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The Isomorphism and Catalytic Properties of Silicates with the Zeolite Structure

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The properties of a new group of catalysts based on crystalline silicates with the zeolite structure†, containing the multicharged Be^{2+}, B^{3+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Mo^{6+}, Se^{6+}, etc. cations occluded in the hydrothermal crystallisation process, are described. The state of the multicharged cations in the silicates has been characterised by physical methods (NMR, EPR, and X-ray diffraction). The selectivity and catalytic activity of such silicates in the formation and other reactions of hydrocarbons and hydrocarbon mixtures are examined.
The bibliography includes 174 references.

CONTENTS

I.	Introduction	231
II.	General rules governing the limitation of the degree of isomorphous substitution	232
III.	Hydrothermal synthesis	232
IV.	The state of multicharged cations in silicates with the zeolite structure	238
V.	Catalytic properties	244
VI.	Conclusion	247

I. INTRODUCTION

According to Pauling's theory[1] and Tanabe's later revised versions,[2] the acid–base properties of binary oxides are determined by the incomplete compensation of the charges of the corresponding ions by the oxygen atoms in the environment. Any isomorphous heterocharge substitution of Si^{4+} cations in the silicon–oxygen skeleton of silicates by other cations of the type $Si^{4+} \rightleftharpoons M^{n+}$, where $n \neq 4$, should then impart to silicates a capacity for acid–base catalytic activity. Crystalline silicon oxides, including silicalite,[3] with an extensive system of pores are indeed adsorbents, but they do not possess catalytic properties. The catalytic properties of aluminosilicates, including zeolites, are determined by the fixation of aluminium cations in isomorphous positions in the silicon–oxygen skeleton as a result of the exchange $SiO_4^{4-} \rightleftharpoons AlO_4^{5-}$.

The idea that the above isomorphous heterocharge substitution takes place in zeolites, constituting a precondition for the formation of catalytically active centres, has been confirmed by a large number of data. For example, a dependence of the unit cell constant on the aluminium content in the zeolite crystals has been established.[4,5] It has been shown by ^{27}Al NMR that the vast majority of aluminium atoms in zeolites are in a tetrahedral oxygen environment.[6,7] It has been observed by ^{29}Si NMR [8–10] that the second coordination sphere of the Si^{4+} ion in the silicon–oxygen skeleton may contain between 1 and 4 aluminium atoms in groups of the type $[Si(OAl)_n]^{n-}$. A statistical model has been developed for the distribution of such groups with respect to the quantity n as a function of the overall aluminium content in the zeolite.[11] It was later suggested[7,12–15] that the change in the conditions of hydrothermal synthesis and in the subsequent treatment of zeolites can induce a deviation of this distribution from the statistical average in one direction or another.

It has been established that, as cations are eliminated[15,16] and also as a result of treatment of the specimens with acids,[17,18] $SiCl_4$,[19,20] and water vapour,[21,22] a signal with $\delta = -3$–0 p.p.m., assigned to Al atoms in an octahedral oxygen environment, i.e. outside the skeleton, appears in the ^{27}Al NMR spectra of zeolites together with a signal having the chemical shift $\delta = 55$–61 p.p.m. (which corresponds to Al^{3+} in a tetrahedral coordination with oxygen ions, i.e. in the silicon–oxygen skeleton. The solid-phase reactions

$$\underset{(I)}{[Si(OAl)_n]^{n-}} \rightarrow \underset{(II)}{Si[(OAl)_{n-1}]^{(n-1)-}} + \frac{(n-1)}{3} Al^{3+},$$

leading to the appearance of the centres (II), probably occur during the cation elimination process ["decationation"] and in the course of thermochemical treatment. A group of type (II) can be regarded as a conjugate acid and base, capable of two-centre interaction with the reactant molecule. According to the literature,[12,15] the selectivity and stability of the catalytic action of zeolites depend both on the distribution of the groups $[Si(OAl)_n]$ with respect to n and on the concentration of groups of type (II).

Zeolites have found applications as catalysts in petroleum processing and in petrochemical processes. Different questions concerning their synthesis, investigation, and application have been considered in many reviews and monographs.[23–25] A series of studies devoted to new generation zeolites, of the ZSM type or pentasils, have been published during the last decade.[26,27] However, any zeolites constitute merely a special case of the manifestation of isomorphism, because they are all silicates with the same type of isomorphous substitution: $SiO_4^{4-} \rightleftharpoons AlO_4^{5-}$ or $Si^{4+} \rightleftharpoons Al^{3+}Na^+$.

A series of studies have been made in which silicates with the zeolite structure have been synthesised without adding sources of aluminium but in the presence of multicharged cations or Group I–VIII elements (M^{n+}), which created preconditions for the isomorphous substitutions $Si^{4+} \rightleftharpoons M^{n+}$ in the silicate skeleton formed.[23,28–30] This method of synthesis of silicates differs significantly from the methods of preparation of zeolites, in which multicharged cations are introduced by ion exchange. A zeolite behaves in ion exchange as a polyacid salt in which the chemical composition of the macroanion does not change and only the chemical nature of the cation, compensating for the negative charge

†We shall henceforth refer to crystalline silicates with the zeolite structure, obtained under hydrothermal conditions from mixtures to which aluminium compounds had not been added before hydrothermal synthesis, as elementosilicates or ex-silicates.

of the skeleton, is altered:

$$[Si(OAl)_n]^{n-}M_1^{n+} \xrightarrow[-M_1A^-]{+M_2A^-} [Si(OAl)_n]^{n-}M_2^{n+}.$$

The state of the cations fixed in zeolites in this way has been characterised in a large number of studies[31-33] (see also the relevant reviews[25,34]).

The introduction of multicharged cations M^{n+} into the initial silica gel before its hydrothermal crystallisation leads to the possibility of altering the chemical composition of the anionic part of the silicon–oxygen skeleton:

$$[Si(OM)_n]^{n-} \text{ and } [Si(OM)_{n-1}]^{(n-1)-} \frac{n-1}{n} M^{n+}.$$

The uncompensated charge of the anionic component of the silicate and hence also the strength of the centres with acid–base properties should depend on the nature of the cation M^{n+}.

II. GENERAL RULES GOVERNING THE LIMITATION OF THE DEGREE OF ISOMORPHOUS SUBSTITUTION

The ideas about isomorphism are widely used in geochemistry and crystal chemistry. According to definitions,[35,36] isomorphism is a result of the capture of impurities in the course of the crystallisation of the system with substitution of some of the atoms by the impurity atom without change in the type of crystal structure of the original state. Approximate relations between the thermodynamic parameters of the system and the degree of isomorphous substitution have been examined in a review.[37] The principal postulates which must be taken into account in estimating the probability of isomorphous substitution reduce to the following:

1. By virtue of the existence of a definite relation between the enthalpy of formation of the system with isomorphous substitution and the ratio of the radii (R) of the interacting ions A and B, the limits of the mutual substitution are smaller the greater the difference between the values of R. It has been suggested[38] that the isomorphous exchange A ⇌ B is possible provided that $\Delta R/R \leq 0.15$.

2. The ions A with larger R substitute the ions B with smaller R more readily than in the case where substitution is accompanied by a decrease in the coordination number of the ion A and, conversely, the substitution is more difficult if it is accompanied by an increase in the coordination number of the ion A.[38]

3. The limits of isomorphous substitution depend on the ratio of the electronegativities χ and ionisation potentials of the interacting ions.

4. In the isomorphous substitution A ⇌ B there is a possibility of a shift of the central atoms with retention of the symmetry of the environment in the main system. The minimum in the free energy of the system is attained when the atoms A and B shift by (0.025–0.03)R.

5. Since the exchange A ⇌ B does not alter the long-range electrostatic interaction, a long-range order in the disposition of A and B may be absent, but a short-range order should exist as a condition for the attainment of the energy minimum.[39]

6. The substitution A ⇌ B can occur when the charges differ by 1, 2, and 3 units. The compensation of the excess charges generated can be non-local (via the formation of electronic and hole centres) and local, when a species with a balancing charge is located in the immediate vicinity to the excess charge. Local defects can have uncompensated magnetic moments and can interact with an external magnetic field, which leads to the possibility of their investigation by EPR.

7. The distribution of ions in the crystal lattice can be statistically uniform or non-uniform.[40,41]

8. The mutually substituting cations should be chemically inert in relation to one another.

Examples of pairs of cations whose mutual substitution can take place with a high probability have been published:[35] the substitution of Si^{4+} by the Ge^{4+}, Al^{3+}, Be^{2+}, Fe^{3+}, Ga^{3+}, P^{3+}, and Ti^{4+} ions is most probable for the $Si^{4+} \rightleftharpoons M^{n+}$ system.

The parameter ρ, introduced by Pauling,[1] can also be used as a criterion for the selection of cations capable of mutual substitution. By definition,[1] ρ is a criterion of the stability of the state of the cation in the given coordination environment and is a function of the attractive and repulsive forces of the ions in the first coordination sphere. To a rough approximation, ρ can be set equal to the ratio of the radii of the cation and anion. The critical values of the parameter ρ for oxides (ρ_c) outside the limits of which the coordination environment of the cation should change, calculated in accordance with Pauling's approximations, are listed in Table 1. The table also includes the values of ρ for different cations. [The ionic radii R taken from Bokii [42] and $R_{O^{2-}} = 1.36$ Å [43] were used in the calculation of ρ.)

Table 1. The parameter ρ for the M^{n+} cations.[1]

Group 1 ($\rho_c = 0.732$; C.N. = 8)		Group 2 ($\rho_c = 0.414$; C.N. = 6)		Group 3 ($\rho_c = 0.225$; C.N. = 4)		Group 4 ($\rho_c = 0.147$; C.N. = 3)	
M^{n+}	ρ	M^{n+}	ρ	M^{n+}	ρ	M^{n+}	ρ
Pb^{2+}	0.926	In^{3+}	0.676	Al^{3+}	0.419	B^{3+}	0.147
Sn^{2+}	0.750	Mn^{2+}	0.669	Mn^{4+}	0.382		
Tl^{3+}	0.772	Zn^{2+}	0.610	Ge^{4+}	0.323		
Nd^{3+}	0.73	Hf^{4+}	0.603	V^{5+}	0.294		
Eu^{3+}	0.71	Cu^{2+}	0.589	Si^{4+}	0.287		
		Sn^{4+}	0.492	Cr^{6+}	0.257		
		Fe^{3+}	0.492	P^{5+}	0.257		
		Mo^{6+}	0.478	Se^{6+}	0.257		
		Ti^{4+}	0.470	Be^{2+}	0.250		
		Pt^{4+}	0.470				
		Cr^{3+}	0.470				
		Sb^{3+}	0.470				
		Ga^{3+}	0.456				
		Sb^{5+}	0.456				
		V^{4+}	0.449				

According to Pauling's criterion,[1] only cations comprising Group 3 in Table 1 should be fixed in a stable tetrahedral environment. Vernadskii's isomorphous series, within the limits of which cations in natural formations are believed to be capable of isomorphous mutual substitution, is widely known: Si^{4+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Cr^{3+}, V^{4+}, Mn^{2+}, Mg^{2+}, Ti^{4+}.[35] It is assumed[35] that, within a narrow range of concentrations of the substituting ion (less than 1 at.%), isomorphism is possible in virtually all inorganic compounds.

III. HYDROTHERMAL SYNTHESIS

The principal procedures in the synthesis of zeolites and ez-silicates are the same. The initial mixtures contain in both cases a source of silicon, alkali, and salts of multicharged cations but in the synthesis of elementosilicates a source of aluminium is not added. There is a possibility of synthesising elementosilicates incorporating simultaneously several types of cations, with the substitution $Si^{4+} \rightleftharpoons M_1^{n+} + M_2^{n+}$.

In the preparation of elementosilicates with the structure of zeolites of the pentasil or ZSM type, organic surfactants, namely quaternary ammonium bases, polyamines, amino-

alcohols, alcohol, etc., are also introduced into the initial mixture. An aqueous silica sol, water glass, and silica gel are used as sources of silicon. A mixture consisting of a source of silicon, a source of M^{n+}, organic additives, alkali, and, sometimes, a seed is homogenised and then placed in an autoclave, where it is kept under hydrothermal conditions for 1–30 days at 80–200 °C. After the completion of crystallisation, the deposit is filtered off, washed, and dried. Before catalytic tests, the solid product is annealed at 520–550 °C in order to eliminate organic inclusions and cations are removed by treatment with NH_4OH + NH_4Cl solutions or solutions of inorganic acid.

We shall consider briefly the characteristics of the chemical behaviour of the SiO_2–H_2O and SiO_2–M_nO_m–H_2O systems in hydrothermal treatment. It is known[44] that $Si(OH)_4$ coagulates in the range 6 < pH < 8, dissolution and depolymerisation begin at pH ≥ 9, while at pH > 10.5 complete depolymerisation of $(SiO_2)_n$ is observed. In the pH range from 12 to 13.56, the system contains predominantly disilicate ions of the type $[Si_2(OH)_{10}]^{2-}$ whereas at pH ≥ 13.83 the monosilicate ions $[Si(OH)_5 2H_2O]^-$ predominate.

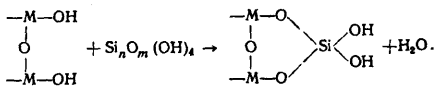
Thus polymerised silicon-containing ions of the type $[Si_nO_m(OH)_p]$, in which the coordination number of Si^{4+} is 4, predominate in aqueous media in the range 6 < pH < 10. As a result of the surface reactions $[Si_nO_m(OH)_p] + 20H^- \rightarrow [Si_nO_m(OH)_pO]^= + H_2O$, such species require a negative charge.

