Effects of the Method of Introducing Iron and Iron Concentration on the Acid and Catalytic Properties of Zeolite

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Abstract—The effects of the method of introducing iron and iron concentration on the acid properties, catalytic activity, and stability of a zeolite in methanol conversion to hydrocarbons were studied. The state of active sites in the zeolite depends on the distribution of the metal in its structure, which depends on the method of zeolite modification. The addition of iron to zeolite increased the catalyst run time between regenerations, and the samples in which iron was introduced at the stage of hydrothermal synthesis exhibited the maximum catalytic stability.

INTRODUCTION

High-silica zeolites (HSZ) are promising catalysts for oil-processing and petrochemical industries. They can be used in practically important processes such as the catalytic dewaxing of petroleum fractions; the cracking of gas–oil fractions; the isomerization, disproportionation, and alkylation of aromatic hydrocarbons; and the conversion of methanol to hydrocarbons [1–3].
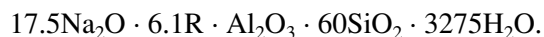
One efficient method for controlling the activity and selectivity of zeolite catalysts is to modify them with various metals. The state of active sites in a zeolite mainly depends on both the nature of a modifier element and modification methods.

The synthesis of ferrosilicates with a pentasil structure and the studies of active sites on their surface by IR spectroscopy have been reported in recent years [4–7]. The catalytic properties of H-form ferrosilicates were studied in the reactions of *n*-hexane and *n*-octane [7]. However, insufficient attention was paid to studies of methanol conversion over Fe-containing zeolite catalysts and other zeolite systems with transition elements introduced at the stage of synthesis. At the same time, this reaction over HSZ provides an opportunity to determine the duration of stable catalyst operation with a sufficient accuracy in a short time interval [8]. We studied the catalytic stability of HSZ containing Ga^{3+}, Cr^{3+}, or B^{3+} ions in methanol conversion to hydrocarbons. We found that these elements, unlike Fe^{3+} ions, do not essentially affect the time of the stable operation of the zeolite.

The goal of this work was to study the effects of the method of introducing iron and the concentration of iron on the acid properties, catalytic activity, and stability of HSZ in methanol conversion to hydrocarbons.

EXPERIMENTAL

The starting zeolite (K-1) ($SiO_2/Al_2O_3 = 60$) containing no iron was synthesized under hydrothermal conditions at 175°C from alkaline aluminosilica gels with the composition

$$17.5Na_2O \cdot 6.1R \cdot Al_2O_3 \cdot 60SiO_2 \cdot 3275H_2O.$$

Hexamethylenediamine (HMDA) was used as an organic component (R). The synthesized HSZ was transformed into the active H form by twofold decationation with a 25% NH_4Cl solution followed by calcination at 540°C for 6 h (concentration of Na_2O in H-HSZ was lower than 0.05%).

The modification of HSZ with iron was carried out by the following methods:

(1) Mechanical mixing of the starting HSZ in the hydrogen form with Fe_2O_3 in a KM-1 vibrating ball mill for 15 min (sample K-2).

(2) Treatment of the starting H-HSZ with an aqueous solution of iron nitrate followed by evaporation and calcination at 540°C for 6 h (sample K-3).

(3) Isomorphous substitution of Fe^{3+} ions for Si^{4+} ions in the zeolite crystal lattice at the stage of hydrothermal synthesis through partial or complete replacement of aluminum with iron in the starting aluminosilica gel $SiO_2/(Al_2O_3 + Fe_2O_3) = 60$ (samples KZh-2–KZh-9).

The amounts of iron introduced into samples K-2, K-3, and KZh-5 were equal to 2.0 wt % Fe_2O_3. The iron contents of samples KZh-2–KZh-9 varied from 0.5 to 3.7 wt %, and sample KZh-9 did not contain Al ($SiO_2/Fe_2O_3 = 60$).

