of the oxidising properties of the well characterised Cr/H-ZSM-5 system is therefore clearly of interest.

Results on the oxidation of CH_4 at 500 °C [60–62] are shown in Fig. 13. The specific activity of the chromium in the zeolite system is very high, much higher than that of chromium on amorphous substrates. Note that if, instead of relating the activity to the whole of the chromium, it is related to the number of isolated Cr^{5+} cations (broken line in Fig. 13) the specific activity is almost constant over a wide range of total chromium concentration in the zeolite (0.5–3.5%). It is therefore likely that the excess chromium which is present on the outer surface in the form of α-Cr_2O_3 crystals, makes no contribution to the activity, which is determined by the number of isolated cations (which are able to change their oxidation state easily). The extremely high activity of these isolated ions is due to their stabilisation in a coordinately unsaturated enviroment, as is found in the H-ZSM-5 zeolite.

The same reaction has been studied on Cu/H-ZSM-5 specimens with a copper content between 0.25 and 2.8 mass% which were obtained by solid state reactions.[60–64] The dependence of the activity of specimens heated at 550 °C on the copper concentration is shown in Fig. 14. The activity increases for 5–10 min and then reaches a stationary value which shows no decrease during treatment at 500 °C for 10 h. Heating in air at 550 °C for 15 h also gives no reduction in catalytic activity, but heating Cu-H-ZSM-5 at 800 °C for 2 h reduces the activity by a factor of 1000.

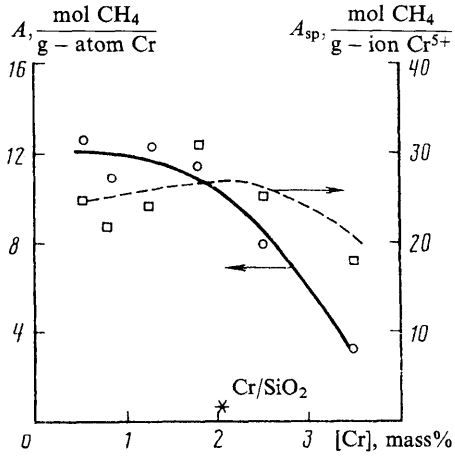


Figure 13. Specific activity of Cr/H-ZSM-5 in the complete oxidation of alkanes.[60]

The relationship shown in Fig. 14 indicates non-uniformity of the active centres. An analysis of catalytic data[63,64] and aspects of the copper distribution which have been thoroughly studied indicate that the high catalytic activity is due mainly to the formation of very coordinately unsaturated (square planar) isolated Cu^{II} ions. In the specimen containing 0.25% copper, which has a low activity, the number of such ions is very small and most of the ions have square pyramidal coordination. Increasing the total copper concentration to 1.0% leads to a significant increase in the concentration of square-planar Cu^{II} ions and there is a good correlation between this and the increase in activity. When the concentration of isolated Cu^{II} ions reaches a maximum (1.5–2.0% Cu) the activity of the catalyst also reaches a limit (see Fig. 14), which remains unchanged when the copper concentration is increased to 2.8 mass%. Therefore an excess of CuO on the outer surface of the zeolite crystals makes no contribution to the catalytic activity of Cu-H-ZSM-5 in the complete oxidation of CH_4.

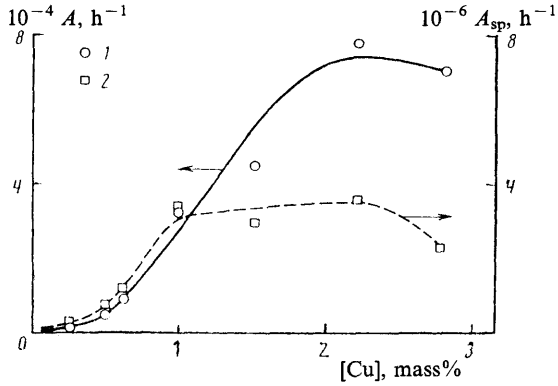


Figure 14. Activity of Cu/H-ZSM-5 specimens in the complete oxidation of CH_4 at 500 °C:[61] *1*, total activity; *2*, activity per 1 g copper.