The polymerisation condensation of silicate ions includes reactions proceeding via an ionic mechanism with participation of OH^-. The condensation leads to the formation of siloxane linkages and the probability of the synthesis of cyclic structures is therefore high.

As a result of polymerisation condensation processes, silicate ions incorporating individual elements or individual structural blocks comprising crystalline varieties of silicates may be formed in an aqueous medium. Such structural blocks may be four- and six-membered rings of tetrahedra. The six-membered rings can be combined to form secondary structural blocks: an individual six-membered ring (beryl) and one-dimensional (amphiboles), two-dimensional (pyroxenes), and three-dimensional (elements of ultramarine, α-quartz, tridymite, and cristobalite) chains of rings.

The multicharged ions hydrolyse in aqueous solutions with formation of positively charged species and liberation of a proton to the outer sphere of the complex. The p*K* for the acid hydrolysis of multicharged cations have been published.[45,46] In alkaline media the hydroxides of Zn^{2+} and Si^{4+} are more basic than $Si(OH)_4$, while the hydroxides of the cations listed below are more acid, their acidity decreasing in the sequence $Ti^{4+} > Fe^{2+} \cong Fe^{3+} \cong Ga^{3+} > Th^{4+} > Al^{3+} > B^{3+} > In^{3+} > Si^{4+}$. The multicharged B, Ge, Tl, Cr, Mo, W, and V ions can hydrolyse with formation of negatively charged species. There is also a possibility of the polymerisation of hydroxides with formation of dinuclear and polynuclear complexes.[47]

The addition of metal salts facilitates the coagulation and polymerisation of silicate ions. In the presence of multicharged hydrolysed M^{n+} ions, the solubility of silicate ions falls in the first place owing to heteropolymerisation reactions:



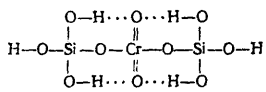
The condensation process is catalysed by hydroxide ions in this case also. The higher the charge of the ion, the greater its capacity for coagulation in relation to silica sol.

The Al^{3+} cation interacts most effectively with the monomeric silicate ion at pH 9. In the pH range 5–7, there is a possibility of the formation of the $[Al(OH)_2]^+$ and $[Al_2(OH)_5]^+$ ions. The complexes $NaAl_{13}(OH)_{32}(SO_4)_4(H_2O)_x$ are formed in the presence of SO_4^{2-}. The cation $[Al(OH)_4]^-$ is formed at pH 9–11.[47]

The interaction of Fe^{3+} with the surface Si–OH groups proceeds via heteropolymerisation processes, which has been demonstrated by the fact that at pH 6–8 the precipitation of $Fe(OH)_3$ on the macrosilicate ions is not observed in an SiO_2 containing system.[44]

As regards the character of its interaction with $(SiO_2)_n$, the cation Cr^{3+} differs greatly from Al^{3+}. The reason is that the chromite ion is not formed as readily as AlO_2^-; furthermore, Cr^{3+} is much larger than Al^{3+} and cannot be incorporated in the SiO_2 lattice with formation of stable anions.

The chromate ion, containing Cr^{6+}, retards the polymerisation of $Si(OH)_4$ at pH 0.5–3.0. It has been suggested[44] that the silicate ions dimerise in the presence of Cr^{6+} with formation of species of the type



The chemical properties of the Be^{2+} cation resemble those of Al^{3+}; solutions of beryllates, like those of aluminates, contain polymeric anions of the type $Be_2O_3^{2-}$ and oxo- and hydroxo-complexes. The hydrolysed Be^{2+} ion is capable of being strongly adsorbed on silica.[44]

The rate of interaction of silicic acid polymers with molybdic acid is higher the lower the molecular weight of the polymer. The interaction is preceded by the successive dissociation of the silicate ions to the monomer, which results in the formation of molybdosilicic acid.[44] The reaction of the silicate ion with H_3PO_4 represents condensation without the participation of water.[44] The Si–O–P and Si–O–B linkages hydrolyse in aqueous solutions. The precipitation of zinc salts by sodium silicate entails the mutual coagulation of zinc hydroxide and silica without the subsequent crystallisation of an amorphous deposit.[48,49]

Table 2. Conditions in the synthesis of beryllosilicates with the zeolite structure.

Type of structure	Source of Be^{2+}	Source of Si^{4+}	*t*, °C	*τ*, days	SiO_2/BeO*	Refs.
D, orthorhombic	$Be(NO_3)_2$ + $NaAlO_2$	32% SiO_2 sol	175	2	12–60	[50]
Faujasite	$Be(NO_3)_2$	Na silicate	100	2	14.3	[51]
Zeolite Y	$NaBeO_2$	Na silicate	70–130	1–2	10	[52]
Faujasite	$NaBeO_2$	SiO_2 sol	70–100	2	—	[53]
Zeolite A, X	—	—	100	2–5	2.5–6.0	[54, 55]
TRS-27, -41, -42	$Be(NO_3)_2$ in alcohol***	TEOS**, SiO_2 sol	155–200	0.5–1.0	12–100	[56]

*Molar ratio in solid product.
**TEOS = tetraethyl orthosilicate.
***Organic additives—tetrapropylammonium hydroxide and triethanolamine.

Thus, when the precipitation process is carried out in the range of mixture compositions and pH in which zeolites are formed, the sources of Si^{4+} and M^{n+} enter into the composition of polymeric blocks. The heteropolymerisation takes

place via the interaction of polymers. The direction of this interaction depends on (a) the ratio of the basicities of the polymers containing Si^{4+} and M^{n+}, (b) the sign and charges on the species, and (c) the degree of polymerisation and dehydration of the monocationic polymers in the initial mixture for hydrothermal synthesis.

On the basis of general considerations, one can assume that the synthesis of the crystalline silicate should be preceded by the following stages: (1) the hydrolysis of the source of M^{n+} and the formation of monocationic polymers containing the Si^{4+} or M^{n+} ions; (2) the heteropolymerisation of the monocationic polymers; (3) their depolymerisation; (4) the oriented fixation of the polymeric blocks accompanied by the establishment of long-range order in the arrangement of ions in the skeleton.

The rate of crystallisation of the silicate system should depend on the ratios of the rates of processes involving the aggregation of the polymeric species, on the one hand, and their depolymerisation and orientation, on the other. The depolymerisation and reorientation stages require a definite activation energy and their rate should therefore increase with increase in the temperature of the hydrothermal treatment and should also depend on the presence of an initiator and, what is especially important, on the nature of the ion-transferring component. The rate of reorientation of the blocks is higher the larger the polar species of the deposit

Table 3. Conditions for the synthesis of borosilicates with the zeolite structures.

Type of structure	Source of B^{3+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/B_2O_3	Remarks	Refs.
Zeolites A, X, and P, H-sodalite, analcime	borosilicate glass	Na silicate	—	80	7—9	—	—	[57]
Zeolite A	Na_3BO_3	Na silicate	—	45—170	—	1.78	—	[58]
Faujasite	B_2O_3	—	—	—	—	0.24—2.02	—	[59]
Faujasite	Borosilicate	kaolin, quartz	—	1100	0.02	—	—	[60—62]
Zeolite-like	$B^{3+}+Al(OH)_3$	aerosil	HMDA	100—200	5	145	conversion of methanol into unsaturated hydrocarbons	[63]
Pentasil	$H_3BO_3+Al(OH)_3$	aerosil	HMDA, DPDA, TEDA, PDA, DETA	150	5	33	synthesis of olefins from methanol and dimethyl ether	[64, 65]
—	B_2O_3	soluble glass	MEA	170	1	—	carrier, adsorbent	[66]
ZSM-5	—	—	—	—	—	31.7	conversion of methanol and ethylene into aromatic and aliphatic hydrocarbons	[67]
ZSM-5	borosilicate glass	—	HMDA	150	5	168	reforming, alkylation	[68]
Borolite: A, B, ..., I, AMS-1, -11, -12	H_3BO_3	TEOS	TPAOH, TEAOH, TBABr, EDA	150—170	6—17	4—13.9	cracking, hydrocracking, isomerisation of xylenes	[69, 70]
AMS	H_3BO_3	30% SiO_2 sol	TPABr	165	7	—	isomerisation and disproportionation of C_2 and higher hydrocarbons	[71]
Eu-1, Eu-2	—	solid SiO_2	HMDA derivative	85—250	1—30	—	separation of aromatic hydrocarbon	[72, 73]
Pentasil	H_3BO_3	silica sol	TPABr	165	7	44.4—104.5	isomerisation of xylenes	[74]
ZSM-5	H_3BO_3	40% SiO_2 sol	EDTA + TPA	168 166 185	7 10 3.5	—	conversion of methanol into dimethyl ether	[75]
ZBM-30	H_3BO_3	SiO_2 (pyrogenic)	DPDA, TEDA, PDA, DETA	170 200	5 0.5	80	synthesis of olefins from methanol and dimethyl ether	[76]
ZHB	H_3BO_3	aerosil	DEG, TEG, HMDA	80—200	0.5—5.0	10—50	conversion of hydrocarbons	[56, 77, 78]

Notation: TEOS = tetraethyl orthosilicate, HMDA = hexamethylenediamine, TPAOH = tetrapropylammonium hydroxide, TEAOH = tetraethylammonium hydroxide, TBABr = tetrabutylammonium bromide, EDA = ethylenediamine, TPABr = tetrapropylammonium bromide, DPDA = dipropylenediamine, TEDA = triethylenediamine, DEG = diethylene glycol, and TEG = triethylene glycol.

or the larger the charge of the elementary blocks.[48] The nature and concentration of the sources of the multicharged ions as well as the nature of the organic additives playing the role of ion-transferring agents therefore influences strongly the crystallisation of silicates with a particular structure.

The conditions for the synthesis of silicates described in the literature are described systematically in Tables 2–6. In the synthesis of beryllosilicates (Table 2), the source of beryllium employed is its nitrate or sodium beryllate, while the source of silicon is silica sol or sodium silicate. The reactant ratio and the crystallisation temperature influence the type of crystal structure of the final product. The crystalline zeolite-like orthorhombic silicate with a SiO_2/BeO ratio of 12–60 has been obtained by the hydrothermal treatment of a mixture consisting of sodium aluminate, beryllium nitrate, and an aqueous solution of silica sol for 24 h at 175 °C.[50] Silicates with structures of type A, X, and Y zeolites have been obtained by the crystallisation of mixtures of definite composition at 70–130 °C.[51–55] A zeolite, designated by TRS, with the ratio $SiO_2/BeO > 12$ in the solid product (of the ZSM type), has been obtained from a mixture of beryllium nitrate and tetraethyl orthosilicate in the presence of tetrapropylammonium hydroxide in an alcoholic medium over a period of 12–17 h at 155–200 °C.[56]

Table 3 presents the conditions for the synthesis of borosilicates, the composition of the solid phase synthesised, and also the reactions in which silicates have been investigated. A borosilicate of the type of a zeolite with the ratio $SiO_2/B_2O_3 = 1.78$ has been obtained from sodium silicate and borate at 45–170 °C.[57–59] A zeolite of the faujasite type has been synthesised from a mixture of borosilicate, boron oxide, kaolin, and quartz after it had been sintered at 1110 °C.[60–62] High-silica borosilicates with the structure of pentasils[63–78] have been obtained by the crystallisation at 150–170 °C of mixtures incorporating a source of boron (H_3BO_3), freshly prepared aluminium hydroxide, aerosil, and organic amines. The use of monoethanolamine[66] and hexamethylenediamine as the organic compound together with borosilicate[67,68] glass or soluble glass enabled the authors to obtain zeolites of the ZSM-5 type.

The main conditions for the synthesis of silicates with the zeolite structure, containing Group III, IV, V, and VI elements, are presented in Table 4. Numerous phosphorus-containing silicates with the analcime, chabazite, phillipsite, sodalite (HS) and type A, X, Y, P, and L zeolite structures have been synthesised.[79–81] The crystallisation was carried out from the gel at 80–200 °C using reactive phosphorus-containing compounds as the sources of phosphorus, usually orthophosphoric acid. The presence of an organic compound [tripropylamine (TPA)] in the crystallising system promoted the crystallisation of a silicate with the type ZSM zeolite structure.[82,83] A sulphur-containing zeolite has been obtained by introducing sulphuric acid into the crystallising mixture instead of phosphoric acid.[82] Silicates with the ZSM structure have also been obtained from systems incorporating silica sol, TPABr, hexamethylenediamine (HMDA), and also arsenic, tin, indium, or tellurium salts.[83,85–88] A zeolite-like silicate, whose composition incorporates iron and arsenic cations, is formed in an acid medium at 220 °C.[84]

Gallo- and germano-silicates (Table 5) were synthesised for the first time from aqueous solutions of sodium gallate and germanate and silica sol at 100 °C.[90] The silicates obtained proved to have the same structures as zeolites X, A, and P and thomsonite, which was demonstrated by X-ray diffraction. It was noted that zeolite A crystallises only from sodium aluminogermanate gels, while zeolite X crystallises from a mixture of sodium gallogermanate and sodium aluminogermanate. Zeolite P is formed on recrystallisation of zeolite A in an alkaline solution.[90] An analogue of zeolite X has been obtained from sodium metasilicate and $GaCl_3$ in an alkaline solution.[91,93–95] The zeolite chabazite has been synthesised from the potassium galloaluminosilicate system, while phillipsite has been obtained from the sodium gallosilicate system.[96,97]

The crystallisation of $HGaCl_4$ and sodium silicate for different periods at 200 °C is accompanied by the formation of several types of zeolites.[92] Analogues of faujasite having the aluminosilicate composition have been obtained in an alkaline medium from sodium and potassium germanates at temperatures not above 100 °C,[93–95,98–100] Zeolites of the

Table 4. The principal conditions for the synthesis of silicates with zeolite structures containing Group III, IV, V, and VI elements.

