[7] are close to each other (150-160°C). It is not precluded that this coincidence may be related to the need for participation of atomically adsorbed hydrogen in hydrogenation on copper. Such a concept agrees with the assumed hydrogenation mechanism [7, 8].

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CONCLUSIONS

1. Isotope exchange between H_2 and D_2 occurs on metallic-copper powder and on reduced copper-containing catalysts at 100-200°C, which indicates dissociative hydrogen adsorption on them.

2. The absence of exchange on oxidized samples of the same catalysts indicates that dissociative hydrogen adsorption occurs on the reduced metal surface.

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TRANSFORMATIONS OF n-PENTANE IN THE PRESENCE OF HYDROGEN SULFIDE ON PENTASILS

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Certain data are given in a review [1] on the aromatization of n-alkanes on high-silica zeolites of the pentasil type. The aromatization of n-pentane on these catalysts was studied in a flow-type [2] and pulsed [3] systems. No data are available on the conversion of n-pentane on pentasils in a hydrogen sulfide medium into aromatic hydrocarbons. Nevertheless they are of definite interest for treatment of effluent gases from petrochemical processes.

In the present work we studied the catalytic properties of the H-form of TsVM and Cr-TsVM zeolites in the transformation of n-pentane in the presence of hydrogen sulfide.

EXPERIMENTAL

In this investigation a decationated TsVM type zeolite (SiO_2/Al_2O_3 = 42) was used. The decationation was carried out using a 25% aqueous solution of NH_4Cl with heating, according to a method described in [4]. After calcination in air for 3.5 h at 500°C and decationation, the Na content was 0.26%. Chromium-containing catalysts were prepared by impregnation of H-TsVM at 65°C with an aqueous solution of $(NH_4)_2Cr_2O_7$, calculated for 1.5, 5.0, and 10% Cr_2O_3 content, evaporation on a water bath, followed by drying for 6 h at 120°C, and calcination in air for 3.5 h at 500°C. Starting materials: "pure" grade n-pentane and hydrogen sulfide (98-99% purity), obtained by condensation of the gas evolved from

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TABLE 1. Aromatization Characteristics of H-TsVM and Cr-TsVM Zeolites in Conversion of n-Pentane (550°C, $v_{mass} = 0.8\ h^{-1}$)

Ord. No.	$H_2S : C_5$, molar	Yield of liquid catalyzate, wt. %	Composition of catalyzate, %: benzene	toluene	ethylbenzene	xylenes		aromatic hydrocarbons		thiophenes	Ratio of hydrocarbons $\Sigma C_6-C_7 : \Sigma C_8 : \Sigma C_9-C_{14}$
						m, p	o	C_9	$C_{10}-C_{14}$		
						H-TsVM					
1[a]	Without H_2S	38,0	20,4	38,2	2,1	15,4	4,2	4,0	8,7	–	4.6 : 1,7 : 1
2	»	40,5	29,3	38,5	1,9	10,9	3,3	4,5	10,3	–	4.6 : 1,1 : 1
3[a]	3,0	31,5	23,0	43,8	1,9	14,1	4.2	4,6	5,8	Traces	6,4 : 1,9 : 1
4	1,9	41,5	35,4	36,5	1,2	7,8	2,5	3,2	12,1	»	4,6 : 0,8 : 1
5[b]	3,0	48,0	34,1	40,8	1,1	8,9	2,7	3.2	8,3	0,3	6,5 : 1.1 : 1
6	3,0	47,0	34.2	40,3	1,5	7,4	2,3	2.9	10,8	Traces	5,4 : 0.8 : 1
7	4,0	35,5	32,7	45,6	1,4	9,4	3,0	2,5	4,4	0,3	11,3 : 2,0 : 1
8	6.0	31,0	35,5	43,4	1,2	8.3	2,4	3.7	1,6	0,5	15.0 : 2,3 : 1
9[c]	Without H_2S	30,0	24,7	45,8	2,1	15,7	4,6	3,7	3,4	–	9,9 : 3,2 : 1
						1,5% Cr-TsVM					
10	3,0	41,0	39,5	35,2	1,4	6,4	1,8	5,3	9,4	1,0	5,0 : 0,7 : 1
						5% Cr-TsVM					
11	3.0	46,5	31,7	36,4	1,0	7,2	2,3	2,8	16,3	1,4	3,6 : 0,5 : 1
12	Without H_2S	43,5	32,3	38,3	1,3	8,3	3,1	3,4	12,7	–	4,4 : 0,8 : 1
						10% Cr-TsvM					
13	3,0	44,0	32,4	34,5	1,0	6,1	1,8	8,4	10,1	2,3	3,6 : 0,5 : 1