The quality of the samples was monitored by IR spectroscopy and X-ray diffraction (XRD) analysis. The IR spectra of the zeolites were recorded on a UR-20 spectrophotometer in the region 2000–400 cm^{-1}.
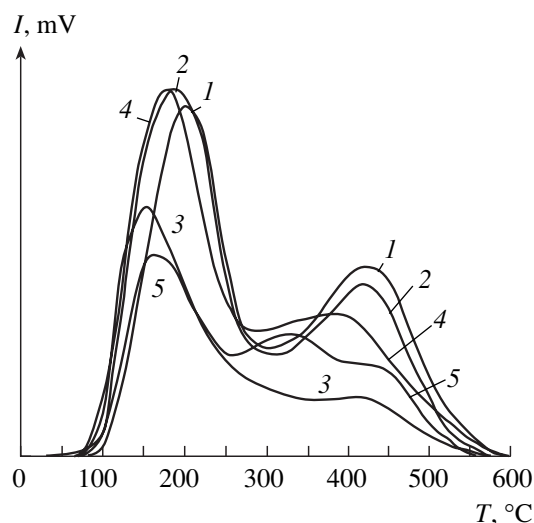
Fig. 1. TPD spectra of HSZ modified with iron: (*1*) K-1, (*2*) K-2, (*3*) K-3, (*4*) KZh-5, and (*5*) KZh-9.

The XRD analysis was performed on a DRON-3 instrument (Cu anode, Ni filter).

The acid properties of the zeolites were studied by the temperature-programmed desorption (TPD) of ammonia, which makes it possible to determine the strength distribution and the amount of acid sites. These studies were carried out on a thermal desorption setup with the programmed heating of the sample. The detector signal was recorded on a PDP4-002 plotting potentiometer. The TPD procedure was described previously [4]. To calculate activation energies, the desorption of ammonia from the sample was performed at several heating rates: 5, 10, 15, and 20 K/min. The activation energies were determined according to the published procedure [9].

The catalytic activity and stability of the zeolites were studied in methanol conversion to hydrocarbons. Tests were performed in a fixed-bed flow reactor ($V =$ 5 cm^3) at atmospheric pressure, a space velocity of 1 h^{-1}, and a temperature of 390°C. The extruded samples without a binder (a fraction of 0.25–0.50 mm) were used. The reaction products were analyzed by GC. The times of stable operation of the zeolites were determined by a rapid method based on monitoring the movement of the reaction heat front along the catalyst bed. The temperature front was monitored with an automated system providing the linear movement of an iron–Constantan thermocouple 1 mm in diameter along the catalyst bed [8].

RESULTS AND DISCUSSION

All the samples synthesized, irrespective of the preparation method, had a high degree of crystallinity according to IR-spectroscopic and XRD data, and they were classified as ZSM-5 zeolites. The degree of crystallinity of the starting zeolite was 94%. With an increase in the iron content, the degrees of crystallinity of the Fe-HSZ samples prepared by hydrothermal synthesis decreased from 90% for KZh-2 to 74% for aluminum-free ferrosilicate (KZh-9). The modification of the starting H-HSZ by mechanical mixing with Fe$_2$O$_3$ or by impregnation with a solution of iron nitrate had almost no effect on the degree of crystallinity.

Figure 1 presents the ammonia TPD spectra for K-1 and HSZ modified with iron. As can be seen, the presence of two peaks is typical of all of the samples. The peaks are evidence for the adsorption of ammonia on the acid sites of two types. The high-temperature peak was attributed to the adsorption of ammonia on strongly acidic OH groups bound to Al(III) or Fe(III) atoms occupying the tetrahedral positions of the zeolite framework.

The quantitative characteristics of acid sites in the modified HSZ are shown in Table 1. The introduction of iron resulted in a shift of the thermal desorption peaks (T_{max}) to the low-temperature region and in a decrease in the total concentration of acid sites. The most pronounced changes in the concentration and strength of acid sites were observed in HSZ modified by impregnation with an aqueous iron nitrate solution under the conditions that simulated ion exchange followed by evaporation (K-3) and in ferrosilicate prepared by isomorphous substitution (KZh-9). The total concentrations of acid sites in these samples were 280.1 and 257.0 µmol/g, respectively, whereas the total concentration of acid sites in the unmodified HSZ was 457.9 µmol/g. Changes in the total concentrations of acid sites in samples K-2 and KZh-5 were less pronounced. At the same time, the strength distribution of acid sites was changed: the number of low-temperature acid sites increased and that of high-temperature acid sites decreased. The third high-temperature peak in a region of 420–500°C with a maximum at 473°C appeared in the TPD spectrum of Fe-silicate (KZh-9) (Fig. 1). This fact indicates the formation of acid sites with enhanced strength on the surface of HSZ.