Element introduced	Type of structure	Source of M^{n+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/M_nO_m	Refs.
P(Al*)	analcime	H_3PO_4 + Al, Na phosphates	SiO_2 (colloidal)	—	230—450	1—68	—	[79]
P	zeolites X, Y, A, L, P, S, and HS	K_3PO_4	clays, zeolite	—	230—530	4—5	—	[80]
P	analcime, chabazite, zeolite A, phillipsite	H_3PO_4	**	—	60—70	—	—	[81]
P	zeolite Y, ZSM-5	H_3PO_4	40% SiO_2 sol	TPABr	145	2	—	[82]
P	ZSM-5	PCl_3	zeolite	TPABr	150	0.05	12	[83]
S	ZSM-5	H_2SO_4	40% SiO_2 sol	TPABr	145	2	—	[82]
As	OTW	KH_2AsO_4, As ferrite	SiO_2	—	220	0.05	—	[84]
As	ZSM	As_2O_3	aerosil	HMDA	150	5	1380	[85]
Sn	ZSM	$SnCl_4 \cdot 5H_2O$	SiO_2 (colloidal)	TPABr	150	1	32	[86, 87]
Te	ZSM	H_6TeO_6	SiO_2 (colloidal)	TPABr	150	1	32	[88]
Pb	faujasite	$PbSiO_3$	Na silicate	—	100	4	—	[89]
In(Ce*)	ZSM	$In_2(SO_4)_3$	SiO_2 sol	TPABr	150	0.05	12	[83]

*Introduced together with the element.
**Synthesis carried out by the coprecipitation method.

type of pentasil and ZSM-11 crystallise at 150 °C in the presence of HMDA and tetrabutylphosphonium chloride respectively.[72,73,103]

Table 5. Conditions in the synthesis of silicates with the zeolite structure containing the Ga^{3+} and Ge^{4+} cations.

Type of structure	Source of M^{n+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/M_nO_m	Refs
Thomsonite, zeolites A, X, and P	Ga_2O_3, GeO_2	—	—	100—200	3	—	[90]
Analcime, natrolite, nepheline, gismondine, H-sodalite	$HGaCl_4$	Na silicate	—	200	5—10	—	[92]
Zeolite 13X	$GaCl_3$	Na silicate	—	102	0.25	2.6	[91]
Zeolite A	Ga_2O_3 $Ga(OH)_3$	Na silicate SiO_2 sol	— —	150 93	7 12	5 4.5	[93]
Zeolite 13X	Na gallate	SiO_2 sol	—	170	3	5	[94, 95]
Chabazite	K gallate	K silicate	—	100	7	—	[96]
Phillipsite	Na gallate	Na silicate	—	100	7	—	[97]
Faujasite	GeO_2 in KOH	—	—	90	2.5	2.02	[98]
Faujasite	Ge^{4+}	—	—	—	—	—	[100, 101]
Zeolite	Ga^{3+} substitutes Al^{3+}	Ge^{4+} substitutes Si^{4+}	—	—	—	—	[102]
ZSM-11	Ga^{3+} substitutes Al^{3+}	Ge^{4+} substitutes Si^{4+}	TBP	150	4	—	[103]
Eu-1, Eu-2	Ga^{3+}, Ge^{4+}	solid SiO_2	HMDA	85—150	1—30	—	[72, 73]

Notation: TBP = tetrabutyl phosphate; HMDA—see reference to Table 3.

The data in Table 6, where the conditions in the synthesis of silicates crystallising in the presence of transition metal cations and platinum group elements are presented,[104–128] permit the following conclusions. The crystallisation of a silicate system, into the composition of which the above cations have been introduced together with quaternary ammonium compounds, leads to the formation of systems isostructural with type ZSM zeolites in alkaline media at 100 °C and above. The sources of cations are their salts and oxides and acids based on them. The sources of silicon and organic ions are the reagents indicated in Tables 2–5.

The characteristic features of the crystallisation of silicates in the presence of multicharged cations have been studied systematically as a function of the nature and content of the latter.[129–137] The influence of the temperature, crystallisation time, component ratio, and the nature of the modifying cation on the content of the zeolite-like silicate phase has been investigated. For the ratios $OH/SiO_2 = 0.1–0.2$, $TBABr/SiO_2 = 0.11–0.15$, and $H_2O/SiO_2 = 20–50$ and temperatures in the range 140–200 °C, the silica sol crystallises predominantly with formation of a product having the X-ray diffraction parameters of a type ZSM-11 zeolite regardless of the nature of the source of M^{n+}. In many cases the solid product may contain α-quartz or an amorphous phase depending on the temperature, crystallisation time, and the type of cation. With increase of crystallisation temperature from 140° to 200 °C for the same crystallisation time, the constant of the crystalline zeolite phase (CZP) passes through a maximum in the range 140–150 °C in many cases (Fig. 1). As the CZP crystallisation temperature increases further, the content of α-quartz diminishes and increases. This result confirms the available data showing that the zeolite phase is formed as an intermediate in the hydrothermal treatment of the $SiO_2–H_2O–M(OH)_m$ system; after a time, it recrystallises and denser and thermodynamically more stable structures, including α-quartz, are formed.[23]

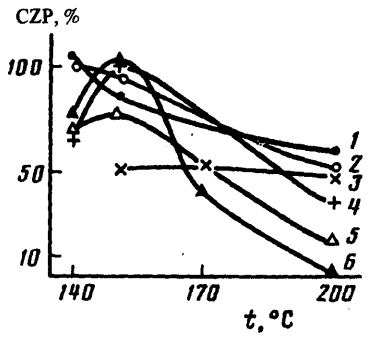


Figure 1. The influence of the temperature of the hydrothermal treatment (t, °C) of silica sol on the content of the ZSM-11 phase in the solid product obtained after the introduction of various cations M^{n+}: *1*) Mn; *2*) Cr; *3*) Eu; *4*) Fe; *5*) Cu; *6*) Zn.[133]

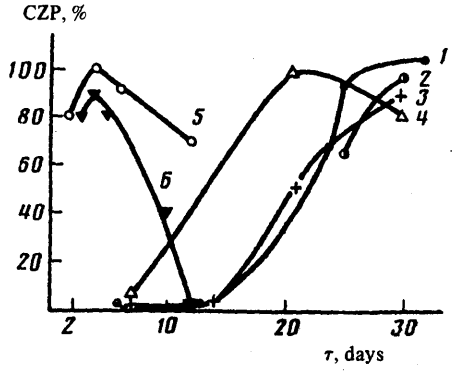


Figure 2. The influence of the duration of the hydrothermal treatment (τ, days) on the content of the ZSM-11 phase in the solid product obtained after the introduction of various cations M^{n+}: *1*) Ti; *2*) Cr; *3*) Cu; *4*) Zn; 5) B; *6*) Eu.[137]

Changes in the CZP content of the same character are observed after an increase in the duration of the hydrothermal treatment of silica sol, keeping the temperature and the composition of the initial mixture unchanged (Fig. 2): the content of the ZSM phase usually increases during the first 2–5 days and then gradually diminishes.[133]

A common feature is the decrease of the content of the ZSM phase with increase of the amount of M^{n+} in the initial mixture (Fig. 3); this means that the crystallisation reactions of silicate ions are retarded in the presence of M^{n+}.[44] The

cause of this phenomenon has not been investigated in detail. However, presumably in the presence of the M^{n+} hydrolysis product either the solubility of the silicate increases or the degree of coagulation diminishes and the stability of the silica sol increases as a result of the adsorption of the $[M_nO_m(OH)p]$ groups on the surface of the polymeric species of the silicate system. The adsorbed polymeric ions containing M^{n+} can prevent the establishment of long-range order in the silicate system.

According to Pauling's criterion, stabilisation in an eight-membered oxygen environment is most likely for the cations in groups 1 (Table 1). It has been shown[137] that most of

Table 6. Principal conditions for the synthesis of silicates with zeolite structures containing transition elements.

Element	Type of structure	Source of M^{n+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/M_nO_m	Refs.
Ti	silicate	$TiOCl_2$	Na silicate	—	95	1,5	5—20	[104, 105]
	TRS-1 . . . TRS-64	$TiOCl_2$, TE-Ti, $TiCl_4$	TEOS	TPAOH	145—175	10	3	[106]
Ti	ZSM-5	$TiCl_4$	SiO_2 (pyrogenic)	HMDA	100—200	0,5—5	—	[76]
V(Al)	VK-2	V_2O_5	Na silicate	—	60	2,5	2—4	[107]
V	zeolite	VCl_3	soluble glass	HMDA	150	5	127	[108]
V	ZSM-5	V_2O_5	Na silicate	TPABr	96	5—6	—	[56]
V	TRS-48	H_4VO_3	TMOS	TPAOH	175	6	17	[106]
Cr	silicate	Cr_2O_3	chabazite	—	100	—	—	[109]
Cr	ZSM-5	$CrK(SO_4)_2$	Na silicate	TPABr	96	5—6	—	[110]
Cr	TRS-28	$Cr(NO_3)_3$	TEOS	TPAOH	155	13	38	[106]
Cr	zeolite-like	Cr sulphate, hydroxide, and oxide	soluble glass	HMDA	150	5	164—399	[111, 112]
Cr	AMS-1	$NaCrO_2$	30% SiO_2 sol	TPABr	150	2—20	16	[113]
Cr	CZS	Cr nitrate and sulphate	SiO_2 sol	TPAOH	165	15	—	[114, 115]
Fe	—	ferroalloy	SiO_2 (dust)	—	100	0,5	—	[116]
Fe	silicate	Fe_2O_3	chabazite	—	100	—	—	[109]
Fe	zeolite-like	Fe-phosphoric acid	—	—	350	1	1	[117]
Fe	zeolite	Fe nitrate	SiO_2 sol	TPAOH	148	2	32	[118—120]
Fe	zeolite	Fe sulphate, oxide, and hydroxide	soluble glass	—	150	5	81	[121—123]
Fe	ZBM-30	Fe sulphate and oxide	SiO_2 (pyrogenic)	HMDA	170	5	—	[124]
Ni	ZSM-5	Ni nitrate	SiO_2 (colloidal)	TPABr	100	19	160	[125]
Co	ZSM-39	$Co[Co(NH_3)_2]^+$	SiO_2 (colloidal)	C_4H_8NH	210	5	—	[126]
Zn	A	Na_2ZnO_2	Na metasilicate	—	95	—	1—1,5	—
Zn	ZSM-5	Zn nitrate	SiO_2 (colloidal)	TPABr	100	14	50	[84]
Zn	TRS-66	Zn nitrate	TEOS	TPAOH	197	6	15	[106]
Zn	ZSM	$Zn_2B_8O_{11}$	Na silicate	TPABr	96	5—6	—	[56]
Zr	silicate	$ZrOCl_2$ (KOH)	Na silicate, SiO_2 sol	—	200	1,5	—	[104, 105]
Zr	ZSM	ZrO_2	SiO_2 (colloidal)	TPABr	150	25	—	[121]
Zr(Al)	zeolite	$ZrOCl_2 \cdot 8H_2O$	Na silicate	TPAOH	160	5	—	[127]
Mo(Al)	silicate	MoO_3	Na silicate	—	100—160	2	150	[128]
Mo	ZSM	H_2MoO_4	SiO_2 sol	TPABr	96	5—6	—	[56]
Ru	ZSM	$RuCl_2$	SiO_2 sol	TPABr	96	5—6	—	[56]
Ag	ZSM	$Ag(CH_3COO)$	SiO_2 sol	TPABr	96	5—6	—	[56]
Pt	ZSM	H_2PtCl_6	sol, soluble glass	TPABr, TEABr	96	5—6	—	[56]
Hg	ZSM	$HgCl_2$	SiO_2 (colloidal)	TPABr	96	5—6	—	[56]

Notation: TMOS = tetramethyl orthosilicate, TEBr = tetraethyltitanyl.

the group 1 cations contained in the initial silica sol are not entrained by the solid phase on crystallisation; the solid product obtained after filtration, washing, and the elimination of cations contains 3–20 times less of M^{n+} than the amount introduced into the initial silica sol. A mainly amorphous phase is obtained in the presence of Tl^{3+} and Sn^{2+}.