[a] T = 500°C, 1.5-2% of n-pentane, 2% of C_6-alkanes.

[b] After 3 h of continuous use of the catalyst.

[c] $N_2 : n\text{-}C_5 = 6$ (molar).

treated monoethanolamine after purification of hydrocarbon gases from the processing of sulfur-containing oils.

The experiments were carried out in a flow-type apparatus in a quartz reactor at atmospheric pressure, for 1 h [5]. Prior to the start of the experiment, the catalyst was heated at 500°C for 1 h in a nitrogen current. The catalyst was regenerated in air, flowing at a rate of 2.6 liters/h at 500°C for 3 h. The liquid reaction products were analyzed on an LKhM-8MD chromatograph with a catharometer with temperature programming in the range of 35-175°C at a rate of 8 degrees/min, on a 3 m x 2 mm column. Polyethylene glycol adipate (15% on chromosorb P) was used as the liquid phase, and helium as the carrier gas. The analysis of the gaseous products was carried out on two columns at 20°C, as described in [6]. The C_2-C_4 hydrocarbons were separated on a 7 m x 3 mm column filled with zeolite 545 with 18% triethylene glycol dibutyrate; N_2, O_2, CH_4, C_2H_6 and C_2H_4 were determined on the same column, using nitrogen as carrier gas.

DISCUSSION

The transformation of n-pentane in the presence of hydrogen sulfide was studied at various temperatures (Fig. 1) on H-TsVM, $v_{mass} = 0.8\ h^{-1}$ ($\tau = 92.6$ g·h/mole) and at a molar ratio $H_2S : n\text{-}C_5 = 3$. With increase in the temperature from 400 to 550°C the yield of the liquid catalyzate increases from 32 to 44-48%. The content of benzene in the liquid catalyzate increases from 5 to 34%, of toluene from 20 to 40 and of ΣC_9-C_{14}, from 4 to 14%. At the same time, the content of ΣC_8-hydrocarbons decreases from 23 to 11%.

If we compare the data obtained for H-TsVM in the presence of hydrogen sulfide ($H_2S : n\text{-}C_5 = 3$) and in its absence (see Table 1), we can see that with H_2S at 500 and 550°C, $v_{mass} = 0.8\ h^{-1}$, the yield of the aromatization products is higher due mainly to the increase in the benzene and toluene content in the catalyzate. The composition of the gaseous products with H-TsVM is not very different with increase in the temperature from 500 to 550°C. They contain 20% of H_2, 20% of CH_4, 17% of ΣC_2, 4% of C_3H_8 and 2% of C_3H_6. Carrying out the reaction in hydrogen sulfide ($H_2S : n\text{-}C_5 = 1.9$) also does not cause appreciable changes in the above composition.