The deactivation of the catalysts after heating at 800 °C [63,64] may also indicate the role of the coordinately unsaturated, isolated active centre: the number of accessible isolated Cu^{2+} cations is not appreciably reduced by heating at 800 °C but the ligand environment of the Cu^{II} changes considerably. Heating at 800 °C leads to the complete disappearance of the very unsaturated square-planar coordination of Cu^{II} and instead the specimens contain two distinct types of cation with distorted square-pyramidal coordination. Cu^{2+} ions in an HM zeolite or on the surface of SiO_2 (where there is no square-planar copper) have a specific activity that is lower by a factor of 100 than that of Cu^{2+} in H-ZSM-5 which has been heated at 500–550 °C. Such sharp differences in activity also demonstrate clearly the effect of the coordination of the isolated Cu^{2+} ion on its catalytic properties.[63,64]

Systems with a number of other cations (V, Fe, Ni, Co, Mn) have been investigated for comparison with Cu/H-ZSM-5 and Cr/H-ZSM-5.[60-62] The V/H-ZSM-5 system, in which the isolated V^{4+} cations are coordinately unsaturated but incapable of changing their oxidation state, shows a complete absence of catalytic activity in the oxidation of methane. In Fe/H-ZSM-5 specmens micro-crystals of iron oxide on the outer surface of the zeolite make an appreciable contribution to catalysis but the overall activity is not large. However systems containing nickel, cobalt, and manganese ions show significant catalytic activity in the oxidation of methane.

The influence of the local topography of the isolated active centres on the oxidation of C_2H_6 on Cu/H-ZSM-5 has been analysed.[65] The studies were performed on the same catalysts, prepared by solid state reactions, as were used in the work discussed above[63,64] but different conditions were used (low degrees of conversion, temperatures of 270–500 °C). It was shown that the

specific activity of an isolated Cu^{2+} ion in the complete oxidation of C_2H_6 can be varied by a factor of 1000 depending on the coordination of the cation. Cu^{2+} ions with low coordination (square planar) display the highest activity and using a zeolite containing such centres the reaction will proceed at an appreciable rate at 270–300 °C.[65]

VI. Conclusion

HS-zeolites modified by various cations can be used to analyse catalytic processes at the atomic-molecular level because it is possible to produce in them distinct sets of isolated active centres with different topologies. However the standard ion-exchange method cannot be used for the introduction into these matrices of the majority of transition metal ions which are of most interest from a catalytic point of view. The potentialities of this field can be extended by using topochemical methods of introducing cations by means of solid state reactions. The following conclusions can be drawn from a generalisation of the results currently available.

Solid state reactions can be used as a new, environmentally clean method for modifying HS-zeolites with one or more multivalent transition metal cations (Cu^{2+}, Fe^{3+}, V^{4+}, Cr^{5+}, Mo^{5+}, Ni^{2+}, Co^{2+}, Ga^{3+}, Mn^{2+}, Zn^{2+}), the majority of which cannot be introduced into these matrices by other methods.

The ions can be introduced by a solid state reaction because of the presence of free acidic centres in the HS-zeolites. These centres can be regarded as energy traps for migrating cationic species. The potentialities of the method can be extended considerably by using transition metal compounds with different anionic fragments and carrying out the reactions in different gaseous media.

Solid state reactions can be used to replace one highly charged cation by another and also to introduce different cations into the HS-zeolite simultaneously. The different cations occupy the same sites and the processes of their location are competitive and dependent on the conditions used for the solid state reaction.

A distinctive feature of the pentasil matrices is that the isolated cations are stabilised in environments with high coordination unsaturation (low-symmetry crystal fields). A result of this is the very high reactivity of the cations towards various adsorbates.

Pentasil-based systems with distinct isolated centres form unique subjects for physicohemical studies and a proper analysis of the relationship between the local structure and the properties of the isolated transition metal cation. The isolated cationic centres formed in pentasils display an abnormally high and stable catalytic activity in the complete oxidation of alkanes and the decomposition of nitrogen oxides. Therefore, in spite of the low density of active centres produced in the solid state reactions, transition metal cation/pentasil catalysts may be of interest for both theoretical studies and environmental protection.

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Received 31st March 1992