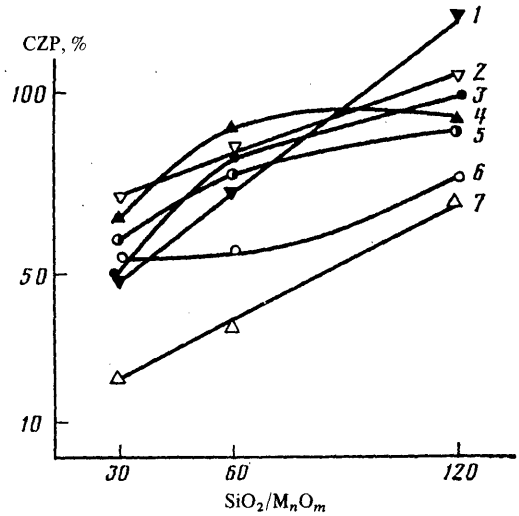


Figure 3. The content of the type ZSM-11 type zeolite phase in the final crystallisation product as a function of the concentration of the added cation in the initial silica sol: *1*) Ga; *2*) Fe; 3) Cr; 4) Mn; 5) Sb; 6) Eu; 7) In.[133]

Table 7. The Si/M^{n+} ratios (mole fractions) in the "decationated" products of the crystallisation of silica gel with the initial ratio $Si/M^{+} = 60$ (crystallisation temperature 150 °C).[137]

Cation	Si/M^{n+}	CZP, %	Cation	Si/M^{n+}	CZP, %
Mo^{6+}	700	100	Ga^{3+}	50	125*
Se^{6+}	1000	100	Al^{3+}	70	100
Zn^{4+}	1000	100	B^{3+}	67	100
Ti^{4+}	480	100	Pb^{2+}	150	50
Tl^{3+}	750	70	Sn^{2+}	280	80
Nd^{3+}	700	100	Mn^{2+}	119	100
Eu^{3+}	1300	70	Zn^{2+}	119	100
In^{3+}	330	80	Co^{2+}	27	100
Fe^{3+}	95	100	Cu^{2+}	73	80
Cr^{3+}	56	95	Be^{2+}	36	100

*The content of the zeolite phase of the ZSM-11 type was considered in relation to a standard, for which silicalite was used.

Six-membered coordination by oxygen is stable for group 2 cations (Table 1). Only traces of these cations have been detected in the solid products of the crystallisation of mixtures containing Ti^{4+}, Mn^{2+}, Zr^{4+}, and Mo^{6+} (Table 7).[137] For systems with the Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Ga^{3+}, B^{3+}, Be^{2+} cations, the ratios Si/M^{n+} in the initial gel and its solid crystallisation product are similar. In these systems, the presence of M^{n+} does not prevent the crystallisation of silica sol and the M^{n+} cations are mostly occluded by the crystalline phase formed. The probability of occlusion depends on the size of the cation. Indeed the cations enumerated have the smallest values of ρ among the group 2 cations.

Regardless of the value of ρ, cations with the 4+, 5+, and 6+ charges are not retained by the silicate in any of the groups. Thus the Se^{6+}, Pt^{4+}, Mo^{6+}, and Zr^{4+} cations are present in the crystalline product in trace amounts, which are much smaller than in the initial silica sol. When the alkalinity of the system is the same as under conditions where the silicate crystallises, the cations forming part of the composition of the anion $[NaM_nO_m]^-$ are probably present in a dissolved state.

A high degree of crystallinity of the solid products and similar Si^{4+}/M^{n+} ratios in the initial mixture and in the crystalline phase have been observed for systems with group 3 and 4 cations.[137] Mixtures containing the highly charged V^{4+} and Se^{6+} cations, which are removed from the solid deposit already in the filtration and washing stages, constitute an exception in this instance. Owing to the high alkalinity of the system, vanadate and selenate ions are probably formed and remain in the liquid phase on crystallisation. The presence of compounds containing V^{4+} and Se^{6+} for Si^{4+}/M^{n+} ratios ranging from 15 to 30 hinders the zeolite formation process.[132]

IV. THE STATE OF THE MULTICHARGED CATIONS IN SILICATES WITH THE ZEOLITE STRUCTURE

The state of the multicharged M^{n+} ions in the product of the crystallisation of the $SiO_2–M_nO_m–H_2O$ system can be various and depends both on the composition of the initial mixture and on the nature of M^{n+}. Thus, apart from the fixation of M^{n+} in the silicon–oxygen skeleton in positions isomorphous with Si^{4+}, there is a possibility of occlusion of M^{n+} in salts or oxides within silicate channels or on the outer surface of the crystals and also of their localisation near groups incorporating oxygen ions with an uncompensated charge (in cationic positions). Various methods have been used to investigate the state of the M^{n+} ions: (1) X-ray diffraction (the incorporation of M^{n+} in the skeleton is inferred from the change in the crystal lattice parameters[50,51,54,58–61,64,71]); (2) high-resolution NMR which makes it possible to determine the symmetry of the coordination environment and the composition of the second coordination sphere of the silicon atoms;[132,133,135–138] (3) EPR and Mössbauer spectroscopy (when paramagnetic cations are introduced into the composition of the silicates[131,134,139]). The principal results of these studies are considered below.

1. The State of Mn^{2+}

The state of the Mn^{2+} cations in the elementosilicates obtained from silica gel with added $MnCl_2$ has been investigated by EPR.[134] EPR spectra with an isotropic *g*-factor of ~2.00 have been recorded for all the manganese-containing silicates with the structure of the type ZSM zeolite. The spectrum of the Mn^{2+}-containing elementosilicate at 77 K (Fig. 4) can be represented by a superposition of two signals with a Lorentzian shape and a width of 1250 and 450 G and a 6-component spectrum in which the splitting between the third and fourth components is 93 G. Their relative contributions to the overall intensity are 91, 8.5, and 0.5% respectively. The Mn^{2+} cations, to which the signals of the first two types correspond, are probably present in a state with a weak interaction. In the EPR spectra of cations of the third type the splitting between the hyperfine structure

components is 90–98 G; the splitting increases as the temperature of the recording is reduced and on passing to the *Q*-range. This spectrum can be attributed to Mn^{2+} cations in an octahedral oxygen environment. In this case, as in type X and Y zeolites,[138] the width of the EPR line is determined by the relaxation due to the periodic modulation of the crystal field caused by the distortion of the solvation shell of the ion and the anisotropic movement of the solvated ion.

The Mn^{2+} ions responsible for the hyperfine structure (HFS) in the EPR spectrum are apparently not "built into" the zeolite skeleton and are separated from the oxygen atoms of the skeleton by the solvation shell. An additional confirmation of this conclusion has been obtained in a study of the EPR spectra of specimens of elementosilicates heated at 500 °C and a pressure of 10^{-5} mmHg for 2 h. Instead of the superposition of several signals, single lines were observed in the EPR spectra of these specimens, whose width depended on the amounts of water and oxygen adsorbed after the activation of the specimen. On the basis of the form of the EPR spectra, one may claim that there are no Mn^{2+} ions in the test specimen in a tetrahedral environment of oxygen atoms. We may note that the EPR method by no means permits the detection of all the manganese ions introduced into the specimens.[134]

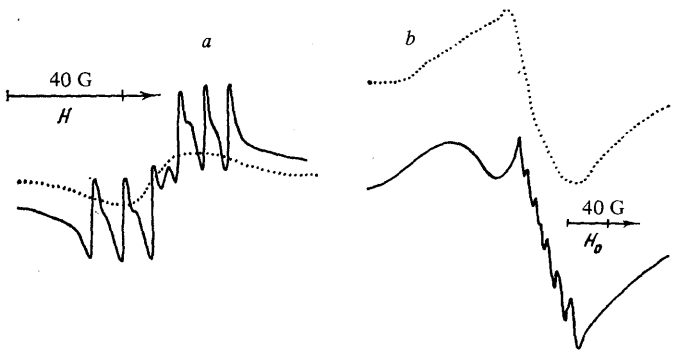


Figure 4. The EPR spectrum of the Mn^{2+} cations of a manganese-containing silicate recorded in the *X*-range (*a*) and *Q*-range (*b*) at 20 °C (dashed lines) and −110 °C (continuous lines).[134]

2. The State of Cr^{3+}

The EPR spectra of specimens of elementosilicates containing chromium exhibit a symmetrical signal with $g = 1.98$ and $\Delta H = 600$ G,[131] which may be assigned to the disperse chromium hydroxide [$Cr(OH)_3.nH_2O$]. After heating the specimens at 300 °C and above, the intensity of this signal diminishes together with an increase in its width. This may be caused by the dehydration of the hydroxide with formation of the antiferromagnetic Cr_2O_3, or, which is most probable, the oxidation of the Cr^{3+} ions in the chromium oxide particles. The latter hypothesis has been confirmed by the appearance of a signal due to the Cr^{5+} ions, whose intensity increases with increase of the heat treatment temperature. The distribution of the chromium ions detected by EPR on the surface of silicate crystals is indicated by the change in the spectra of the Cr^{5+} ions following the adsorption of pyridine.

3. The State of Cu^{2+}

Signals of mainly two types (I and II) are observed in the EPR spectra of specimens of elementosilicates[131,139] synthesised in the presence of Cu^{2+} ions:

$$g_{\parallel}^{I} = 2.30 \quad A_{\parallel}^{I} = 160\ \text{G} \quad g_{\perp}^{I} = 2.055 \quad A_{\perp}^{I} = 25\ \text{G}$$
$$g_{\parallel}^{II} = 2.32 \quad A_{\parallel}^{II} = 157\ \text{G} \quad g_{\perp}^{II} = 2.058 \quad A_{\perp}^{II} = 26.5\ \text{G}$$

The parameters of these signals correspond to Cu^{2+} ions fixed in an octahedral oxygen environment. The difference between the parameters of the ions of types I and II is probably determined by the existence of tetrahedral distortions for the type II Cu^{2+} ions. After the specimens have been heated at 250 °C and above, the intensity of the EPR signals of the Cu^{2+} ions is found to increase. It is noteworthy that some of the detected Cu^{2+} ions are inaccessible to the adsorbed molecules, which is indicated by the absence of changes in the EPR spectrum after the adsorption of pyridine. The copper ions interacting with pyridine give rise to an EPR spectrum with the $g_{\parallel} = 2.26$, $A_{\parallel} = 1.86$ G and $g_{\perp} = 2.08$, $A_{\perp} = 40$ G signals, which is due to the formation of pyridinates.[131]

Overall, the hydrothermal synthesis of elementosilicates from silica gel containing copper compounds results in the stabilisation of the bulk of the copper (~90%) in a state undetectable by EPR, probably in the form of an oxide phase. A small proportion of the copper (~10%) is stabilised in the form of isolated ions and, after treatment with thionyl, in a specific form with antiferrodistortion order.[139]

The crystal lattice parameters of the copper-containing zeolite do not differ from those of the unmodified zeolite, which provides additional grounds for the assumption that the isomorphous substitution of silicon atoms by copper atoms with tetrahedral coordination does not occur. It is more likely that the copper cations are localised in the channels of the zeolite structure and that the exchange interaction between them takes place via silicon–oxygen bridges or via oxygen atoms which do not belong to the zeolite skeleton.

4. The State of V^{4+}

The character of the X-ray diffraction patterns of specimens of vanadium-containing elementosilicates shows that the systems synthesised are mixtures of three phases: silicalite (crystalline SiO_2 with the zeolite structure), α-quartz, and an admixture of amorphous SiO_2. With increase in the amount of VO_2^- introduced into the initial sol, the content of the crystalline silicate phase in the specimen diminishes, as a result of which the actual SiO_2/V_2O_5 ratio in the solid phase is smaller by a factor of 4–10 than in the initial gel.

Low values of the HFS constant for the parallel orientation as well as the dependence of the character of the EPR spectrum on the temperature of the measurement are to be expected for a V^{4+} ion in a tetrahedral coordination.[140]

The EPR spectrum of vanadium-containing silicates obtained by hydrothermal synthesis is characteristic of V^{4+} ions in an octahedral coordination with tetragonal distortion ($g_{\parallel} = 1.93$, $A_{\parallel} = 1.95$ G and $g_{\perp} = 1.96$, $A_{\perp} = 56$ G) in the isolated (as part of the composition of VO_2^-) and exchange-linked states. Since the intensity of the EPR signal of V^{4+} proved to be many times smaller than might have been

expected from chemical analysis, it was concluded that the main bulk of the V^{4+} ions present in the silicate are bound by a strong exchange interaction and are present in the composition of polymers. The EPR spectrum of the V^{4+} ions in this state has not been observed.[141]

Thus there are no grounds for the assumption that the V^{4+} cation is "built into" the silicon–oxygen skeleton in tetrahedral positions in the course of the hydrothermal synthesis of silicates with a zeolite structure.

5. The State of Fe^{3+}

The incorporation of Fe^{3+} ions into the composition of type A, X, and Y zeolites in the hydrothermal synthesis of the latter has been frequently established.[142–147] The source of Fe^{3+} consists of the admixture of iron compounds present in the components of the initial mixture. Thus it has been shown[142] that 0.01% of Fe^{3+} cations are occluded in type Y zeolites obtained by hydrothermal synthesis. Three signals, with $g = 4.27$, 2.4, and 2.0, have been observed in the EPR spectra. The signal with $g = 2.4$, whose width was 1600 G and which diminished with increase of temperature, was assigned to magnetite Fe_3O_4, which has ferromagnetic properties. The Curie point, determined from the magnetic susceptibility, was at 572 °C and was attributed to the highly defective nature of the phase produced. The EPR spectrum of Fe^{3+} occluded in the zeolite NH_4Y and mordenite was found to contain three signals:[143] with $g = 4.3$ (narrow), 2.3, and 2.0 (both broad). The first was assigned to Fe^{3+} fixed in a tetrahedral oxygen environment with pronounced orthorhombic distortion. The signal at $g = 2.0$ was assigned to all the cations in the octahedral environment incorporating three oxygen atoms and three OH groups at cationic sites.

The EPR spectra of the Fe^{3+} ions forming part of the composition of a type Y zeolite[144–146] have been interpreted in the same way: the signals with $g = 2.2–2.3$ were explained by the presence of an amorphous oxide phase[143] and an occluded salt,[145] in which the Fe^{3+} cations are in a state with strong exchange interaction. The fraction of Fe^{3+} cations in a tetrahedral environment ($g = 4.3$) was ~4% of the total Fe_3O_4 content in the zeolite. The part of Fe^{3+} forming part of the composition of the phase giving rise to the signal with $g = 2.2–2.3$ was most readily extracted.

