HETEROCYCLIZING PROPERTIES OF FERRISILICATE IN THE REACTION OF **n**-PENTANE WITH HYDROGEN SULFIDE

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Unlike the iron-modified pentasil, the ferrisilicate has high heterocyclizing activity in the formation of 2-methylthiophene from hydrogen sulfide and n-pentane. During the reaction and the subsequent regenerations a considerable proportion of iron ions leaves the ferrisilicate lattice. The heterocyclizing activity is probably related to the formation of a highly dispersed Fe sulfide phase in the zeolite channels.

Ferrisilicates (FS) are used as catalysts in the transformations of hydrocarbons [1, 2], in oligomerization and aromatization of ethylene [3, 4], etc. According to the data in [5, 6] a considerable proportion of Fe^{3+} ions in FS is present in the lattice, substituting of the Al^{3+} ions in it isomorphously. It is known [7] that the isomorphous substitution of ions in the zeolite lattice is an effective means for its modification in order to change its acid and catalytic properties.

It was of interest to examine the possibility of using the FS as catalysts in the heterocyclization reaction, using as an example the reaction of H_2S with *n*-pentane with the formation of methylthiophenes, which virtually does not occur on high silicon zeolites of the pentasil type [8]. In the presence of the latter, *n*-pentane is converted into C_6-C_{14} aromatic hydrocarbons, while H_2S promotes this reaction. For comparison, we also studied an iron-modified up-rated Natrolite zeolite (UNZ). Using the EPR, information was obtained on the change in the stage of iron ions in FS under heterocyclization and regeneration conditions.

EXPERIMENTAL

A high silicon FS was used in the investigation, which was synthesized at the All-Union Scientific Institute of Petroleum Products, having the composition (wt. %): $Fe_2O_3 - 1.43$, $Al_2O_3 - 0.39$, $Na_2O - 0.67$; $SiO_2/Fe_2O_3 = 181$ mole/mole; $SiO_2/Al_2O_3 = 424$ mole/mole. Its structure was determined by x-ray phase analysis. The presence of Fe in a tetrahedral coordination was shown by a high resolution NMR method in the solid phase [3]. The FS was subjected to double decationation by an NH₄Cl solution [9]. The catalyst having the composition: 1.43% Fe₂O₃/UNZ was prepared by impregnation of UNZ ($SiO_2/Al_2O_3 = 42$, $Na_2O = 0.025\%$) with a Fe(NO_3)₃·9H₂O solution, evaporation on a water bath, drying at 120°C and calcination at 500°C for 3.5 h.

"Pure" grade *n*-pentane was used as the starting hydrocarbon, and the hydrogen sulfide was 98-99% pure. The experiments were carried out in a quartz reactor, 20 mm in diameter and 360 mm long at atmospheric pressure for 1 h, on a catalyst preliminarily calcined in a N₂ current. The amount of the catalyst used was 1.7-6.7 g, and its regeneration was carried out by air (2 liters/h) at 500°C for 3 h. The liquid reaction products were analyzed on a LKhM-8 MD chromatograph with a catharometer in a temperature programming regime from 35 to 150°C (8 K/min) on a 3 m × 2 mm column). Poly(ethylene glycol adipate) (15% on Chromosorb P) was used as the liquid phase and helium served as carrier gas. The composition of the C₅ hydrocarbons was also determined on a 10.5 m × 3 mm column with 12% of tricresyl phosphate on celite-545 at 35°C, using a catharometer as detector and helium as carrier gas. The

