- N. V. Palishkina, Ya. I. Isakov,
- E. G. Khelkovskaya-Sergeeva,
- B. K. Nefedov, and Kh. M. Minachev

The effectiveness of high-silica (HS) zeolites with the ZSM structure as catalysts for various chemical reactions has made these zeolites the focus of a large amount of research in recent years [1-4].

Previously, we had investigated the aromatization of ethane in the presence of a number of modified HS zeolites [5]. Here we are reporting on a study of the catalytic activity and selectivity in conversions of ethylene, n-hexane, and 1-hexene on a series of zeolites of the Pentasil type - TsVM and TsVK-1 - differing in preparation method and composition. With the aim of showing up the acidic function more clearly, these zeolites were tested in the H, HNa, and Na forms. The hydroxyl cover of some of these zeolites was investigated by IR spectroscopy in diffuse-scattered light.

The catalysts used in this study were HS zeolites in the Na, HNa, and H forms (Table 1). The Na forms of TsVM and TsVK-1 were obtained by crystallization of alumina-silica gels under hydrothermal conditions. In the synthesis of the TsVK-1, we used a tetrabutylammonium base; the crystallization of the TsVM was accomplished by a new technology without the use of or-ganic components. As a result, we obtained samples I and II (see Table 1) with respective SiO_2/Al_2O_3 ratios of 33 and 70 for the TsVM and TsVK-1.

The corresponding H forms were prepared by ion exchange, replacing the Na^+ by NH_4 in aqueous solution of NH₄Cl or NH₄NO₃, or by treatment with 0.1 NH₄Cl solution at 70°C. In the interest of a more nearly complete removal of Na⁺, the zeolites were treated twice, with an intermediate calcination at 550°. By these procedures, samples III, IV, and VI were obtained (see Table 1) with residual Na₂O contents below 0.1%. Sample V was obtained by replacing Na⁺ by NH4⁺, using an NH4Cl solution containing 0.43 equivalents of NH4⁺ per equivalent of Na⁺ in the zeolite sample (degree of exchange ~43%, residual NaO content 1.7%); sample VII was obtained from VI by impregnating it with the calculated quantity of CH₃COONa (Na₂O content ~0.4%); the corresponding Na form of TsVK-1 contained 1.3% Na20. The reactants used in this work were ethylene, 1-hexene, and n-hexane with purities of 98-99% (GLC). The experiments were performed in a flow unit at 300-500° and 1 atm, following procedures given in [6]. The catalyst charge was 1.7-1.8 g (2.5 cm³); the rate of ethylene feed was 300 ml/h; the space velocity for 1-hexene and n-hexane was approximately 1 h^{-1} . Before use, the zeolites were heated for 5 h in a stream of air at 550°; between experiments (each of which lasted for 4 h), the catalysts were heated for 2 h. The maximum yield of liquid products from the reaction is reached in the second or third hour of catalyst operation, and these are the results shown in Table 1 and Fig. 1. The catalyst activity, under the indicated conditions of treatment, generally remains the same throughout the entire series of experiments, a period of more than 50 h. The reaction products were analyzed chromatographically [6].

DISCUSSION OF RESULTS

On the Na forms of the TsVM and TsVK-1 zeolites at $300-550^{\circ}$, ethylene did not undergo any appreciable conversion. The replacement of Na by H (either through the NH₄ form or directly by treatment with HCl) led to the appearance of catalytic activity for the aluminosilicates; the greater the degree of replacement of Na by H⁺, the higher was the C₂H₂ conversion and the yields of liquid products and aromatic hydrocarbons (AHC) (Fig. 1 and Table 1).

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O. V. Bragin, T. V. Vasina,



Fig. 1. Yield of liquid products from reaction (a, b) and total yield of AH (c) as functions of reaction temperature in conversion of ethylene: I) Na-TsVM; II) Na-TsVK-1; III) H-TsVM; V) HNa-TsVM; VI) H-TsVK-1; VII) HNa-TsVK-1.

On the H form of the TsVM, under optimal conditions, 85% liquid catalysate was obtained, with very nearly quantitative conversion of the original ethylene. These results point out the important role of the acidic centers in the oligomerization and aromatization of ethylene on HS zeolites. Above 500°, the quantity of liquid products from C₂H₄ conversion was much smaller, owing to intensification of processes of cracking and gas formation in the presence of catalysts of the TsVM type.