Thus, the procedure of introducing a modifier affects the acid characteristics of HSZ, which depend on the state of iron distributed in the zeolite matrix. A decrease in the concentration and strength of acid sites upon the mechanical mixing of HSZ with Fe$_2$O$_3$ is due to the blocking of a fraction of the acid sites by iron arranged on the external surface of zeolite crystals as a highly dispersed phase. As a result, the number of zeolite acid sites accessible to adsorbate molecules decreases.

Upon the impregnation of HSZ and the subsequent calcination, iron can occur as extraframework cations or low-nuclear complexes located inside the micropore system of zeolites to change the localization of active sites, the electronic state of the metal, and, consequently, the acid characteristics of the zeolite.

When Fe-HSZ samples were prepared by hydrothermal synthesis, iron occurred as isolated ions in the

crystal lattice and isomorphously substituted for silicon atoms in tetrahedral positions. The acid sites due to the bridging hydroxyl groups formed upon the incorporation of iron ions into the zeolite lattice exhibit a lower acid strength as compared to Al. This is confirmed by thermal desorption data. According to published data [5], the number of iron atoms in an iron-containing zeolite is limited and the optimum saturation is reached at a Fe_2O_3 concentration of about 2 wt %. With a further increase in the Fe content of zeolite, a significant amount of iron leaves the framework to form large clusters of extraframework iron, which do not exhibit acidic properties [10]. A fraction of iron introduced into zeolite at the stage of hydrothermal synthesis can also occur in the cationic positions, and it can be occluded within zeolite channels or at the external surface of the crystals as salts or oxides [6]. As a result, the amount of acid sites differing in strength increases, as evidenced by the broadening of the high-temperature peak (Fig. 1, spectrum *5*). Thus, the state of zeolite active sites is determined by the metal distribution in its structure, which, in turn, depends on the zeolite modification procedure.

Table 2 summarizes the results on methanol conversion to hydrocarbons over HSZ modified with iron by various methods. The mechanical mixing of HSZ with Fe_2O_3 resulted in an increase in the yield of gaseous hydrocarbons, whereas their fraction decreased upon modification by impregnation (K-3). The fractions of C_2–C_4 olefins increased in the reaction products obtained over the iron-containing zeolites. This increase was most pronounced over HSZ modified by isomorphous substitution (KZh-5). The increased olefin content of the gaseous products can be explained by the low activity of ferrosilicates in secondary reactions, for example, in hydrogen redistribution. An increase in the yield of C_1–C_4 alkanes over K-2 is likely due to the enhanced hydrogenating activity of iron occurring on the surface of zeolite crystals.

The total yield of C_{5+} hydrocarbons changed only slightly with the method of HSZ modification, whereas the ratios between various hydrocarbons in the reaction products differed significantly. The main products of methanol conversion are aromatic hydrocarbons, isoalkanes, and cycloalkanes. The products of methanol conversion over the sample modified by impregnation contained a greater amount of aromatic hydrocarbons compared to other samples. The lowest yield of aromatic hydrocarbons (32.7%) was found over the HSZ modified by isomorphous substitution. Since the amount of metal introduced by all modification methods was the same, the differences observed in the catalytic activity and selectivity can be explained by the different localization and different electronic states of iron in zeolites. A combination of several types of the active sites likely occurs: the Brønsted sites with different strengths due to the isomorphous substitution of Al^{3+} or Fe^{3+} for Si^{4+}, the Lewis sites due to the extraframework Fe^{3+} ions, and the hydrogenating–dehydrogenating sites formed by the reduction of Fe^{3+} ions.