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| Reaction conditions | | | Comp. of the catalyzate | | | | | Yield,* wt. % | | | |
|---------------------|-----------------------|-----------------------------------|-------------------------|-------------------------|------|------|------|---------------|------|------|------|
| т, °С | v, h ⁻¹ | H ₂ S/n-C ₅ | n-C ₅ | other C ₅ | Т | 2-MT | 3-MT | 2-МТ | | 3-MT | |
| | | | | | | | | A | B | A | В |
| | |] | | | | | | | |] | |
| 500 | 0.8 | 3 | 70.7 | 15.1 | 0.3 | 12.2 | 1.7 | 12.2 | 41.4 | 1.7 | 5.2 |
| 510 | 0,8 | 3 | 73,8 | 8,3 | 0,6 | 11.2 | 5,7 | 11.2 | 43,8 | 5,7 | 21,2 |
| 525 | 0,8 | 3 | 52,1 | 16,9 | 1,6 | 18,8 | 10,1 | 18,9 | 38,5 | 10,1 | 20.8 |
| 550 | 0,8 | 3 | 37,0 | 20,2 | 3,5 | 23,4 | 15,7 | 23,4 | 37,1 | 15,7 | 24,9 |
| 580 ** | 0.8 | 3 | 18,3 | - | 13,1 | 46,5 | 7,7 | 34,5 | 40,1 | 5,7 | 6,4 |
| 525 | 0,3 | 3 | 27,9 | 17,8 | 2,7 | 30.8 | 19,7 | 30,8 | 42,8 | 19,7 | 27,3 |
| 525 | 0,5 | 3 | 39,4 | 19,9 | 2,0 | 23,1 | 15,0 | 23,1 | 38,0 | 15,0 | 24,8 |
| 525 | 1.2 | 3 | 63,2 | 14,2 | 1.2 | 15.1 | 6.3 | 15,1 | 40.5 | 6,3 | 16,9 |
| 525 | 0.8 | 1 | 56,9 | 14.0 | 0,8 | 14,7 | 3,7 | 14.0 | 34,3 | 3,5 | 8,5 |
| 525 | 0,8 | 3 | 56,2 | 14.3 | 1,1 | 21,5 | 6,9 | 21,5 | 49,1 | 6,9 | 15,9 |
| 525 | 0.8 | 6 | 57,2 | 10,5 | 1.2 | 26.6 | 4,5 | 26,6 | 62,1 | 4,5 | 10.6 |
| -525 | 0.8 | 8 | 68,3 | 10.8 | 1.1 | 17,7 | 2,2 | 17,7 | 55.8 | 2,2 | 6.8 |
| 525 | 0,3 | 6 | 34,3 | 15,5 | 2.2 | 37,6 | 9,7 | 37.6 | 57,5 | 9,7 | 14.9 |
| 525 | 0,5 | 6 | 44.1 | 15,0 | 1,6 | 31,2 | 8.1 | 31,2 | 55,4 | 8,1 | 14.3 |
| 525 *** | 0,5 | 6 | 42,9 | 14.7 | 1.8 | 34,0 | 5.5 | 34,0 | 59,6 | 5,6 | 9.9 |
| 525 **** | 0.5 | 3 | 46.1 | 13.9 | 2,8 | 31.6 | 5,6 | 30,8 | 56,3 | 5.5 | 9,9 |

TABLE 1. Heterocyclizing Properties of Ferrisilicate in the Reaction of n-Pentane with Hydrogen Sulfide

*A — percentage of passed through *n*-pentane, B — percentage of

reacted *n*-pentane.

**Yield of liquid catalyzate 74.5%.

*******After 4 h of operation.

**** After 10 h of operation.

activity of the catalyst was evaluated from the yield of reaction products as a percentage of the n-pentane passed through.

The UV spectra of the products were obtained on a "Specord UV-VIS" spectrophotometer. The presence of alkylthiophenes was confirmed by the presence of an absorption band at λ 234 nm. The EPR spectra of the FS samples were obtained on a deflecting type spectrometer (λ 3.2 cm) at 20 and -198°C, using diphenylpicrylhydrazyl (DPPH) as a standard.

The experimental data are given in Table 1 and Figs. 1, 2.

RESULTS AND DISCUSSION

In the reaction of *n*-pentane with H_2S on FS, together with the unreacted *n*-pentane, pentenes, 2- and 3methylthiophenes (MT) and thiophene (T) as well as unreacted *n*-pentane were detected in the products. In the reaction of *n*-pentane with H_2S on FS, heterocyclization, isomerization, dehydrogenation and cracking of *n*-pentane take place, as in the case of a chromium oxide catalyst [10-12].

In most of the experiments, the yield of liquid catalyzate is 100%. The catalyzate also contains 0.4% of benzene and 0.3% of toluene. In the C₅ fraction, besides *n*-pentane, there are 8.8% of 1-pentene, 18.8% of trans-2-pentene, 19.3% of cis-2-pentene, 8.7% of 2-methyl-1-butene, 23.6% of 2-methyl-2-butene, 1.3% of 3-methyl-1-butene, 6.8% of trans-piperylene, 6.3% of cis-piperylene, 1.4% of 2-methyl-1,3-butadiene, and 5.3% of cyclopentadiene (mean values for experiments at 500-550°C).