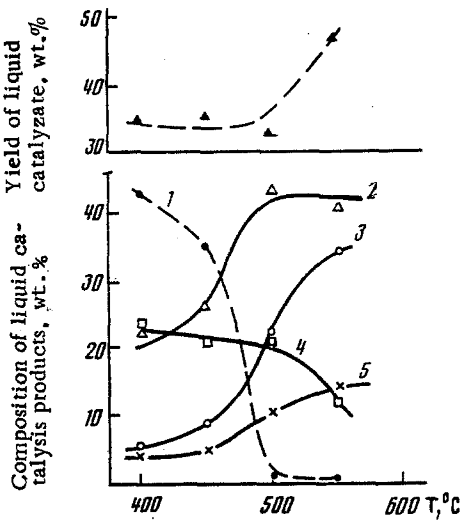

Fig. 1

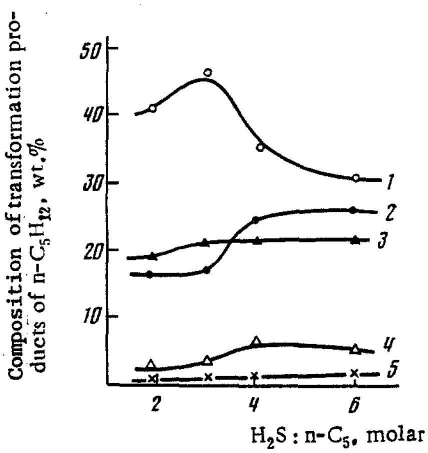

Fig. 2

Fig. 1. Influence of temperature on the composition of liquid conversion products of n-pentane on H-TsVM in the presence of H_2S (v_{mass} = 0.8 h^{-1}, H_2S : n-C_5 = 3, molar): 1) n-pentane; 2) toluene; 3) benzene; 4) Σ C_8-aromatic hydrocarbons; 5) Σ C_9-C_{14}-aromatic hydrocarbons.

Fig. 2. Composition of conversion products of n-pentane as a function of the change in the molar ratio H_2S : n-C_5 on H-TsVM (550°C, v_{mass} = 0.8 h^{-1}): 1) Σ C_6-C_{14}-aromatic hydrocarbons; 2) C_2H_4 and C_2H_6; 3) CH_4; 4) C_3H_8; 5) C_3H_6.

The authors of [2] showed that the main product in the catalysis on H-TsVM (SiO_2/Al_2O_3 = 52) at 450°C and at τ = 14.6 g·h/mole is propane; the yield of the aromatic hydrocarbons was ~15%. With increase in the reaction temperature to 500 and 550°C, at a complete conversion of n-pentane, the yield of propane decreases sharply, while the yield of methane and C_2 hydrocarbons and aromatic hydrocarbons increases to 18 and 23%, respectively. It has been suggested [2] that aromatization proceeds through the stage of propane formation. We obtained a similar pattern of the distribution of the aromatization products of n-pentane on H-TsVM without hydrogen sulfide.

The influence of molar ratio H_2S : n-C_5 = 1.9; 3.0; 4.0 and 6.0 on the aromatization properties of H-TsVM was studied under conditions of complete conversion of n-pentane at 550°C and v_{mass} = 0.8 h^{-1} (Fig. 2 and Table 1). The data obtained show that when the H_2S : n-C_5 ratio is increased threefold, the yield of the aromatic hydrocarbons decreases from 41.5 to 31%. The content of toluene in the liquid products increases from 36.5 to 43.4% and the yield of the C_{10}-C_{14} hydrocarbons decreases sharply from 12.1 to 1.6%. The ratio ΣC_6-C_7 : ΣC_8 : ΣC_9-C_{14} becomes 15.0 : 2.3 : 1, instead of 4.6 : 0.8 : 1. The highest yield of the aromatic hydrocarbons was obtained at a molar ratio H_2S : n-C_5 = 3. It was found that the C_{10}-C_{14} fraction contains up to 50% of naphthalene and 15% of anthracene. The presence of the latter was confirmed not only by GLC, but also by UV spectroscopy. The UV spectra were run on a Specord UV-VIS recording spectrophotometer. The absorption curve has several bands characteristic of naphthalene λ_{max} 220 nm and anthracene λ_{max} 340-480 nm. Figure 2 shows that with increase in the molar ratio of H_2S : n-C_5 from 1.9 to 6 in the gaseous reaction products, the total content of the C_2 hydrocarbons increases from 17 to 26%, while the amount of methane, propane and propylene remains constant, and is equal to 19-20, 2-5, and 2%, respectively. Moreover, insignificant amounts, namely, 0.1% of n-butane, 0.14% of C_4H_8-1, 0.05% of C_4H_8-2-cis and 0.02% of C_4H_8-trans were also detected. It was found by special experiments that dilution with nitrogen (N_2 : n-C_5 = 6.0, molar) also influences the selectivity of H-TsVM. However, in the presence of hydrogen sulfide and in the absence of nitrogen, the content of benzene and C_8-aromatic hydrocarbons was 35.5 and 10.7%, instead of 24.7 and 20.3%, respectively (see Table 1). Hence, hydrogen sulfide intensifies the acid function of the zeolite, promotes cracking of n-pentane and further formation of propane, the precursor of aromatic hydrocarbons.

