SYNTHESIS OF OLEFINS FROM METHANOL ON ERIONITE AND MORDENITE WITH ISOMORPHOUS SUBSTITUTION OF Si^{4+} CATIONS BY B^{3+}, Ga^{3+} OR Fe^{3+}

N.V. Kljueva, Nguen Duc Tien, K.G. Ione

Institute of Catalysis, Novosibirsk 630090, USSR

ABSTRACT

The peculiarities of erionite and mordenite crystallization in the presence of polycharged cation salts and their catalytic properties in methanol transformation have been studied. It is shown that the capability of zeolites, in which part of Si^{4+} cations are isomorphously substituted by B^{3+}, Ga^{3+} or Fe^{3+}, to accelerate hydrogen redistribution reactions of olefins differs from that of aluminosilicate catalysts of the same crystal structure but without polycharged cations.

INTRODUCTION

As is known, the formation of acid-base centers in zeolites is a result of isomorphous substitution of Si^{4+} by Al^{3+} cations. It was shown earlier [1-3] that introduction of E^{3+} cations, where E^{3+} = B^{3+}, Ga^{3+}, Fe^{3+} into ZSM zeolites changes their catalytic properties in methanol conversion to hydrocarbons due to isomorphous substitutions, $Si^{4+} \rightleftharpoons E^{3+}$ and $Al^{3+} \rightleftharpoons E^{3+}$, and formation of active centers of peculiar compositions. In the present work zeolites with the erionite and mordenite structures were synthesized. Part of Al^{3+} cations in the initial reaction mixture was substituted by the same amount of B^{3+}, Ga^{3+} or Fe^{3+} cations. Crystallization fields in systems $Na_2O-K_2O-Al_2O_3-E_2O_3-SiO_2-H_2O$ and $Na_2O-Al_2O_3-E_2O_3-SiO_2-H_2O$, where $E_2O_3 = B_2O_3$, Ga_2O_3 or Fe_2O_3, were studied.

EXPERIMENTAL

The initial reaction mixture for erionite synthesis was prepared by mixing solutions of NaOH, KOH, aluminium, gallium and iron sulphates, boric acid and sodium silicate. Molar ratios of OH/SiO_2 and SiO_2/Al_2O_3 were varied from 0.60 to 0.90 and from 20 to 100, respectively. When thoroughly stirred, the mixture was placed into a steel autoclave in a Teflon tube and was held at 120°C for 1-30 days.

Mordenites were synthesized by crystallization of the initial mixture under hydrothermal conditions at 150°C for 3-7 days. 30% sili-

ca sol, sodium hydroxide, salts of iron, gallium, boron, aluminium were used as reactants, with water and mordenite powder as a seed added in a quantity of 1 wt%. Reactant molar ratios were varied in the range: $SiO_2/Al_2O_3 = 30{+}80$, $OH/SiO_2 = 0.25{+}0.60$, $SiO_2/E_2O_3 = 26{+}60$ at constant $SiO_2/Al_2O_3{+}E_2O_3 = 20$ and $H_2O/SiO_2 = 35$.

X-ray spectra were recorded using CuK_α-monochromatic radiation at reflection angles ranging over $2° < \Theta < 20°$. The crystalline phase was determined from the comparison of reflex intensities within 10-15° of the resulted product and reference zeolite. This latter was synthesized as described above without addition of inorganic salts.

The efficient specific surface area of silicates (S_{sp}, m^2/g) was calculated from the values of argon adsorption at the temperature of liquid nitrogen.

^{29}Si, ^{27}Al, ^{11}B, ^{71}Ga NMR spectra were recorded[*] using a Bruker CXP-300 spectrometer. In some cases magic angle spinning was employed Prior to spectra registration, the samples were held in a desiccator over the saturated solution of NH_4Cl at room temperature until the constant weight.

ESR spectra were taken[**] on a Bruker EP 201 spectrometer. Silica glass with Fe^{3+} admixture ions, whose ESR spectrum was characterized by the line with a g-factor of 4,28, was used as a reference. Relative line intensities were found by comparing peaks of line intensities for the sample under study and the reference.