The heterocyclizing properties of FS were studied in dependence on the temperature, per volume feed rate of *n*-pentane, the H_2S/n -pentane molar ratio and the duration of the catalyst operation (Fig. 1a-d). Increase in the temperature from 500 to 580°C (Fig. 1a) at 0.8 h⁻¹ and H_2S/n -C₅ = 3 leads to increase in the yield of 2-MT from 12 to 34.5%. The yield of 3-MT increases from 1.5 to 15.7% on increase of the temperature from 500 to 550°C and decreases



Fig. 1. Dependence of the yield of 2-methylthiophene (1), 3-methylthiophene (2) and thiophene (3) on FS, on: a) the reaction temperature ($v = 0.8 h^{-1}$, $H_2S/n-C_5 = 3$); b) feed rate of *n*-pentane (525°C, $H_2S/n-C_5 = 3$); c) *n*-pentane/H₂S (525°C, $v = 0.8 h^{-1}$); d) time of operation (525°C, $v = 0.5 h^{-1}$, $H_2S/n-C_5 = 3$).

Fig. 2. EPR spectra of FS samples: a) starting FS; b) FS after 3 h of operation and three regenerations; c) after 10 h of operation and regeneration; d) after 10 h of operation. T, $^{\circ}C$ -196 $^{\circ}C$ (a) and 20 $^{\circ}C$ (b-d).

to 5.7% at 580°C. The cracking of *n*-pentane on FS is inappreciable and up to a temperature of 550°C the yield of T does not exceed 2-3%; with further increase in temperature to 580°C, the yield of T increases to 9.7%. It is possible that under these conditions T is also formed due to demethylation of 3-MT.

Thus, increase in the reaction temperature from 550 to 580°C promotes the intensification of both the heterocyclizing and cracking properties of the FS. However, after performing the reaction at 580°C and on subsequent regeneration, the FS loses its initial activity, which may due to its degradation. In fact, it was shown in [6] that at $T \ge 600^{\circ}$ C, Fe³⁺ leaves the skeleton of the zeolite, and therefore in further experiments, the reaction temperature was not allowed to exceed 550°C. Increase in the feed rate of *n*-pentane from 0.3 to 0.8 h⁻¹ at 525°C and H₂S/*n*-C₅ = 3 leads to a decrease in the heterocyclizing activity; the yields of 2- and 3-MT decrease from 30.8 to 18.9% and from 19.7 to 10%, respectively. Further decrease in the feed rate of *n*-pentane to 1.2 h⁻¹ does not influence the yield of alkylthiophenes appreciably.

A change in the $H_2S/n-C_5H_{12}$ ratio at 525°C and $v = 0.8 h^{-1}$ from 1 to 6 promotes an increase in yield of 2and 3-MT. Further increase in the ratio to 8 leads to a decrease in the yield of the alkylthiophenes.

Under optimal conditions: $T = 525^{\circ}C$, $v = 0.3 h^{-1}$ and $H_2S/n-C_5 = 6$, the yield of 2-MT as a percentage of *n*-C₅ passed through is 37.6% and as percentage of reacted *n*-C₅ is 57.5%. Under these conditions, the yields of 3-MT and T on the basis of the passed-through *n*-C₅ are equal to 9.7 and 2.2%, respectively.

The FS regains its initial heterocyclizing activity completely in the formation of the main product (2methylthiophene) after 5-6 regenerations, while the high isomerizing activity of a fresh sample of FS in the formation of 3-MT decreases after several regenerations. Thus, the yield of 3-MT on FS after five regenerations decreases from 10.1 to 2.2%. This change in the isomerizing activity of FS as a result of its oxidative heat treatment may be due to the decrease in the content of iron in the skeleton of the zeolite. The authors of [13] using IR spectroscopy and EPR methods found that under the aromatization and oligomerization reaction conditions of ethylene and oxidative regeneration of FS, iron is partially removed form the zeolite lattice with the formation of an Fe_2O_3 phase inside the zeolite channels. This leads to a decrease in the concentration of the OH groups bound with the iron in the skeleton, which are responsible for the catalytic activity of FS. It was shown by special experiments that after 10 h of operation, the FS practically does not lose its heterocyclizing activity (Fig. 1d). The mean yield of 2-MT is 27.3%, 3-MT 7.4% and T 4.2%. The isomerizing activity of FS in the formation of 3-MT thus decreases somewhat. After 10 h of operation, the yield of 3-MT decreases from 12.9 to 5.5%.

The data in Fig. 2a show that in the initial FS the Fe^{3+} ions are mainly present in a tetrahedral coordination in the zeolite lattice (g = 4.3, $\simeq 6$ and $\simeq 8$). However, examination of the samples after the catalytic experiments confirms that during the operation and regenerations, the distribution of iron changes substantially, and the concentration of isolated Fe^{3+} ions in the lattice decreases considerably. As has been noted above, the heterocyclizing activity does not change after several regenerations. In other words, in contrast to isomerization, the activity in this reaction cannot be related to the concentration of the iron in the lattice.