Ethylene was subject to similar conversions on the TsVK-1 zeolites (see Table 1 and Fig. 1). However, there were certain differences. In the first place, the activity of the H-TsVK-1 at 300-500° with respect to the formation of liquid hydrocarbons was found to be considerably lower than that of the H-TsVM. In the second place, the H and HNa forms of the TsVK-1 in contrast to the TsVM series, have very similar activities. In the third place, in the 250-550° interval, the liquid catalysate yield on the TsVK-1 remained very nearly constant. These differences are apparently due to nonidentical conditions of synthesis and to the composition of the zeolites (the SiO_2/Al_2O_3 ratio in the TsVM is 33, and in the TsVK-1 it is 70), and also to certain features of their structure: According to [7], TsVK-1 is similar to ZSM-11 in the structure of its crystal lattice, whereas the TsVM is analogous to ZSM-5.

The H-TsVM catalyst has a considerably greater aromatizing capability at $300-500^{\circ}$ than does the H-TsVK-1 (see Fig. 1c). On either zeolite, as the temperature is increased, the composition of the products from ethylene conversion changes substantially. At $400-500^{\circ}$, the liquid products obtained on H-TsVM consist to the extent of 85-100% of AHC. As the temperature is increased, we observe a considerable increase in the relative fraction of C_6-C_8 AHC, particularly toluene; with this H-TsVM catalyst, the total content of xylenes and ethylbenzene passes through a maximum at 400° (Fig. 2); the concentration of C_9-C_{12} AHC gradually decreases, and at 550° becomes lower than at 300° by a factor of 1.5-2. The increase in selectivity of benzene and toluene formation in comparison with C_8 and C_9-C_{12} AHC as the temperature is increased can be seen from the plots in Fig. 3. These results show that the H-TsVM is appreciably higher in selectivity than the HNa-TsVM with respect to AHC formation; apparently this is also due to the difference in the acidic properties of these catalysts.

The character of the relationships that we have obtained (Figs. 2 and 3) suggests that part of the benzene and toluene from ethylene conversion is obtained by dealkylation of C_{8} - C_{12} AHC. As the temperature is increased, there is also a significant increase in the rate of desorption of light AHC from the channels of the zeolites, and this may influence the selectivity of ethylene aromatization.

The higher catalytic activity of the H-TsVM in the overall conversion of C_2H_5 and in the formation of AHC, in comparison with the H-TsVK, is apparently due to the larger content of Al_2O_3 in the former catalyst and hence the relatively higher total concentration of OH groups. According to [8, 9], the Brønsted acidity of the H-form of high-silica zeolites is characterized by the OH structural groups that give an absorption band at 3610 cm⁻¹ in the IR spectra. Hence we can assume that these OH groups (bridge groups) are responsible for the oligomerization and aromatization of C_2H_4 on these pentasils. Consistent with this assumption are two facts: 1) the absence of catalytic activity for the Na forms of the TsVM and TsVK-1 in ethylene conversion, and 2) the "intermediate" activity manifested by the HNa-TsVM catalyst (see Fig. 1). Actually, the HNa-TsVM (1.7% Na₂O, degree of exchange 43%), which



Fig. 2. AHC composition as a function of reaction temperature with H-TsVM (a) and H-TsVK-1 (b): 1) benzene; 2) toluene; 3) Σ xylenes; 4) Σ C₉-C₁₂ AHC.



Fig. 3. Ratios $\Sigma C_6 - C_7 / \Sigma C_8$ AHC (A) and $\Sigma C_6 - C_7 / \Sigma C_8 - C_{12}$ AHC (B) as functions of ethylene conversion temperature for H-TsVM (III), HNa-TsVM (V), H-TsVK-1 (VI), and HNa-TsVK-1 (VII).