A zeolite of the ZSM-5 type, in which the Fe^{3+} cations were introduced before the hydrothermal crystallisation of silica gel, has been synthesised[146] in the presence of hexamethylenetetramine. The general character of the EPR spectrum resembles that described above.[142–145] After the reductive treatment of the specimen, the intensity of the signal with $g = 2.02$ diminished markedly, while the intensity of that with $g = 4.28$ remained almost unchanged.

A characteristic signal with $g = 4.3$ (Fig. 5a), which can be assigned to isolated Fe^{3+} ions, was observed[131] in the EPR spectra of iron-containing elementosilicates with the ZSM structure. The transitions near $g = 4.3$ in the low-field part of the spectrum refer to Fe^{3+} ions whose ligand environment is appreciably distorted (type I). The main transitions noted in Fig. 5 can be assigned to Fe^{3+} ions stabilised in a weakly distorted octahedral environment (type II) (D, $E \lesssim h\nu$). Analogous spectra have been observed for Fe^{3+} ions in the hexa-aquo-complexes formed on dissolution of iron salts in water at low concentrations. The absence of a significant temperature dependence of the EPR of type II Fe^{3+} ions also indicates the fixation of the iron cations predominantly in the form of isolated ions. A symmetrical line in the vicinity of $g = 2.00$ (type III), characteristic of exchange-bound Fe^{3+} ions, can be observed in the EPR spectrum of the specimens obtained at 200 °C.

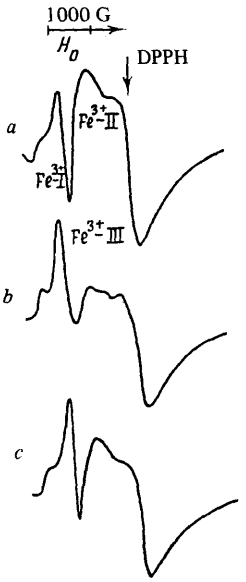


Figure 5. The EPR spectrum of the Fe^{3+} cations of an iron-containing silicate: *a*) initial specimen; *b*) after dehydration at 400 °C; *c*) after the adsorption of pyridine on the specimen and subsequent dehydration at 400 °C.[131]

The assignment of the signal with $g = 4.23$ in the Fe^{3+} EPR spectra to Fe^{3+} ions in a tetrahedral coordination does not alone justify the claim that the corresponding Fe^{3+} ions are fixed in the silicon–oxygen skeleton at sites isomorphous with those of Si^{4+}. Indeed the iron oxide compounds can incorporate Fe^{2+} and Fe^{3+} cations fixed in tetrahedral cavities.[140] Some evidence for the view that the Fe^{3+} cation giving rise to the EPR signal with $g = 4.23–4.3$ enters into the composition of the silicon–oxygen skeleton of a type ZSM zeolite has been obtained.[147]

The intensity of the signal with $g = 4.27$ in the EPR spectrum of the products of crystallisation of the $Na_2O.nFe_2O_3.SiO_2.mH_2O$ mixture increased almost in proportion to the content of the zeolite phase (Fig. 6), but diminished after ion exchange. On the other hand, the intensity of the signal with $g = 2.0$ was independent of the degree of crystallinity of the specimen but increased with increasing Fe_2O_3 content for the well crystallised specimens. In the studies enumerated above, it was shown that the intensity of the signal of the type I ions is very low. In one study[145] it corresponded to 4% of the total amount of the Fe_2O_3 present in the type Y zeolite. In another study[147] the signal intensity ratio $I_{4.27}/I_{2.0}$ was 20–30.

Thus the literature data permit the conclusion that a small proportion of Fe^{3+} ions are built into the silicon–oxygen skeleton of the elementosilicate in the course of hydrothermal synthesis; most of the ions remain in the iron oxide phase or in cationic sites. These data indicate the possibility of the formation of the $[Si(OFe)_n]^{n-}Fe^{3+}$ groups in the skeleton.

After the removal of cations by acid or NH_4OH solutions, there is a possibility of the rupture of both Si–O–Fe–O–Si and Si–O–Al–O–Si linkages as a result of hydrolysis.

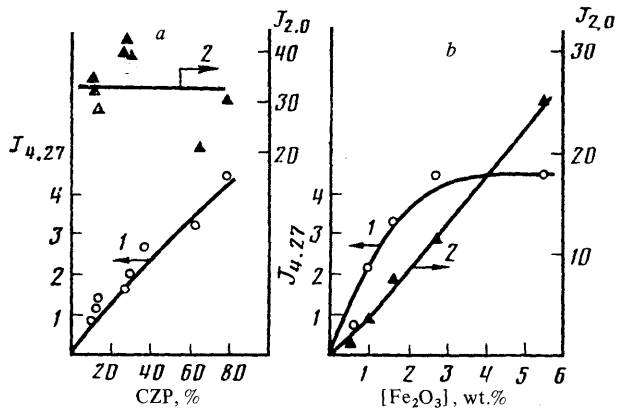


Figure 6. The relative intensities of the EPR signals of the Fe^{3+} cations with $g = 4.27$ (curves *1*) and $g = 2.0$ (curves *2*) for a silicate occluding Fe^{3+} ions during hydrothermal treatment as a function of the content of the crystalline phase (*a*) and the content of Fe_2O_3 in the crystallisation product (*b*).[137]

The state of Fe^{3+} at various sites in the silicon–oxygen skeleton of faujasite[148] for Si/Al = 1 has been calculated by the semiempirical LCAO-MO SCF method in the CNDO/2 valence approximation. The authors[148] concluded that the Fe^{3+} cations must be bound to the oxygen atoms in the zeolite skeleton by strong donor–acceptor bonds whose strength is comparable to that of the bonds involving Al^{3+}. Comparison of the charge density and Wiberg indices of the $FeSi_5O_6$. $.(OH)_{12}Na$ and $AlSi_5O_6(OH)_{12}Na$ clusters formed on isomorphous substitution of Si^{4+} in the six-membered silicon–oxygen ring showed that the Al^{3+} and Fe^{3+} ions have identical effects on the properties of the skeleton; the Fe–O bond is stronger than the Al–O bond.

6. The State of Be^{2+}

The isomorphous substitution of the atoms of the silicate skeleton by Be^{2+} ions has been observed in natural minerals: in helvin $Mn_4Be_3O_{12}S$, whose structure is similar to that of sodalite $Na_4Al_3Si_3O_{12}Cl$, with a three-dimensional skeleton formed by the linkage of silicon–oxygen tetrahedra, and in tugtupite,[149] where the isomorphous substitution is of the type $2Al^{3+} \rightleftharpoons Be^{2+}Si^{4+}$. Beryllosilicates with the analcime structure have been synthesised[150,151] at 150–400 °C in the course of 1–3 weeks from gels having the composition $NaBe_{1.5}Si_2O_6$ and $Na_3Be_{1.5}.Si_{4.5}O_{12}.NaCl$. The formula $Na_{16}Be_8Si_{40}O_{96}(H_2O)_{16}$ has been proposed for the final product. Its derivatograms showed an exothermic peak at 150–500 °C. The authors attributed its appearance to the removal of zeolitic water.

It has been noted[151] that the size of the unit cell and the refractive index of the products formed decrease linearly with increasing degree of isomorphous substitution $2Al^{3+} \rightleftharpoons Be^{2+}Si^{4+}$. These facts are regarded as proof of the occurrence of isomorphous substitution. Thus the unit cell of $Na_3Al_{2x}Be_{1.5-x}Si_{5-x}O_{13(4-2x)}$, synthesised under condtions with $0 \leq x \leq 1.5$, varies from 13.72 Å for the zeolite without Be^{2+} cations to 13.36 for beryllosilicate, while the refractive index varies correspondingly from 1.48 to 1.519.

The state of the Be^{2+} cations in the solid state can be investigated by NMR. The interpretation of the ^9Be NMR spectra is made difficult by the high sensitivity of the spin–lattice relaxation, which requires an exact determination of the strengths of the pulse for each specimen analysed, and by the low intensity of the signal obtained. The $[Be(H_2O)_4]^{2+}$ ion gives rise to a narrow resonance line at 50 and 1000 Hz, which indicates a symmetrical tetrahedral environment with quadrupolar interaction whose extent is close to zero.

It has been concluded[152] that a Be^{2+} ion in a tetrahedral environment gives rise to an NMR signal in a stronger field than the same ion in the tricoordinate state. A Be^{2+} ion in a three-membered environment gives rise to a ^9Be NMR signal with a chemical shift δ, relative to $[Be(H_2O)_4]^{2+}(NO_3)_2$, ranging from −21 to −11 p.p.m., while the same ion in a tetrahedral environment gives rise to a signal ranging from −12 to +1 p.p.m. The substitution of the negative ions of the environment by ions with a higher negative charge leads to a downfield shift of the signal. The introduction of strong bases into the environment of Be^{2+} causes an upfield shift of the signal. For example, the substitution of CH_3^- by Cl^- in the first coordination sphere of the Be^{2+} cation results in a shift of the NMR line from −4.2 to −5.5 p.p.m. The ^9Be NMR spectra of $BeCl_2$ in dimethyl sulphoxide, diethyl ether, and ammonia have $\delta = -5.5$, −3.1, and −1.7 p.p.m. respectively.

The state of Be^{2+} in beryllosilicates with the zeolite ZSM structure was investigated by the ^9Be NMR method for the first time by Ione and co-workers.[132,133,137] The spectra consisted of a single signal, whose chemical shift relative to that of ^9Be in the spectrum of sodium beryllate was −5.8 p.p.m. (Fig. 7*a*). The character of the spectrum differs also from that of beryllium oxide. The intensity of the ^9Be NMR signal is proportional to the amount of beryllium determined by chemical analysis. Comparison of the ^9Be NMR signal intensity and the Be^{2+} content determined by chemical analysis showed that most of the Be^{2+} ions in the silicate synthesised are fixed in the crystalline silicon–oxygen skeleton.[153]

7. The State of P^{5+}

Like Si^{4+}, the P^{5+} cation can have a tetrahedral oxygen environment and can form a three-dimensional phosphorus–oxygen skeleton. Bearing in mind the similarity of the radii of the above cations, one may expect the occurrence of the isomorphous substitution $PO_4^{3-} \rightleftharpoons SiO_4^{4-}$. In nature, this phenomenon has been observed in the mineral viséite, which is a structural analogue of analcime.[24]

Phosphorus-containing crystalline silicate with the analcime, chabazite, phillipsite-harmotome, and type A, L, and B(P) zeolite structures, containing 5–25% [of phosphorus? (Ed.of Translation)], have been synthesised.[154] It has been established that the lattice constant diminishes with increasing P_2O_5 content in the type Y zeolite (thus a = 12.249 Å in the presence of 5.2% of P_2O_5 and a = 12.232 Å in the presence of 10% of P_2O_5). The increase of the cell parameter is caused

by the fact that the length of the P–O bond (1.54 Å) is smaller than those of the Si–O (1.61 Å) and Al–O (1.75 Å) bonds. With increase of the P_2O_5 content in the type A zeolite, the intensity of the refraction also changes almost linearly. These data enabled the authors[154] to conclude that the $Si^{4+} \rightleftharpoons P^{5+}$ isomorphism occurs in the type A zeolite synthesised.

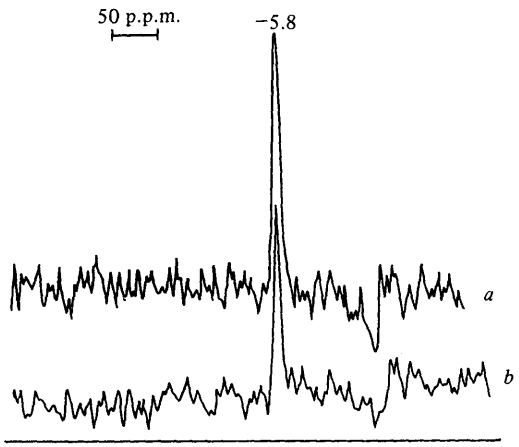
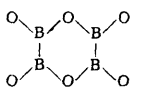


Figure 7. The ^9Be NMR spectrum of crystalline beryllosilicates; SiO_2/BeO_2 ratio in initial hydrogel: *a*) 60; *b*) 30.[137]

8. The State of B^{3+}

It has been established that B^{3+} cations in a tetrahedral coordination are present in the BF_4^-, BH_4^-, $[HB(OR)_3]^-$, and $[B(C_6H_5)_4]^-$ anions. In compounds with oxygen, boron forms either a planar structural BO_3^- unit with angles of 120° between the bonds or boron–oxygen tetrahedra (in glasses). In solutions, $B(OH)_3$ polymerises with formation of cyclic polymers, whose presence has been established also in crystalline borates. The latter include both BO_3^- groups and BO_4^- groups and consist of six-membered rings of the type



This has been demonstrated by ^{11}B NMR.