Experiments were carried out by a pulse method in a fluidized catalyst bed microreactor. The samples were pre-calcined in air flow at 500°C. Methanol conversion was studied in the temperature range 350-450°C at an input methanol concentration of 21 vol%, the rest being helium, and at contact time $1{\pm}0.2$ s. The reaction mixture at the reactor outlet was chromatographically analyzed using columns filled with polyethylene glycol and sodium-modified γ-Al_2O_3. The selectivity of methanol conversion into i-product was calculated from the formula

$$S_i = \frac{C_i}{\sum_i C_i} \cdot 100\% \text{ , where}$$

C_i is the concentration of i-product in the gas mixture at the reactor outlet in $g \cdot dm^{-3}$. Olefin yield was estimated from the formula

---

[*] NMR spectra were taken by V.M. Mastikhin
[**] ESR spectra were taken by V.F. Yudanov

$$W = \frac{V \cdot \Sigma C_{en}}{m} \quad , \text{ where}$$

V – space velocity of the gas mixture in $dm^3 \cdot h^{-1}$; C_{en} – olefin concentration in the gas mixture at the reactor outlet, $g \cdot dm^{-3}$; m – catalyst weight in g.

RESULTS

Hydrothermal treatment of bialkaline aluminosilica gels with B^{3+}, Ga^{3+} or Fe^{3+} additives at molar ratios of $OH/SiO_2 = 0.70 \div 0.90$, $SiO_2/Al_2O_3 + E_2O_3 = 20$ and at 120°C leads to the formation of erionite. Polycharged cations considerably affect the formation rate of a zeolite phase. Thus, crystallization of erionite is markedly accelerated after introduction of B^{3+} and is somewhat slowed down upon addition of a Ga^{3+} source. In the presence of Fe^{3+} the selectivity of the erionite phase formation decreases (Fig. 1).
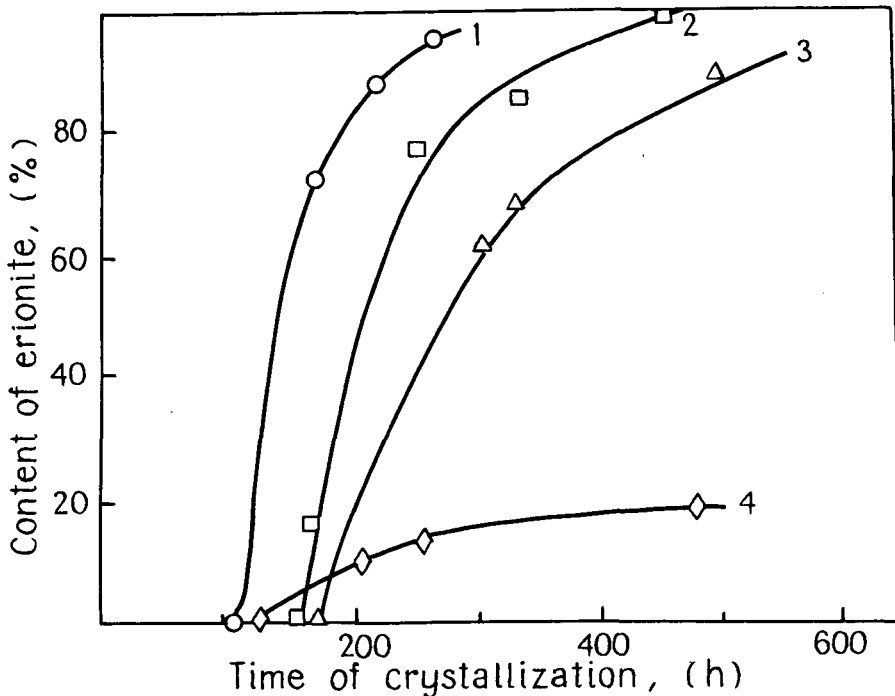

Fig. 1. Content of erionite phase in a solid product versus the time of crystallization in the presence of B^{3+}, Ga^{3+}, Fe^{3+} cations. 1 – BEr, 2 – Er, 3 – GaEr, 4 – FeEr.