Thus, it was shown under selected catalytic conditions that the increase in the molar ratio H_2S : n-C_5 from 1.9 to 6 does not influence the general aromatizing activity of H-TsVM appreciably, but leads to a change in the selectivity of the catalyst in the direction of the formation of benzene and decrease in the yield of the aromatic hydrocarbons with high molecular weight. These data may be of interest for the use of pentasil in the processing of C_5 petroleum fractions containing hydrogen sulfide.

Similar results with respect to the influence of hydrogen sulfide on the aromatization of propylene at 600°C and its complete conversion on H-ZSM-5 are given by a patent [7]. A five-fold increase in the propylene:hydrogen sulfide ratio leads to an increase in the yield of benzene from 28.7 to 34.5%, and decrease in the yield of benzene from 28.7 to 34.5%, and decrease in the yield of toluene from 17.5 to 12.5%, of the C_8-aromatic hydrocarbons, from 8.8 to 2.1%, C_9 and higher aromatic compounds from 15.5 to 13.3% at an overall selectivity of the conversion of propylene to aromatic hydrocarbons of ~50%.

All the above data indicate that the aromatization of n-pentane on H-TsVM precedes cracking with the formation of mostly C_3 hydrocarbons, and that hydrogen sulfide intensifies the selectivity of this reaction.

It should be noted that under selected catalytic conditions, the H-TsVM samples become completely regenerated, and retain the same activity after seven regenerations. It was also shown that at 550°C, $v_{mass} = 0.8\ h^{-1}$ and H_2S : n-C_5 = 3, the catalyst does not lose the aromatizing activity after 3 h of operation.

We have previously comprehensively studied the properties of oxide chromium-containing catalysts in the reaction of n-pentane with hydrogen sulfide in the formation of 2-methylthiophene [5]. It was therefore of interest to study the catalytic properties of pentasil containing chromium oxide in this heterocyclization reaction. The data obtained for catalysts containing 1.5, 5 and 10% of Cr_2O_3 on H-TsVM show that the yield of the aromatic hydrocarbons remains practically the same as for H-TsVM, while the ratio of the aromatization products changes only slightly. From comparison of the data obtained on H-TsVM, and, for example, for 5% Cr_2O_3-TsVM (550°C, $v_{mass} = 0.8\ h^{-1}$ and H_2S : n-C_5 = 3) it is seen that in the aromatization product, the content of toluene and the C_{10}-C_{14}-aromatic hydrocarbons increases (see Table 1). The yield of thiophene and 2-methylthiophene is very slight, and with increase in chromium oxide concentration increases from 1.0 to 2.3%. It is thus evident that the heterocyclization reaction practically does not proceed on these catalysts.

The results obtained for pentasils containing chromium oxide also provide indirect proof for the fact that on H-TsVM, under selected catalytic conditions, the cleavage of the n-pentane molecule in the presence of hydrogen sulfide proceeds mainly with the formation of C_3-hydrocarbons, from which 2-methylthiophene cannot be formed.

CONCLUSIONS

1. The influence of hydrogen sulfide on the activity of H-TsVM in the aromatization of n-pentane was established. Under conditions of complete conversion (550°C, $v_{mass} = 0.8\ h^{-1}$ and H_2S : n-C_5 = 3, molar), the yield of the C_6-C_{14}-aromatic hydrocarbons increases from 40 to 48%.

2. Increase in the molar ratio H_2S : n-C_5 from 1.9 to 6 influences the selectivity of H-TsVM and leads to increase in the yield of C_6-C_7- and decrease in the yield of C_9-C_{14}-aromatic hydrocarbons.

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