TABLE 1. Liquid Products from Ethylene Conversion (space velocity 120 $h^{-1})$

Sam-	Catalyst	T., °C	Composition, %*						
ple No.			C ₄ -C ₈ ali- phatic hy- drocarbons	C_6-C_{12} aromatic hydrocarbons					
				benzene	toluene	xylenes	С ₉ -С ₁₂ АНС		
I	Na-TsVM	300-550	Inactive						
II	Na-TsVK-1	300-550	*						
1117	H-TsVM, decat. NH ₄ Cl	300 400 500 550	34 2 Trace	2 12 25 33	3 25 30 33	7 20 12 10	54 41 33 24		
IV†	H-TsVM, decat. HCl	300 400 500 550	30 14 Trace —	$2 \\ 3 \\ 20 \\ 25$	5 16 27 34	7 22 13 17	56 45 40 24		
V†	HNa-TsVM	$300 \\ 400 \\ 500 \\ 550$	28 10 1 Trace	3 3 14 17	4 15 34 36	8 21 19 22	57 51 32 25		
VI .	H-TsVK-1	300 400 500 550	$28 \\ 5 \\ 1 \\ Trace$	2 10 17 33	8 32 34 30	22 22 20 11	40 31 28 26		
VII	HNa-TsVK-1	300 400 500 550	5 9 Trace »	3 12 24 39	17 36 32 36	20 22 15 12	55 21 29 13		

*For yields of liquid products from reaction, see Fig. 1. [†]Ethylene conversion at 300-400 °C was 97-99%. On samples III-V, above 400°, the concentration of C₂H₄ in the reaction products was higher because of secondary processes.

Sam-			Yield of	Composition, %					
ple No.	Catalyst	т., °С	gaseous products, %	CH.	C₂H₄	C_2H_6	C'H',	C₃H₅	ΣC_4
111	H-TsVM, decat. NH ₄ Cl	300 400 500 550	15 28 25 55	2 3 14 24	6 1 12 20	3 8 25 33	3 5 3 8	39 66 46 15	47 17 Trace
IV	H-TsVM, decat. HCl	300 400 500 550	10 39 39 36	1 3 19 28	6 8 14 22	2 6 29 38	1 2 2 5	48 61 36 7	42 20 Trace »
v	HNa-TsVM	$300 \\ 400 \\ 500 \\ 550$	47 55 31 52	2 6 11 21	$4 \\ 2 \\ 6 \\ 24$	11 7 23 28	23 12 6 8	17 57 46 16	
VI	H-TsVK-1	300 400 500 550	57 63 52 52	Trace 1 12 37	1 2 3 5	$2 \\ 9 \\ 25 \\ 51$	1 1 4 1	$52 \\ 64 \\ 48 \\ 6$	44 23 8 —
VII	HNa-TsVK-1	300 400 500 550	68 60 60 60	1 3 13 32	$\begin{array}{c} 16\\ 2\\ 5\\ 7\end{array}$	4 9 30 48	$2 \\ 2 \\ 4 \\ 4$	$30 \\ 67 \\ 45 \\ 9$	47 17 3 Trace

TABLE 2. Gaseous Products from Ethylene Conversion (space velocity 120 h^{-1})

was obtained by partial decationization of the original Na-TsVM sample $(3.3\% \text{ Na}_20)$, was lower in acidity than the H-TsVM. In the case of the TsVK-1, the relative similarity of catalytic properties of the H and HNa forms of the TsVK-1 is still difficult to explain. We can only suggest that this similarity is due to the relatively small content of alkali metal (0.4%Na₂O) in the latter sample; the original Na-TsVK-1 contained 1.3\% Na₂O.

The hydroxyl cover of the H and Na forms was investigated by IR spectroscopy in diffusescattered light. The spectra were measured in the region of fundamental stretching vibrations of the O-H bond (3300-4000 cm⁻¹), following procedures given in [10]. In the case of the Na-TsVM and Na-TsVK, we observed absorption bands of only the nonacidic hydroxyl groups of the terminal type (v 3740 cm⁻¹), analogous to the silanol groups of silica. Decationization of the zeolites (through the ammonium forms) led to the appearance of an intense absorption band with a maximum at 3610 cm⁻¹ in the IR spectra of the zeolites, this band characterizing vibrations of the acidic OH bridge groups, which, as noted above, are responsible for the Brønsted acidity of the H forms of high-silica zeolites of the pentasil type and mordenites.

Thus, the data that we have obtained indicate that the oligomerizing and aromatizing properties of these HS zeolites depend to a great degree on their acidity (the degree of replacement of Na⁺ by H⁺) and are practically independent of the decationization method (Tables 1 and 2, samples III and IV).