In the $Na_2O-Al_2O_3-E_2O_3-SiO_2-H_2O$ system, at $OH/SiO_2 = 0.30 \div 0.60$ and $SiO_2/Al_2O_3+E_2O_3 = 20$, crystallization temperature 150°C and 1 wt% of mordenite powder as a seed, crystallization of mordenite is observed. Table 1 shows the effect of the nature of substituting elements introduced into the initial reaction mixture on the content of crystalline phases of erionite and mordenite in crystallization products.

Table 1

Chemical composition of silicates with the structure of erionite (Er) and mordenite (M) synthesized under optimal conditions in the presence of B^{3+}, Ga^{3+}, Fe^{3+} sorces.

Sample	Product composition, mol/mol Al_2O_3						S_{sp} m^2/g	Content of crystalline phase,%	Crystalline phase composition
	Na_2O	K_2O	B_2O_3	Ga_2O_3	Fe_2O_3	SiO_2			
Er	0.03	0.30	-	-	-	6.7	630	100	erionite
BEr	0.01	0.22	0.29	-	-	7.3	680	95	erionite
GaEr	0.03	0.21	-	0.21	-	8.3	520	100	erionite
FeEr	0.01	0.24	-	-	1.01	12.1	430	80	Er,P,chabasite
M	0.03	-	-	-	-	11.6	600	100	mordenite
BM-1	0.03	-	0.38	-	-	19.0	610	100	mordenite
BM-2	0.04	-	-	-	-	35.0	560	80	mordenite
BM-3	0.04	-	-	-	-	52.0	420	70	mordenite
GaM-1	0.03	-	-	0.59	-	21.3	610	90	mordenite
GaM-2	0.03	-	-	0.79	-	26.0	580	90	mordenite
GaM-3	0.05	-	-	1.33	-	34.4	560	80	mordenite
FeM-1	0.03	-	-	-	0.45	17.3	570	100	mordenite
FeM-2	0.04	-	-	-	1.98	32.5	530	100	mordenite
FeM-3	0.22	-	-	-	2.96	40.6	500	70	mordenite

^{29}Si NMR spectra of the synthesized silicates have signals with chemical shifts (δ) -99, -105, -119 ppm. The line with $\delta = -113$ ppm is attributed [4,5] to silicon cations, having no aluminium cations in the second coordination sphere, and the line with $\delta = -105$ and -99 ppm is attributed to silicon cations with one and two aluminium atoms in the second coordination sphere, respectively. The chemical shifts of the signals in ^{29}Si NMR spectra of the synthesized element-containing silicates are the same, but intensities of signals with $\delta = -105$ and -99 ppm are less than in the spectrum of aluminosili-

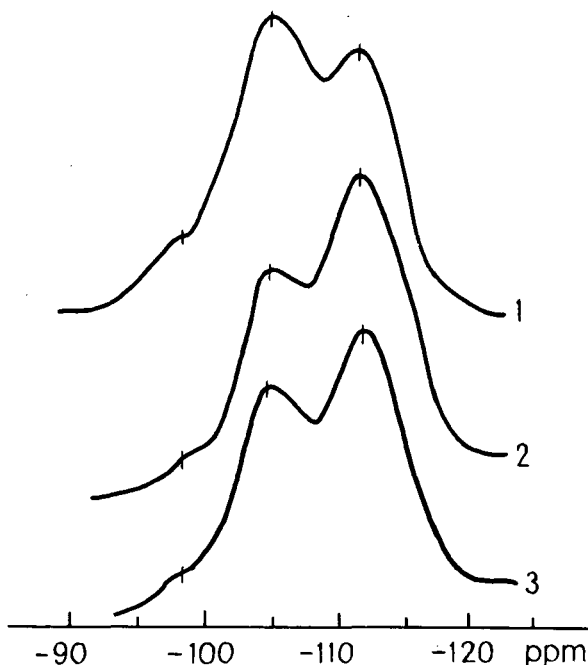cate synthesized without addition of inorganic salts (Fig. 2). This

Fig. 2. ^{29}Si NMR spectra of mordenite samples: 1 - M, 2 - BM-1, 3 - GaM-1, compositions of samples are given in Table 1.

indicates that decreasing of the number of aluminium cations in the second coordination sphere of silicon cations has taken place.