Table 3 demonstrates the effect of the concentration of iron, which was introduced by isomorphous substitution, in zeolites on the composition of methanol conversion products. The concentration of aromatic hydrocarbons decreased with an increase in the amount of iron in zeolite, and the yields of C_2–C_4 olefins, isoalkanes, and cyclic hydrocarbons simultaneously increased. As can be seen in Table 3, the fraction of C_{9+} hydrocarbons in the aromatic hydrocarbons increased with the iron content of zeolite. It is likely that the unit cell parameters in zeolites increase upon the isomorphous substitution of Si^{4+} for Fe^{3+}. As a result of this, the concentration of polyalkylaromatic hydrocarbons with bulky molecules (isopropylbenzene, propylbenzene, ethyltoluene, etc.) in the reaction products increased. A decrease in the total yield of aromatic hydrocarbons and an increase in the yield of olefins with the iron content of zeolite are due to a decrease in the strength and concentration of acid sites in iron-con-

Table 1. Effect of the mode of H-HSZ modification with iron on the acid properties

Catalyst	T_{max}, °C		Concentration*, μmol/g			E_a^{**}, kJ/mol	
	I	II	C_I	C_{II}	C	E_I	E_{II}
K-1	210	435	257.8	200.1	457.9	29.7	119.3
K-2	192	423	280.1	171.6	451.7	23.4	118.6
K-3	148	410	207.0	73.1	280.1	9.3	92.6
KZh-5	178	400	290.1	167.5	457.6	22.7	115.8
KZh-9	165	334	153.9	103.1	257.0	17.7	104.3

  * C_I, C_{II}, and C are the concentrations of type I, type II, and total acid sites, respectively.
 ** E_I and E_{II} are the activation energies of ammonia desorption from type I and type II acid sites.

Table 2. Effect of the mode of HSZ modification with iron on the stable operation time of the catalyst and on the composition of the products of methanol conversion

Products, wt %	Catalyst*			
	K-1 (112)	K-2 (178)	K-3 (330)	KZh-5 (1079)
Alkanes C_1–C_4	42.3	44.3	35.5	31.7
Alkenes C_2–C_4	5.7	6.8	9.4	17.6
Total C_1–C_4	48.0	51.1	45.0	49.3
Alkanes C_{5+}	0.9	0.8	0.9	1.6
Alkenes C_{5+}	0.3	0.2	0.3	1.2
Isoalkanes and cycloalkanes C_{5+}	9.0	8.5	9.2	14.9
Arenes:	40.9	38.4	43.8	32.7
Benzene	1.9	0.7	1.4	0.6
Toluene	10.3	6.4	9.3	4.7
Xylenes	22.9	22.0	25.5	18.7
Arenes C_{9+}	5.8	9.3	7.6	8.7
Total C_{5+}	51.0	47.9	54.2	50.4

* The catalyst operation time, h, is given in parentheses.

Table 3. Effect of iron concentration in zeolite on the composition of methanol conversion products

Products, wt %	Catalyst*								
	K-1	KZh-2 (0.5)	KZh-3 (1.1)	KZh-4 (1.2)	KZh-5 (2.1)	KZh-6 (2.7)	KZh-7 (3.2)	KZh-8 (3.7)	KZh-9 (4.2)
Alkanes C_1–C_4	42.3	42.2	41.8	31.7	31.7	30.4	25.4	24.0	20.1
Alkenes C_2–C_4	5.7	7.3	8.2	17.2	17.6	18.6	20.3	26.7	33.2
Total C_1–C_4	48.0	49.5	50.0	48.9	49.3	49.0	45.7	50.7	53.3
n-Alkanes C_{5+}	0.9	0.7	0.9	1.5	1.6	1.3	1.2	1.4	2.0
Alkenes C_{5+}	0.3	0.3	0.3	0.6	1.2	1.2	1.2	2.2	2.2
Isoalkanes and cycloalkanes C_{5+}	9.0	8.6	9.4	11.9	14.9	14.3	16.7	17.1	16.5
Arenes:	40.9	40.0	38.8	36.7	32.7	33.9	34.9	28.4	25.8
Benzene	1.9	1.6	1.2	0.7	0.6	0.6	0.5	0.6	0.6
Toluene	10.3	9.4	8.2	6.1	4.7	3.7	3.2	2.8	1.4
Xylenes	22.9	23.1	23.3	22.0	18.7	18.4	18.9	15.6	11.1
Arenes C_{9+}	5.8	5.9	6.1	7.9	8.7	11.3	12.4	9.5	12.8
Total C_{5+}	51.0	49.5	49.4	50.7	50.4	50.8	54.0	49.2	46.5