The boron phosphate BPO_4, obtained by the interaction of boric and phosphoric acids, includes a tetracoordinate boron atom; the phosphate contains B–O–P linkages.[140]

Borosilicates and aluminoborates with zeolite structures have been synthesised in many studies. The substitution of Si^{4+} by B^{3+} cations in the zeolite skeleton was not demonstrated by Barrer and Marchilly.[155] It has been suggested[156] that boron cations are occluded in the zeolite cavities in the compound $NaBO_2$ or $NaB(OH)_4$. These conclusions conflict with data[157] according to which all the unit cell parameters of borosilicates decrease almost linearly with increase of their B_2O_3 content (Table 8). The B_2O_3 content was determined from the amount of the carbon-containing precursors of borosilicates. Simultaneously with increase of the ratio B/(B + Si), a transition from the monoclinic to the orthorhombic system was observed.

The state of the B^{3+} ions in a silicate isostructural with the zeolite ZSM-11 has been studied systematically as a function of the conditions of their synthesis;[132,133,135,136] the elementosilicates were synthesised by the method of Ione et al.[130] Two lines were observed in the ^{11}B NMR spectra of borosilicates—a symmetrical narrow line with a width of ~1.7 kHz and a chemical shift of −23.3 p.p.m. (signal I) and a broad line with $\delta = -17 - 64$ p.p.m. (signal II).[135]

Table 8. The unit cell parameters as a function of the ratio B/(B + Si) in borosilicates with the zeolite structure.[157]

B/(B + Si)	*a*, Å	*b*, Å	*c*, Å	*d*, Å	*v*, Å³
0	20.117	19.874	13.371	90.62	5345.5
0.007	20.087	19.852	13.364	90.46	5329.3
0.016	20.050	19.822	13.372	90.00	5314.3
0.022	20.022	19.816	13.340	90.00	5292.6
0.041	20.002	19.805	13.334	90.90	5282.1
0.049	19.974	19.774	13.306	90.90	5255.9
0.109	19.934	19.716	13.269	90.00	5215.0

The NMR spectra of the glasses usually show two types of lines due to the boron atoms in different coordination environments.[158] At a frequency of 30 MHz, a second-order quadrupolar splitting of ~15 kHz occurs for boron atoms in ternary coordination, which corresponds to a quadrupolar interaction constant of ~2 MHz. For tetracoordinate boron atoms, the quadrupolar interaction constant is much smaller. As a result of the latter, the spectrum of boron in a tetrahedral oxygen environment does not exhibit second-order splitting even at low frequencies; the line due to boron atoms in a tetrahedral environment is comparatively narrow and symmetrical. As a result of this, the narrow symmetrical line I, observed in the NMR spectra of borosilicates, can be assigned to boron atoms in a tetrahedral oxygen environment.

With increase of the ratio OH/SiO_2 in the initial borosilica sol, the chemical shift of the ^{11}B NMR signal in the spectra of the resulting borosilicates did not change, but the intensity of the main spectral line with $\delta = -23.3$ p.p.m. (signal I) [135] diminished. The degrees of crystallinity of the corresponding borosilicate change in the same sequence (NaB-0.1 > NaB-0.2 > NaB-0.3) with virtually identical total B_2O_3 contents in these substances (Table 9). The increase of the crystallisation time from 48 to 144 h (NaB-0.1 specimens) led to a comparatively small decrease of the intensity of signal I without change in the chemical shift and line width. The degree of crystallinity of the corresponding specimens (NaB-0.1 series) hardly changed under these conditions, but their B_2O_3 content diminished somewhat. With decrease of the B_2O_3 concentration in the specimens (from 4 to 0.7%), the intensity of signal I in the ^{11}B NMR spectra also fell.

Comparison of all the data enabled the authors[135,137] to postulate that signal I with $\delta = -23.3$ p.p.m. corresponds to boron atoms fixed in the crystalline part of the borosilicate synthesised as part of the composition of the silicate skeleton. Significant differences have been observed between the ^{11}B NMR spectra of freshly prepared specimens and the same specimens after a test in the catalytic conversion of methanol and after subsequent regeneration by annealing in air at 520 °C. The intensity of signal I in the

^{11}B NMR spectra decreases sharply, while the intensity of the broad band increases. In the course of the treatment of borosilicates at elevated temperatures in the presence of water vapour, the Si–O–B linkages are probably hydrolysed with the accompanying displacement of the B^{3+} cations from sites with a tetrahedral oxygen environment.[137]

Table 9. The influence of the ratio OH/SiO_2 in the initial mixture and of the crystallisation time τ on the content of the borosilicate phase isostructural with the ZSM-11 zeolite (crystallisation temperature 150 °C, SiO_2/B_2O_3 = 60).[135]

Specimen	OH/SiO_2	τ, h	$[B_2O_3]$, wt.%	S, m^2g^{-1}	CZP, %	I_{rel}
NaB-0.1	0.1	48	1.6	570	90	1.0
	0.1	78	1.5	580	100	0.9
	0.1	120	1.4	530	95	0.8
	0.1	144	1.2	540	90	0.7
NaB-0.2	0.2	48	1.8	170	30	0.4
NaB-0.3	0.2	120	1.1	120	16	—
	0.3	48	2.1	180	20	0.2

Notation: $[B_2O_3]$ = B_2O_3 concentration in the silicate and I_{rel} = relative intensity of signal I in the ^{11}B NMR spectrum.

9. The State of Ga^{3+}

The structure and properties of the oxygen-containing Ga^{3+} compounds are similar to those of aluminium oxides.[140] Gallium trioxide ε-Ga_2O_3 as well as gallate ions contain both tetracoordinate and octacoordinate Ga^{3+} ions.

Chabazite and phillipsite have been synthesised[159] in the presence of Ga^{3+} cations, but evidence for the isomorphous substitution of Si^{4+} by Ga^{3+} was not published. A type X zeolite has been synthesised[160] in the presence of Ga^{3+} cations and a change in the unit cell parameters was observed. Sodalite with the ratio $SiO_2/(Ga_2O_3 + Al_2O_3)$ = 1.28 and Na-GaX (1.14), Na-GaX (1.42), and Na-GaY (2.17) faujasites have been obtained[16] by the hydrothermal method. The Al_2O_3 content in these silicates was ~1% of the amount of Ga_2O_3 introduced. The state of the Si^{4+} and Ga^{3+} ions in the zeolite was investigated by ^{29}Si and ^{71}Ga NMR respectively and it was shown that the intensity of the NMR signal depends on the Si/Ga_2O_3 ratio, which was determined by chemical analysis.[160,161]

Comparison of the chemical shifts of the ^{29}Si NMR signals of zeolites having the silicon–oxygen composition and their gallium analogues[160,161] showed that the introduction of Ga instead of Al diminishes somewhat the shift of the peaks corresponding to the $Si-(OM)_n$ groups, where M = Ga or Al. The intensity of the peaks corresponding to the Si–OM and $Si-(OM)_2$ groups in the case of Ga-sodalite is smaller than for the Al–Ga-zeolites.

A ^{29}Si NMR signal, whose chemical shift is also smaller than in the case of the aluminium-containing analogues, is characteristic of type X and Y gallium-containing zeolites. The relative intensities of the peaks in the ^{29}Si NMR spectra of Ga- and Al-faujasites are similar, which indicates the identical character of the distribution of the corresponding elements in both cases.

The ^{71}Ga NMR signal of the zeolite Ga-Y, obtained by Thomas et al.[161], is broad and its chemical shift relative to $Ga(NO_3)_3$ is −182.5 p.p.m. The ^{29}Si NMR signal with δ = −75.5 p.p.m. has been assigned to $Si-(OGa)_4$ and that with δ = −81.5 p.p.m. has been assigned to $Si-(OGa)_3$. The ^{29}Si NMR spectrum of Ga-thomsonite includes signals with δ = −82.9 and −83.5 p.p.m. The MAS ^{71}Ga NMR spectrum has been measured[132,137] for a gallosilicate with the ZSM-11 structure, obtained by the method of Ione et al.[130], and was found to contain one broad band with a chemical shift relative to $Ga(NO_3)_3$ of 154–155 p.p.m. (Fig. 8).

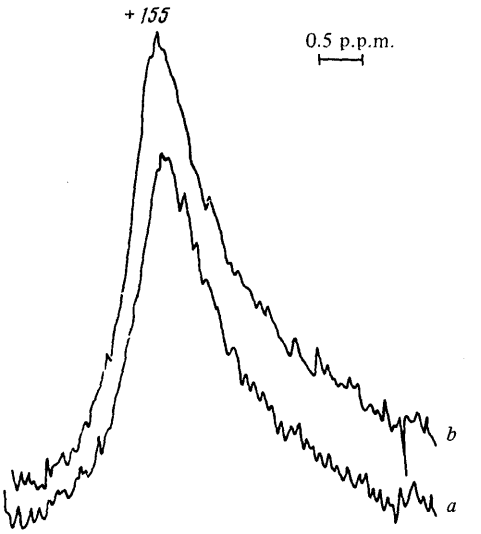


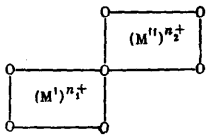
Figure 8. The ^{71}Ga NMR spectrum of crystalline gallosilicates with the ZSM-11 structure; SiO_2/Ga_2O_3 ratio in the initial silica sol: *a*) 60; *b*) 30.[137]

The set of data obtained by the ^{29}Si and ^{71}Ga methods justifies the assumption that the degree of isomorphous substitution and the character of the distribution of the Ga^{3+} ions in the silicon–oxygen skeleton are similar to the corresponding parameters for Al^{3+}.

Thus, depending on the type of the cation and the conditions in the hydrothermal treatment of the initial gel in the thermochemical treatment of the finished products, the modifying element M^{n+} can be fixed (1) in the composition of the individual (oxide or hydroxide) phase within cavities or outside the silicate crystals with the corresponding octahedral (for transition metal cations) and ternary (for boron) coordination, (2) in cationic sites in the form of species neutralising the negative charge of the skeleton, and (3) in the silicon–oxygen skeleton with a tetrahedral symmetry of the environment comprising oxygen atoms at sites isomorphous with respect to those of the Si^{4+} cations. The catalytic properties of the silicates should depend significantly on the state and the degree of coordination of the M^{n+} cations. Thus in the first case the individual phase can behave under the reaction conditions as an inert additive or can exhibit catalytic activity in oxidation-reduction reactions. The conversion of methanol on silicates with such additives can proceed with decomposition to CO and H_2. The M^{n+} cations fixed in silicates in accordance with types 2 and 3 should influence the acid–base properties of the latter.

V. CATALYTIC PROPERTIES

Crystalline silicates with zeolite structures (elementosilicates) are binary oxide systems like zeolites themselves. According to general ideas developed by Pauling[1] and Tanabe,[1,2] the acid–base properties of the binary oxides are determined by the incomplete compensation of the charges of the oxygen ions in polyhedra differing in the charges of their cations. Thus an uncompensated charge Z is generated on the oxygen atoms of the two polyhedra $M'O_4$ and $M''O_4$



with $n_1 \neq n_2$. According to Pauling's second rule,[162] the charge of the anion must be equal to the sum of the electrostatic forces of the bonds between the anion and the surrounding cations. The electrostatic strength of the bond is defined by Pauling as the ratio of the charge of the cation (en_i) to its coordination number (c). Hence the following formula is obtained for oxygen atoms in binary oxides:

$$Z = \frac{en_1}{c} + \frac{en_2}{c}.$$

The formation of a proton-donating centre on a polyhedron with an excess charge takes place (*a*) on substitution of the cation, compensating for the excess charge of the polyhedron, by a proton; for example, we have for silicates with a tetrahedral coordination of the cation

$$[(OSi)_n(OM)_{4-n}]^{(4-n)-} \cdot Na^+ \xrightarrow[-Na^+]{+H^+} [(OSi)_n(OM)_{4-n}]^{(4-n)-} \cdot H^+.$$

(b) In the heterolytic dissociation of water molecules in the field of the oxygen atoms of the polyhedron and the cation compensating for the charge:

$$[(SiO)_n(MO)_{4-n}]^{(4-n)-} \cdot H^+ + \ldots OH^- — M^{n+}.$$

The energy of the $\rangle O \ldots H$ bond in the $\begin{matrix} M \\ \diagdown \\ \rangle O \ldots H \\ \diagup \\ Si \end{matrix}$ group should diminish in a series of polyhedra with the cations $M^+ > M^{2+} > M^{3+}$, because the excess charge on the oxygen atoms decreases in the same sequence. For this reason, if the mobility of the proton in the $[(SiO)_n(MO)_{4-n}]^{(4-n)-}H^+$ group is adopted as a measure of its proton-donating activity, then the mobility should decrease in the sequence $M^{3+} > M^{2+} > M^+$.

Thus the proton-donating activity of silicates incorporating triply charged ions at sites isomorphous with those of Si^{4+} should be greater in the presence of doubly and singly charged cations.

Evidently the strength of the acid centres of silicates incorporating M^{n+} cations with identical charges should depend on the radius of the cations. The strength of the acid centres has been compared[163] with the difference between the electrostatic potentials (ΔV) of the BO_x and AO_y polyhedra at the sites of the B → A substitution:

$$\Delta V = \sum_i (q_i/r_i)_{BO} - \sum_i (q_i/r_i)_{AO},$$

where q_i is the charge of the ion at a distance r_i from the site A in the $BO_x.nAO_y$ matrix.

If one begins with the fact that the degree of polarisation of the O–H bond in the $[(SiO)_n(OM)_{4-n}]^{(4-n)-}H^+$ group depends on the electrostatic potential e/r in the field of the cation M and if the M–O bond length in the silicate is the same as in the oxide of M, then the acidity of the OH group in silicates incorporating triply charged cations should diminish in the sequence $B^{3+} > Al^{3+} > Ga^{3+} > Fe^{3+} > In^{3+}$ with decrease of e/r for these cations. However, this approximation has little predictive power, because the assumption of the equality of the M–O bond lengths in the silicate and the oxide has not been confirmed experimentally.