In ^{27}Al NMR spectra of all solid samples a line with a chemical shift of δ = 54,3 ppm corresponding to Al^{3+} cations in the tetrahedral coordination is observed [6]. The position of this line and, hence, the state of aluminium cations in the zeolite framework is unaffected by introduction of boron or gallium into the silicates, but the intensity of signal and the content of Al cations decrease. In accordance with the NMR data, the aluminium content in the tetrahedral coordination within the experiment error is consistent with the total concentration of Al^{3+} in a solid product derived from chemical analysis data (Table 2).

^{11}B NMR spectra of mordenite and erionite samples have the line with a chemical shift δ = -23.8 ppm with respect to an aqueous saturated solution of H_3BO_3. This signal is attributed [7] to boron cations in tetrahedral oxygen environment, which appear to enter the zeolite framework. Comparison of NMR and chemical analysis data

Table 2

NMR data on the content of Al^{3+}, B^{3+} and Ga^{3+} cations in tetrahedral coordination in erionite samples.

Sample	$\dfrac{Al_2O_3^{tetr.}}{Al_2O_3^{com.}}$	$\dfrac{B_2O_3^{tetr.}}{B_2O_3^{com.}}$	$\dfrac{Ga_2O_3^{tetr.}}{Ga_2O_3^{com.}}$
Er	0.9	–	–
BEr	0.9	0.1	–
GaEr	1.1	–	0.5

(Table 2) reveals that only small part of B^{3+} cations is fixed in the tetrahedral environment of the zeolite framework.

^{71}Ga NMR spectra possess a broad signal with δ =157 ppm ascribed to gallium cations in tetrahedral coordination, i.e. in the framework [8]. Relative intensities of this signal suggest that only part of the overall amount of gallium cations determined by the chemical analysis are in such state (Table 2).

In ESR spectra of Fe^{3+} cations three signals with g-factors of 2.003, 2.3 and 4.28 are observed. The third signal is the weakest. The presence of the g = 4.28 signal extends an evidence for that part of iron cations is in tetrahedral oxygen environment of the crystalline lattice[9].Relative intensities of signals with g-factors of 2.003 and 4.28 versus the total content of Fe^{3+} in samples are given in Fig. 3. Based on the intensity ratios of these signals one may conclude that the major part of Fe^{3+} are in the oxide phase composition and only little part in zeolite framework.

The main reaction products of methanol conversion are light hydrocarbons, C_2-C_4, paraffins and olefins. Aromatic hydrocarbons, mainly ethyl-benzene, toluene, xylene, are present in the reaction products too. Table 3 shows the effect of Al^{3+} concentration in the zeolites, synthesized in the presence of E^{3+} cations on the selectivity of methanol conversion.

The decreasing of the aluminium content in the erionite, as well as in the mordenite, changes selectivity of methanol transformation to hydrocarbons. Thus, in the case of erionites a decrease in the Al_2O_3 content in the solid product from 15,4 down to 7,5 wt% resulted in the increase of the olefin-to-paraffin ratio in methanol conversion products from 1,6 to 3,8. As for mordenite, the decrease in the Al_2O_3 content from 9,4 down to 5,2 wt% leads to a slight decrease of the olefin-to-paraffin ratio in the reaction product and
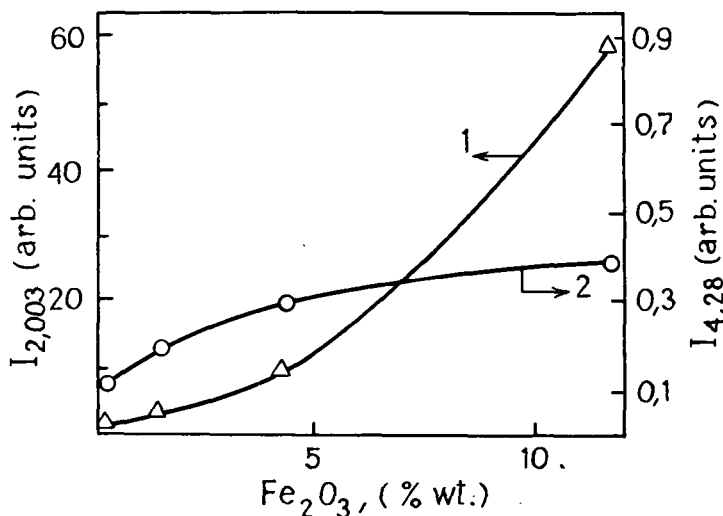
Fig. 3. Relative intensities of signals with g-factors of 2.003 (1) and 4.28 (2) in ESR spectra of Fe-containinf mordenites as a function of the concentration of Fe_2O_3 in the samples.