* The iron content, wt %, is given in parentheses.

taining zeolites. According to published data [11], the electronic states of iron upon isomorphous substitution can be different because a fraction of iron ions enters the zeolite crystal lattice and another fraction occurs in the ion-exchange positions or as an oxide. The Fe^{3+} cations that occur in the tetrahedral positions of the framework can form acid–base sites like $(Si-O-Fe)^-H^+$. At the same time, the Fe(III) ions occupying cationic positions similarly to Al in aluminosilicate can serve as active sites in hydrogen redistribution and aromatization reactions.

The introduction of iron into zeolite irrespective of the procedure results in an increase in the duration of stable catalyst operation in methanol conversion (Table 2). The most substantial increase in the catalyst run time between regenerations was reached when HSZ was modified by isomorphous substitution. This is due to the fact that, at the stage of hydrothermal synthesis, a fraction of Al atoms was replaced by Fe atoms to decrease the strength of acid sites, as follows from data on the thermal desorption of ammonia. As a result, methanol conversion occurs under milder conditions with the predominant formation of low olefins and isoalkanes. The coking rate decreases to prolong the stable operation of the catalysts.

A study of the effect of the amount of iron introduced into HSZ by isomorphous substitution on the time of stable operation of catalysts in methanol conversion showed that the catalyst run time between regenerations increased from 112 h for unmodified HSZ to 1382 h for sample KZh-6 containing 2.7% Fe_2O_3 (Fig. 2). A further increase in the iron content shortened the catalyst run time between regenerations, and ferrosilicate containing no aluminum exhibited a minimum run time. This is likely due to the formation of new active sites, which are characterized by an excessive acidity, on the surface of Fe-silicate. Because of this, the rate of coking on the catalyst surface considerably increases; as a result, the catalyst is deactivated much faster.

Thus, a decrease in the strength and concentration of acid sites in the zeolite catalyst upon modification with iron results in a decrease in the degree of hydrogen redistribution. The concentration of olefins in the reaction products increases, and the fraction of aromatic hydrocarbons decreases. Moreover, the introduction of iron into the zeolite structure leads to a decrease in the rate of catalyst coking to prolong the catalyst run time between regenerations. The catalysts modified by isomorphous substitution have the longest run times, and the zeolite catalyst containing 2.7 wt % Fe_2O_3 is characterized by the maximum time of stable operation.
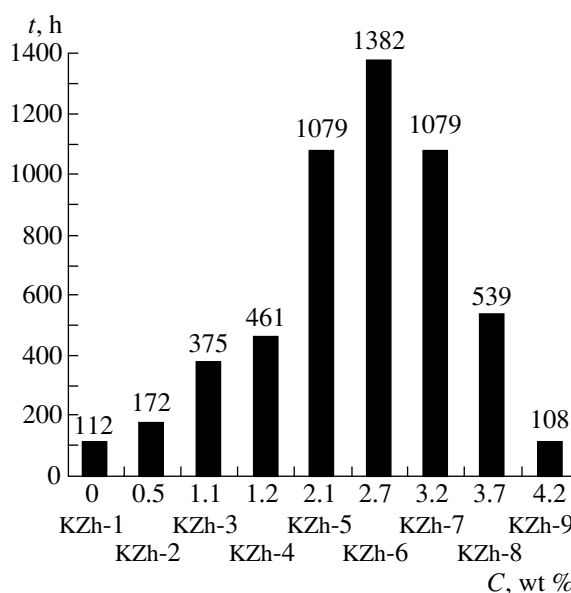

Fig. 2. Effect of iron concentration on the time of stable operation of Fe-HSZ. C is the concentration of Fe_2O_3, wt %.

The complete substitution of Fe atoms for Al atoms results in a dramatic decrease in the catalytic activity and stability of the zeolite.

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