No studies have been published hitherto in which the variation of the strength of the acid centres of silicates was estimated as a function of the nature of the cation M^{n+} substituting Si^{4+} isomorphously in the silicate skeleton. So far there have been few studies in which the strength of the acid centres of such systems has been determined experimentally. Their comprehensive investigation is only beginning. The ^1H NMR method has been applied[164] in a comparative determination of the proton-donating strength of the OH groups in the zeolite ZSM-5 and borosilicate (H-borolite). The authors based their conclusions on the assumption that the chemical shift of the ^1H NMR signal reflects the degree of shielding of the proton nuclear spin by electrons and can serve as a measure of acidity. The authors observed that the ^1H NMR spectra of the two specimens each contain two signals—with δ = 6 and 2 p.p.m. (ZSM-5) and 3.5 and 2 p.p.m. (H-borolite). The signal at δ = 2 p.p.m. was assigned to the Si–OH groups, that with δ = 3.5 p.p.m. to the Si–O–B groups, and that with δ = 6 p.p.m. to the Si–O(H)–Al groups. The authors[164] concluded that the acidity of the OH group also increases in this sequence.

The catalytic activity of the solid surface is known to depend not only on the strength but also on the concentration of the active centres present on it. It has been established[165] on the basis of the relative intensities of the ^{11}B NMR signals of the boron cations having tetrahedral and ternary coordination in borosilicates with zeolite structures that only 5–10% of the total number of the B^{3+} detected in the specimens by chemical analysis is fixed in the former state.

It has been demonstrated[147] by ^{11}B and ^{71}Ga NMR that not more than 10–20% of the total amount of the elements which were determined by chemical analysis in the hydrothermal crystallisation product are present in a tetrahedral oxygen environment in zeolites with the erionite structure synthesised in the presence of the B^{3+} and Ga^{3+} cations.

Thus the true concentration of the cations substituting isomorphously the silicon atom in the silicon–oxygen skeleton and hence also the number of the catalytically active centres can be much less than the total content of the given element in the silicate. The latter factor hinders the determination of correlations between the nature of the M^{n+} cations fixed at isomorphous sites and the catalytic properties of the silicates. Nevertheless the data considered above show that the hydrothermal synthesis of the sources of SiO_2 in the presence of sources of multicharged M^{n+} cations leads to the formation of silicates with the zeolite structure, whose catalytic properties differ from those of aluminosilicate zeolites.

1. Germanium-containing Elementosilicates

The catalytic properties of the NaGe–X faujasite, synthesised from the Al–Ge gel and having the composition $Na_{75.8}(NH_4)_{20.2}(AlO_2)_{96}(GeO_2)_{96}$ have been investigated[166] in the isomerisation reaction of n-butenes at 150–350 °C. Comparison of the properties of the faujasites based on Al_2O_3–SiO_2 (HX and HY) and Al_2O_3–GeO_2 (HGeX) led to the following findings.

1. For high degrees of ion exchange, significant breakdown of the crystal lattice of the germanosilicate is observed as a consequence of the lower stability of the germanium–oxygen zeolite skeleton compared with that of the silicon–oxygen skeleton having an analogous structure.

2. In the presence of HGeX specimens, the isomerisation of n-butenes proceeds in accordance with a first-order equation without change in the kinetic parameters for 3.5 h, while in the presence of HX and HY the first order of the reaction is maintained only in the first 6 min after the start of the experiment. The catalytic activity of the zeolite HY falls during 1.5 h by a factor of 7, while the activity of HGeX does not change during this period.

3. The activation energy and selectivity of the process are close to those observed for HX and HY when the reaction is carried out in the presence of HGeX.

4. The rate of reaction, referred to a single active centre, and the average acidity of the OH groups diminish with increase of the Si, Ge/Al ratio in the zeolite HGeX. The process proceeds, as for the HY and HX catalysts, with participation of Brønsted acid centres.

2. Boron-containing Elementosilicates

Boron-containing faujasites have been investigated in the cracking of cumene[39] and it has been shown that their catalytic properties resemble those of the Al, Si-faujasites.

Data[55,58] concerning the catalytic properties of boron-containing silicates (borolites) in the synthesis of t-butyl methyl ether (TBME) from methanol and isobutene are of great interest. It has been shown that at 150–170 °C it is possible to attain a high degree of conversion of the initial reactant and that the yield of TBME in the presence of type B, C, and D borolites is 96–99.3%. The borolites proved to be highly selective and stable catalysts of the decomposition of TBME to isobutene and methanol over a wide temperature range; they ensure a selectivity of 99.8% and do not induce the subsequent conversion of isobutene and methanol. In contrast to this, in the presence of aluminosilicate zeolites methanol can be dehydrated with subsequent redistribution of hydrogen in the resulting olefins. The type C borolite acts as a catalyst of the alkylation of benzene by ethylene at 450 °C, a space velocity of 4 h^{-1}, and for the ratio benzene/ethylene = 5.[69,70]

According to the data in Ref.71, borolites are catalytically inactive in the synthesis of hydrocarbons from methanol. Bragin et al.[67] arrived at the opposite conclusion having established that borolites with the zeolite structure exhibit a high activity and selectivity in this reaction. The catalytic properties of borosilicates in the synthesis of hydrocarbons from methanol have been investigated[129–137] as a function of the state of the boron atoms in the silicate skeleton and of the content of the Al^{3+} admixture in them. Under the same conditions, the highest degree of conversion was attained in the presence of boron-containing aluminosilicates with SiO_2/Al_2O_3 ratios of 126 and 220 (Table 10, specimens 1 and 2). The catalytic properties of these specimens are typical for type ZSM zeolites with the same SiO_2/Al_2O_3 ratio. At 380 °C the degree of conversion of methanol is close to 100% and the fraction of C_5 and higher hydrocarbons is 57 to 60% of all the hydrocarbon reaction products and includes 16–27% of aromatic compounds.[136]

The borosilicates in which the Al_2O_3 content is very low ($SiO_2/Al_2O_3 > 1000$) and the SiO_2/B_2O_3 ratio is 25 and 46 have sharply different catalytic properties from those of aluminosilicates (Table 10): at 380 °C the main reaction product is dimethyl ether and C_2–C_7 olefins. The content of aromatic hydrocarbons in the reaction products is less than 2%.[135] With increase of the reaction temperature from 380° to 500 °C, the content of dimethyl ether in the reaction product falls (from 54 to 56% for specimens with $SiO_2/B_2O_3 = 30$), while that of aromatic and aliphatic hydrocarbons increases sharply (from 1.2 to 13.6 and from 32.5 to 67.8% respectively). However, after the reaction–regeneration cycle, the selectivity of the action of the catalysts changes: the selectivity diminishes with respect to the higher hydrocarbons and increases with respect to dimethyl ether.

Table 10. The degree of conversion of methanol and the composition of the reaction products in the presence of boron-containing silicates* with the ZSM-11 structure.[36]

Silicate	Chemical composition of silicate			α**, %	Composition of carbon-containing reactions products, %				
	[Na_2O], wt.%	SiO_2/B_2O_3	SiO_2/Al_2O_3		DME***	C_2–C_7 olefins	aromatic hydrocarbons	C_5 and higher fractions	C_1–C_4 fractions
Boroaluminosilicate-1	0.08	37	126	100	traces	—	27.4	57.0	43.0
Boroaluminosilicate-2	0.12	102	220	100	10.2	—	16.2	61.6	28.2
Borosilicate No.3	0.03	25	1000	76	54.3	32.5	1.2	10.4	2.8
Borosilicate No.4	0.05	46	1000	69	79.1	15.6	1.6	4.3	1.0
Borosilicate No.5	0.05	135	1000	42	100.0	0	0	0	0
Silicalite	0.05	—	1500	1–2	100	0	0	0	0

*Reaction temperature 380 °C, contact time (gas phase) 20–30 s, methanol content in mixture 20 vol.%, pressure 1 atm.

**Degree of conversion of methanol.

***Dimethyl ether.

Cyclic compounds were not detected in the reaction products for specimens with $SiO_2/B_2O_3 = 135$ and silicalite (Table 10). These results show that the high catalytic activity of boron-containing zeolites in reactions involving the synthesis of aliphatic and aromatic hydrocarbons from methanol, observed in some investigations, is due to admixtures of aluminium. Nevertheless, there is a relation between the content of B_2O_3 in borosilicates and the degree of conversion of methanol, which supports the hypothesis that the B^{3+} cations enter into the composition of the active centres. However, as shown above, a considerable proportion of the boron cations are displaced from the silicate skeleton on elimination of cations and in the reaction–regeneration cycles. The boron atoms remaining in the tetrahedral coordination at sites isomorphous with those of silicon (or aluminium) atoms apparently constitute a significant proportion of the entire B_2O_3 introduced.

It has been established in a number of studies[167–171] that borosilicates with the structure of type ZSM zeolites are highly selective catalysts of the synthesis of olefins from methanol. The content of aromatic hydrocarbons in the reaction products obtained[168] at 500 °C and for a 100% degree of conversion of methanol in the presence of borosilicates was 5.4–13.8% and the selectivity with respect to the sum of the C_2–C_4 olefins was 56–70.9%. After treating the borosilicate having the ratio $SiO_2/B_2O_3 = 35$ with hydrochloric and hydrofluoric acids, its selectivity with respect to olefins increased to 78.9%. The same result was obtained in other investigations[169,170] at a reaction temperature of 550 °C. It is known that the content of olefins in the products obtained in the presence of aluminosilicate zeolites with the same

structure (pentasil) and under the same conditions is not more than 20–30%, while the content of aromatic hydrocarbons in C_5 and higher fractions is up to 60–80%.

The appreciably lower catalytic activity of borosilicates compared with aluminosilicates containing approximately the same amount of B_2O_3 has been attributed[135,137,171] to two causes: (1) the catalytic activity of the $Si-(OB)_n$ groups of the silicate skeleton in reactions involving an acid–base mechanism is appreciably lower than that of the $Si-(OAl)_n$ groups; (2) the actual content of boron cations in the silicon–oxygen skeleton at isomorphously substituted sites is extremely low.

3. Elementosilicates with Transition Metal Cations

The catalytic properties of silicates where the Cr^{3+}, Pt^{4+}, V^{4+}, Mo^{6+}, and Zn^{2+} cations were introduced into the initial mixture before hydrothermal synthesis have been investigated[82] in the disproportionation of toluene. The disproportionation was carried out in an atmosphere of hydrogen at a pressure of 400 N cm^{-2}, for the ratio H_2/hydrocarbons = 2, and at temperatures in the range 455–593 °C. The degree of conversion of toluene reached 14–31.8%. The same catalysts were tested in the hydrocracking of the petroleum fraction with T_{nb} = 107–185 °C at a pressure of 70 N cm^{-2}, for the ratio H_2/hydrocarbons = 3, and at temperatures in the range 480–540 °C.[106]

Silicates with the ZSM-5 structure, synthesised in the presence of Cr^{3+}, have been investigated in the alkylation of toluene by methanol. It has been established that the chromosilicates (Cr–ZSM) with SiO_2/Cr_2O_3 ratios of 107 and 38.5 differ in the selectivity of their action from aluminosilicates with the same type of crystal structure (Al–ZSM). For a degree of conversion of methanol of 21–23%, the selectivity with respect to the total xylenes in the presence of chromosilicates was 94–99.2%. The content of *p*-xylene among all the xylene isomers then reached 90.9–58.2%, which is much higher than the equilibrium content (25%). For the chromosilicate impregnated with boric acid, the content of xylenes in the reaction products at 450° and for a degree of conversion of toluene of 20.13% was 86.28% and the content of *p*-xylene among all the xylenes was 74.55% under these conditions. At 500 °C and for a degree of conversion of toluene of 24.1%, these values were respectively 92.36 and 72.7%. The authors[172] suggest that the high *para*-selectivity of the chromosilicates is due to several causes: the influence of diffusion-dependent limitations, a higher concentration of strong acid centres than in aluminosilicates, etc. The ferrosilicates with the crystal structure of zeolites of the pentasil group have been tested as catalysts of the isomerisation of xylenes.[173] The content of p-xylene in a mixture of aromatic hydrocarbons containing xylenes and ethylbenzene increased as a result of the isomerisation reactions in the presence of ferrosilicates at 340 °C and atmospheric pressure from 7.4 to 14.5% (to 14.4% in the presence of aluminosilicate), while the content of *m*-xylene diminished from 55 to 40.1%.

The conversion of methanol has been investigated in the presence of a phosphorus-containing silicate with the ZSM structure.[82] The reaction was carried out in an atmosphere of H_2 at a pressure of 3.5 atm, with the ratio H_2/hydrocarbons = 2, and at temperatures of 372° and 400 °C. The specificity of the action of this catalyst compared with aluminosilicate zeolites is difficult to judge on the basis of the data presented,[82] because the content of aluminium in each specimen is not indicated. This precludes the estimation of the influence of the modifying element on the catalytic properties of the silicates synthesised.

Aluminosilicate zeolites with the chabazite and erionite–offretite structures have been synthesised[151] from gels containing sources of boron, titanium, gallium, and zironium. Catalytic data are presented for lanthanum-containing chabazite and erionite. The selectivity in the synthesis of olefins from methanol proved to be higher by 1–2% (82 to 83%) in the presence of these catalysts than in the presence of the H-form of chabazite not containing lanthanum (81%). It was demonstrated in the same studies that the selectivity of the action of type ZSM-5 zeolites, synthesised in the presence of sources of Zr^{4+} and Ti^{4+}, in the synthesis of olefins from methanol is higher by 8–9% (64–65%) than for the usual ZSM-5 zeolite (56%). However data concerning the content of Al_2O_3 in the test specimens and the state of the titanium and zirconium cations are not presented in the above communication.