enhances the selectivity to the formation of aromatic hydrocarbons (Table 3).

Table 3

Selectivity of methanol conversion on silicates synthesized in the presence of B^{3+}, Ga^{3+}, Fe^{3+} sources. Reaction temperature 380°C.

Sample	Content of Al_2O_3 wt%	Selectivity to hydrocarbons, wt%			Yield of olefins $g_{olef}/g_{cat} \cdot h$
		paraffins	olefins	aromat.	
Er	15.4	38.3	61.5	0.2	0.93
BEr	13.9	29.5	69.9	0.6	1.13
GaEr	11.7	20.4	78.0	1.6	0.86
FeEr	7.5	21.4	78.6	0.0	0.07
M	9.4	57.8	41.0	1.0	0.29
BM-1	6.8	64.8	32.6	2.6	0.36
GaM-1	5.2	64.3	27.8	7.9	0.25
FeM-1	6.3	67.0	30.2	2.8	0.12

On further decreasing of Al_2O_3 content down to 2.8 wt% in a solid product the olefin-to-paraffin ratio tends to increase. It is important to note that at the same Al_2O_3 content the lowest selectivi-

ty to olefin formation is observed for B-containing samples and the
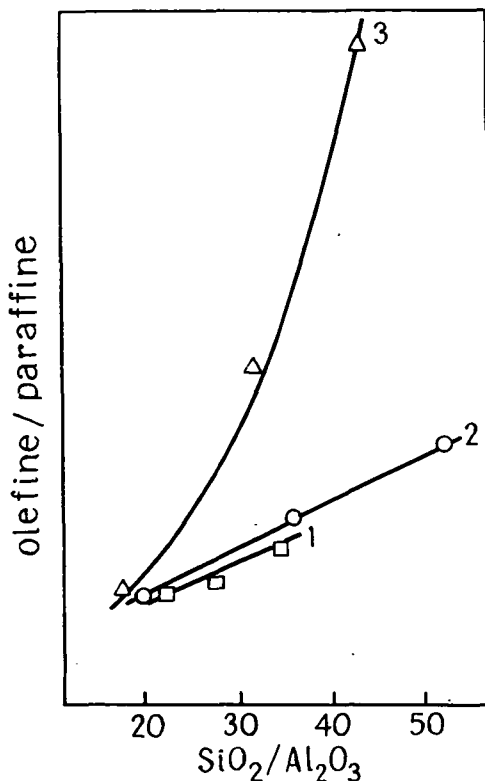highest one for Fe-containing mordenites (Fig. 4).

Fig. 4. Olefin-to-paraffin ratios in methanol conversion
products at 380°C versus the SiO_2/Al_2O_3 mole ratio in mor-
denites: 1 - GaM, 2 - BM, 3 - FeM.

The yield of olefins in methanol conversion in the presence of both
erionites and mordenites decreases in the order (Table 3):

BEr > Er > GaEr > FeEr
BM > M > GaM > FeM

The yield of olefins is the highest for boron-containing zeolites,
and the lowest for ferrozeolites.