The EPR spectra of the regenerated FS samples are characteristic for dispersed Fe_3O_4 or γ -Fe₂O₃ phases (Fig. 2b, c, the asymmetric lines with $\Delta H = 1000-1100$ Oe). In the EPR spectrum of an unreacted sample (Fig. 2d), the ferromagnetic phases are absent. It is probable that the contact of FS with the reaction mixture leads to the formation of a highly dispersed sulfide phase, to which the heterocyclizing activity is related. The loss of the activity of FS after the operation at 580°C may be due to a decrease in the dispersity of the active phase.

In the EPR spectrum of a coked catalyst (Fig. 2d) there occurs a narrow symmetrical line (g = 2.002; $\Delta H = 5.5$ Oe) characterized by a sharp dependence of the intensity on the p_{O_2} . This dependence is characteristic for high-temperature carbons with a high degree of graphitization. It is natural that this polycondensed carbon can be localized only on the external surface of the FS crystals. Since a coked catalyst still retains its heterocyclizing activity after 10 h of operation, it can be assumed that the active centers located mainly inside the zeolite channels are responsible for this activity.

In contrast to FS, the heterocyclization reaction does not proceed on a 1.43% Fe/UNZ. The yield of 2- and 3-MT and T does not exceed 1.5%, while the aromatization of *n*-pentane with the formation of C_6-C_{14} aromatic hydrocarbons is observed. These data agree with the results in [8] on the aromatization of *n*-pentane in a UNZ in a H₂S medium. Introduction of 1.43% of Fe into the UNZ leads to the intensification of aromatization of *n*-pentane and an increase in the yield of C_6-C_7 -aromatic hydrocarbons. Thus, at 525°C, v = 0.8 h⁻¹ and H₂S/*n*-C₅ = 3, 49.0% of C₉-C₁₄-aromatic hydrocarbons is formed as in the case of the UNZ. The ratio of $\Sigma C_6:\Sigma C_7$ increases from 5.4 for UNZ to 6.4, while the $\Sigma C_8:C_9-C_{14}$ ratio remains the same and is equal to 0.8.

In a catalyst obtained by the impregnation method, Fe does not enter into zeolite channels but forms large α -Fe₂O₃ crystals on the external surface [14], which accounts for the low heterocyclizing activity of the system.

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HYDROLYSIS OF BIS(CHLOROMETHYL)PHOSPHONIC ACID p-NITROANILIDE IN AQUEOUS MICELLAR SURFACTANT SOLUTIONS

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The hydrolysis of bis(chloromethyl)phosphonic acid p-nitroanilide has been studied in the pH range 6.86-13.0 and the effects of ionic surfactant micelles on this process have also been examined. The nature of the micellar effects of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS) on this reaction lead us to conclude that both the neutral and anionic forms of the substrate are reactive, and that in the range of pH > pK_a hydrolysis of the ionic form of the anilide predominates, while at pH < pK_b the reaction of the neutral form is predominant. The binding constants for both the neutral and anionic forms of bis(chloromethyl)phosphonic acid p-nitroanilide in micellar CTAB and SDS solutions have been determined using a kinetic method, as well as by measuring the changes in the acid—base properties of the substrate resulting from the influence of micelles.

The hydrolytic stability of phosphonic acid amides in acid media has been widely studied [1-3]. It has been shown that, depending on the structure of the amide, either a dissociative or associative hydrolysis mechanism may be operating. In all cases, however, cleavage of the P--N bond occurs along with formation of phosphonic acid and the corresponding amine. Basic hydrolysis of phosphonic acid amides, on the other hand, has been much less studied. This process takes place only under harsh conditions, namely, at high temperatures and in strongly basic media. For example, the bimolecular rate constant for basic hydrolysis of diphenylphosphonic acid amide at 90°C is equal to $1.42 \cdot 10^{-5}$ liter/mole·sec [2]. In a series of papers [4-6] the hydrolysis of phosphoric acid amide ester derivatives containing several different groups susceptible to cleavage was examined in detail; included was the hydrolysis of amides accompanied by N-H bond dissociation [4]. Phosphonic acid amides which do not contain an ionizable hydrogen atom attached to the nitrogen atom, or which cannot undergo N-H bond cleavage via a bimolecular addition-elimination mechanism involving a pentacoordinate transition state [2].



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