A detailed study has been made of the catalytic properties of silicates with the structure of ZSM zeolites, synthesised in the presence of transition metal cations but without the addition of sources of aluminium, in reactions involving the synthesis of hydrocarbons from methanol.[129–137] The catalytic properties of the silicates synthesised were compared with those of crystalline silicon oxides having the structure of the ZSM-11 zeolite (silicalite) with the composition $0.02Na_2O.Al_2O_3.1000\ SiO_2$ and obtained by a method analogous to that of Ione et al.[130] At 380 °C methanol is converted to an extent not more than 50% in the presence of silicalite and the main reaction product is dimethyl ether (88–99%); hydrocarbons were also formed in trace amounts. The activity of silicalite was accounted for by the presence of the Al^{3+} admixture at sites isomorphous with respect to those of the Si^{4+} cation. A similar low activity and selectivity with respect to C_2–C_{10} hydrocarbons and a high selectivity with respect to dimethyl ether was shown by silicates containing the V^{4+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Eu^{3+}, and In^{3+} cations.

According to the data of Vostrikova et al.[134], the degree of conversion of methanol in the presence of manganese-containing silicates was 2–5% and the main reaction product was dimethyl ether. The low catalytic activity was observed both for the specimen where 90% of the manganese (according to EPR data) was in the state of Mn^{2+} ions and for the specimen in which 90% of the manganese introduced was not detected by EPR.

The silicates of the triply charged Ga^{3+} and Fe^{3+} ions as well as beryllium silicates manifested a high catalytic activity in the conversion of methanol into hydrocarbons.[132,133] The selectivity with respect to C_2–C_{10} hydrocarbons at 410–450 °C was 60–98% (Table 11). In the presence of type ZSM-5 and ZSM-11 zeolites, the degree of conversion of methanol under the conditions investigated was not less than 95–98%. The reaction products contained 22–38% of light C_1–C_4 hydrocarbons and 60–70% of liquid hydrocarbons. Mainly propane and butane were detected in the C_1–C_4 fraction, while the C_5 and higher fractions were found to contain aliphatic aromatic alkyl-substituted compounds. The overall content of products agreed on the whole with that quoted in a review.[26] The amount of aromatic hydrocarbons in the reaction product increased with decrease of the ratio SiO_2/Al_2O_3 in the catalyst. Thus, it amounted to 46% for SiO_2/Al_2O_3 = 38 and to only 22% for SiO_2/Al_2O_3 = 280.[137]

A series of studies have been carried out in which the combined substitution of the Si^{4+} cations by aluminium atoms and another cation (Cu–Al, Al–Fe, etc.) was achieved.[174] The introduction of copper or iron ions into the aluminosilicate at the hydrothermal synthesis stage altered the selectivity of their action. Thus, for the same Al_2O_3 content, the amount of aromatic hydrocarbons in the reaction products, obtained from methanol, was less in the presence

of aluminoferro- and aluminocupro-silicates and greater in the presence of aluminosilicates. A sharp change in the selectivity of the action of silicates was attained after the complete replacement of Al^{3+} by Fe^{3+} in the latter. Thus the amount of aromatic reaction products did not exceed 10% in the presence of iron silicates whose Al_2O_3 content is at the level of impurities (less than 0.1%) and the Fe_2O_3 content is not less than 1.5%. On the whole, the fraction of aromatic hydrocarbons in the product obtained under the same conditions in the presence of catalysts with identical Al_2O_3 or Fe_2O_3 contents (Fig. 9) diminished in the sequence SiO_2–Al_2O_3 > SiO_2–Al_2O_3–CuO > SiO_2–Al_2O_3–Fe_2O_3 > SiO_2–Fe_2O_3.

Table 11. Catalytic properties of silicates with the zeolite structure containing Group I–VIII elements in methanol conversion reactions.

Modifying element	SiO_2/M_nO_m	α, %	Products, wt.%			α, %	Products, wt.%		
			CO, CH_4	DME	C_2–C_{10} hydrocarbons		CO, CH_4	DME	C_2–C_{10} hydrocarbons
		Reaction temperature 380 °C				Reaction temperature 410 °C			
—	1000	2.5	0.4	99.6	—	69.4	2.4	88.1	9.5
Pb	443	41.0	0.2	99.8	—	41.2	3.2	96.8	—
Se	1000	66.0	0.3	99.7	—	76.0	1.7	97.9	0.4
Te	335	6.0	3.0	97.0	—	40.0	0.5	97.5	2.0
Sn	280	25.3	12.3	87.3	—	31.9	21.3	78.7	—
Sb	535	18.0	18.4	81.6	—	29.0	51.2	48.8	—
Eu	1000	25.0	21.5	78.5	—	37.0	46.5	51.2	2.3
Zn	78	5.8	58.3	41.7	—	39.0	80.0	20.0	—
Mn	77	2–5	—	100.0	—	—	—	—	—
Ti	367	2–5	—	100.0	—	29.0	51.2	48.8	—
In	663	29.0	—	100.0	—	57.0	0.4	99.2	0.4
V	480	45.0	—	100.0	—	43.0	—	100.0	—
Cr	112	45.6	7.3	92.4	0.3	61.0	23.0	75.2	1.8
Nd	700	39.0	1.2	97.7	1.1	45.0	1.7	96.6	1.7
Be	91	82.5	0.4	81.0	18.6	87.2	1.1	50.3	48.6
B	46	69.6	1.1	79.0	19.9	74.0	5.3	24.9	69.7
Ga	210	93.5	0.7	6.4	92.9	97.0	0.9	1.0	98.1
Al	58	96.0	0.5	—	99.5	99.6	1.2	—	98.8
Fe	57	84.0	2.0	12.7	85.3	96.5	2.5	2.5	95.0
Fe	109	86.0	0.7	37.4	61.9	92.5	1.2	7.4	91.4

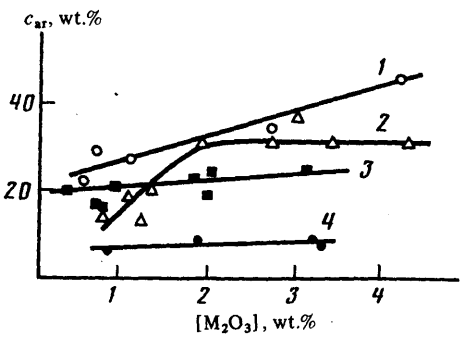


Figure 9. The content of aromatic compounds (c_{ar}) in the hydrocarbon methanol conversion products as a function of the M_2O_3 content in the crystalline silicate with the ZSM-11 structure (for reaction at 380 °C); rate of supply of liquid methanol 1 h^{-1}; composition of silicate: *1*) SiO_2–Al_2O_3; 2) SiO_2–Al_2O_3–CuO; 3) SiO_2–Al_2O_3–Fe_2O_3; 4) SiO_2–Fe_2O_3.[174]

Thus, for the same M_2O_3 content in the silicate, the aromatisation reactions proceed at the lowest rate in the presence of iron-containing silicates and at the highest rate in the presence of aluminosilicates. Analysis of the aliphatic component of the hydrocarbons formed demonstrated that the fraction of hydrocarbons with a chain length of C_5 and above diminishes in the same sequence owing to the increase of the fraction of the light C_3–C_4 paraffins and, in the presence of the SiO_2–Fe_2O_3 system, also the C_3–C_4 olefins.[174]

A dependence of the rate of conversion of methanol (k), referred to one mole of M_2O_3 in a silicate with triply charged cations, on the quantity e/r, where e is the formal charge and r the radius of the cation, has been established[137] (Fig. 10). The character of the variation of $\lg k$ as a function of e/r does not change when the reaction temperature is raised from 380° to 450 °C: in both cases the curve passes through a maximum. At 380 °C the maximum corresponds to gallium silicate and at 450 °C to aluminium silicate (zeolite). The lowest values of $\lg k$ were obtained for indium and boron silicates. The maximum content of the C_2–C_{10} hydrocarbons, including olefins and aromatic compounds, in the reaction products was observed for aluminium and gallium silicates; the maximum yield of dimethyl ether was noted in those cases where the amount of hydrocarbons in the reaction products was lowest.

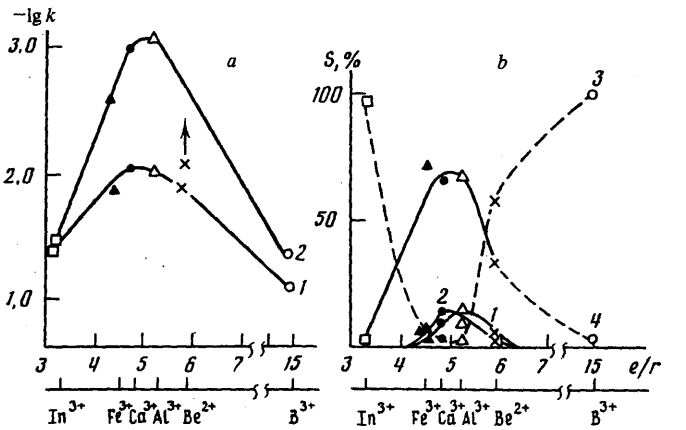


Figure 10. *a*) Dependence of the relative rate of conversion of methanol in the presence of various silicates on e/r at 380 °C (curve *1*) and 450 °C (curve *2*); *b*) dependence of the selectivity S in the formation of various methanol conversion products in the presence of silicates on e/r at 380 °C: *1*) aromatic hydrocarbons; *2*) isoparaffins; *3*) dimethyl ether; *4*) C_2–C_7 olefins.[137]

VI. CONCLUSION

The results presented in the present review show that silicates with the zeolite structure containing cations of only one type (Si^{4+}) exhibit no catalytic activity in reactions involving an acid–base mechanism. Thus hydrocarbons are not formed from methanol in the presence of silicalite. Silicates with the structure of zeolites, whose multicharged cations are fixed predominantly in an octahedral environment (V^{4+}, Cr^{3+}, Mn^{2+}, Cu^{2+}) and do not therefore enter into the composition of the silicon–oxygen skeleton, do not differ from silicalite as regards the selectivity of their action with respect to aliphatic reaction products. At 450 °C and above, methanol decomposition reactions with the predominant

formation of CO and CH_4 (up to 60–90% of all reaction products) take place in the presence of these silicates, which can be due to the catalytic action of the phase comprising the oxides of the corresponding cations.

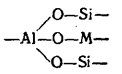
Aromatic hydrocarbons, paraffins, and olefins are formed from methanol in the presence of silicates in which at least some of the cations Fe^{3+}, Ga^{3+}, Al^{3+}, Be^{2+}, or B^{3+} are in a tetrahedral oxygen environment. The EPR and NMR data suggest that the introduction of these cations into the initial gel before the hydrothermal synthesis leads to the formation of active centres having the composition $[Si(OM)_n(SiO)_{4-n}]^{(4-n)-}$.

The dependence of the activity and selectivity of these silicates on the quantity e/r for the cations introduced is not linear, passing through an extremum. The character of the catalytic action is determined by the fact that not only the strength but also the concentration of the active centres depends on the nature of the cation in the silicon–oxygen skeleton. If the length of the M–O bond differs in one direction or another from that of the Si–O bond, then major structural distortions of the silicon–oxygen skeleton should occur. Since the bond length varies in the sequence B–O < Be–O < Si–O < Al–O < Ga–O < Fe–O < In–O, then the greatest distortions in the skeleton are to be expected for the B-, In-, and Fe-containing silicates.

The concentration of the M^{n+} cations in the silicon–oxygen skeleton of silicates should depend on the thermodynamic probability of their fixation in a tetrahedral oxygen environment relative to another, higher, or lower coordination. The energy of the stabilisation of the V^{4+}, Cr^{3+}, Mn^{2+}, and Cu^{2+} ions in an octahedral coordination is very high and the incorporation of these cations in the silicate skeleton in a tetrahedral environment has not been demonstrated. The B^{3+} cations can be fixed in a ternary coordination with a high degree of probability.

The fact that mainly olefins or dimethyl ether are formed from methanol in the presence of silicates containing the B^{3+}, Be^{2+}, and Fe^{3+} cations indicates the slow subsequent conversion of these products into aromatic hydrocarbons and paraffins. Consequently centres having the composition $[Si(OM)_n(SiO)_{4-n}]^{(4-n)-}$, where $M \neq Al$, are much less active in the hydrogen redistribution reactions in unsaturated compounds than the $[Si(OAl)(SiO)_{4-n}]^{(4-n)-}$ groups.

Bonds of the type



may be formed in the synthesis of zeolites (aluminosilicates) in the presence of multicharged cations M^{n+} introduced into the initial silica-alumina gel. For the same Al_2O_3 content, silicates without additives have a higher concentration of the $[Si(OAl)_n(SiO)_{4-n}]^{(4-n)-}$ centres with high values of n than the silicates incorporating the M^{n+} cations.

The introduction of multicharged cations, capable of substituting the Si^{4+} and Al^{3+} cations isomorphously, into aluminosilicates (zeolites) should therefore diminish the number of aluminium atoms in a single active centre and hence the ability of the latter to accelerate the hydrogen redistribution reactions in unsaturated compounds.

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