The selectivity of methanol conversion to aromatic hydrocarbons
is lower on erionites than on mordenites. Different selectivities of
erionite and mordenite samples with respect to aromatic hydrocarbons
seem to be due to geometric peculiarities of erionite porous struc-
ture which prevents the development of hydrogen redistribution reac-
tions [10]. Gallium-containing samples have shown the highest selec-

tivity to the formation of aromatic hydrocarbons.

DISCUSSION

The reported experimental data is an evidence for that the crystallization of erionite and mordenite zeolites with a low content of aluminium cations is possible under hydrothermal synthesis. The crystallization is achieved by introduction of polycharged B^{3+}, Ga^{3+}, Fe^{3+} cations into the initial reaction mixture.

From the character of ^{11}B, ^{71}Ga NMR and Fe^{3+} ESR spectra it may be proposed that during crystallization part of these cations enter the silica-oxygen framework of solid products in isomorphous Si^{4+} positions.

It may be concluded that along with the catalytically active centers of type $[(SiO)_{4-n}Si(OAl)_n]^{n-}$ supposed previously [11], the groups with the composition of $[(SiO)_{4-n}Si(OAl)_{n-m})(OE)_n]^{n-}$ in zeolite structures may also be formed. As reported earlier [11], the ability of zeolites to convert methanol to aromatic hydrocarbons (and coke precursors) depends upon the concentration of the centers of multipoint interaction with reagent molecules $[(SiO)_{4-n}Si(OAl)_{n-1}]^{n-1} \cdot Al^{3+}$. These centers include the framework anions and aluminium cations that have emerged from the framework as a result of hydrolytic rupture of the Si-O-Al bond.

It may be expected that during decationation and thermotreatment procedures of the synthesized element-containing zeolites $[(SiO)_{4-n}Si(OAl)_{n-m-1}(OE)_{m-1}]^{n-2} \cdot Al^{3+} \cdot E^{3+}$ groups may be formed. On the one hand, these groups have a lesser value of "n" in $Si(OAl)_n$ groups and, on the other hand, a lesser concentration of aluminium in cation positions in comparison with zeolites, synthesized without polycharged cations. The appearance of such centers would decrease the rate of secondary reactions of the hydrogen redistribution in olefins and, consequently, change the reaction selectivity. The proposed explanation of variations in the selectivity of zeolite action upon introduction of cations capable of isomorphous substitution of types $Si^{4+} \rightleftharpoons E^{3+}$ and $Al^{3+} \rightleftharpoons E^{3+}$ are consistent with experimental data presented in Table 3 and Fig. 4.

REFERENCES

1. Ione K.G., Vostrikova L.A., Paukshtis E.A., Yurchenko E.N.: Dokl. AN SSSR, 261, 1160 (1981).
2. Ione K.G., Vostrikova L.A., Stepanov V.G.: Certificate of authorship No 1092141, 15.05.84, V.I. No 18.

3. Ione K.G., Vostrikova L.A., Petrova A.V., Mastikhin V M.: Proc. 8th Intern. Congress on Catalysis, v. 4, 519 (1984), W.Berlin.

4. Nagy J.B., Gabelica Z., Debras G., Boudart R., Derouane E.G., Jacobs P.A.: J.Molec.Catal., 20, 327 (1983).

5. Nagy J.B., Gabelica Z., Derouane E.G., Jacobs P.A.: Chem.Lett., 200 (1984).

6. Klinovski J.: Progress in NMR spectroscopy, 16, 237 (1984).

7. Ione K.G., Vostrikova L.A., Petrova A.V., Mastikhin V.M.: Studies in surface science and catalysis, 18, Structure and reactivity of modified zeolites, Elsevier, p. 151-158, 1984 .

8. Akitt J.V.: Ann.Rep.NMR, v. 5, 4 (1973).

9. Dorouane E.G., Mestdaqu M., Vielovye L.: J.Catal., 33, 168 (1974)

10. Weisz P.: Proc. 7th Intern Congress on Catal., Tokyo, 1980, p. 1.

11. Ione K.G., Stepanov V.G., Echevskii G.V., Shubin A.A., Paucshtis E.A., Zeolites, 4, 114 (1984).