Along with the liquid reaction products obtained in C_2H_4 conversion, gaseous hydrocarbons are formed (Fig. 4). The principal processes involved in the formation of gaseous hydrocarbons on these high-silica zeolites are dimerization of ethylene, cracking of the butane-butylene fraction with the formation of C_2-C_3 hydrocarbons, and partial redistribution of hydrogen. As the temperature is increased, the content of C_3-C_4 hydrocarbons passes through a maximum at 300-400°. At 500-550°, the gaseous products consist largely of ethane, ethylene, and methane. In the presence of the HNa forms of the TsVM and TsVK-1, complex relationships are observed in the influence of the process temperature in C_2H_4 conversion on the composition of the gaseous products. The data of Table 2 indicate that as the temperature is increased to 500° with the H or HNa form of the TsVK-1 or TsVM, the gaseous products from ethylene conversion consist mainly of C_2-C_3 saturated hydrocarbons. Thus, in the processes of formation and subsequent conversions of C_3-C_4 hydrocarbons, the two types of HS zeolite behave similarly.

We may suggest that the presence of considerable quantities of C_3 hydrocarbons in the reaction products at relatively low temperatures (300°, see Table 2) is due to cracking of higher-molecular-weight oligomers and also to the formation of unsaturated C_1 fragments as a result of partial decomposition of ethylene when it interacts with the HS zeolites.



Fig. 4. Composition of gaseous products from ethylene conversion on H-TsVK-1 as a function of temperature: 1) CH₄; 2) C_2H_4 ; 3) C_2H_6 ; 4) C_3H_6 ; 5) C_3H_8 ; 6) ΣC_4 .

TABLE 3. Conversion of 1-Hexene* on Na-TsVK-1 (400°, space velocity 0.9 h^{-1} , in stream of Ar at 300 m1/h)

Products from con- version of 1-hexene, after hydrogenation	Compo- sition, %	Products from conversion of 1-hexene, after hydro- genation	Composition, %
$\begin{array}{l} \sum_{i=C_4} - C_5 \\ \sum_{n-C_4} - C_5 \\ 2 - Methylpentane \\ 3 - Methylpentane \\ n - Hexane \\ \sum_{i=C_7} \\ n - Pentane \end{array}$	7,75,526,317,724,39,90,9	Σi -C ₈ n-Octane Σi -C ₉ n-Nonane Cyclopentane Methylcyclopentane Gaseous hydrocarbons	$\begin{array}{c} 3,65\\ 0,3\\ 2,2\\ 0,2\\ 0,2\\ 1,1\\ \text{Trace } C_2C_3\end{array}$

*Conversion of 1-hexene was 92%.

Our data are in agreement with those of [11], where it was noted that considerable quantities of C_3-C_5 hydrocarbons were formed from ethylene on H-ZSM-5.

In the light of the fact that the Na forms of TsVK-1 and TsVM are inactive in the oligomerization and aromatization of ethylene, it seemed important to determine their behavior in other reactions. To this end, we investigated conversions of n-hexane and 1-hexene on Na-TsVK-1 and Na-TsVM. At 400-450°, on either zeolite, the 1-hexene undergoes a number of conversions, the most important of which are skeletal isomerization and disproportionation with respect to carbon, forming C_4-C_5 and C_7-C_9 hydrocarbons (Table 3). For the C_6 hydrocarbons, the concentration ratio $i-C_6:n-C_6 = 1.8$; in the case of the C_7-C_9 hydrocarbons, the relative content of branched structures is considerably higher. Similar results were obtained on the Na-TsVM catalyst. Thus, we can say that regardless of the absence of bridge OH groups in the IR spectra of the Na forms of TsVM and TsVK-1, both zeolites manifest rather high catalytic activities in the isomerization and disproportionation of olefins. Our data indicate that the active centers in the HS zeolites are inhomogeneous, and that various reactions of olefins apparently proceed on active centers that differ in properties. When n-hexane was used as a feed with Na-TsVK or Na-TsVM at 400-500°, no appreciable conversion was noted.

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CONCLUSIONS

1. In the 300-500° interval, the H form of the high-silica zeolite TsVM with a mole ratio $SiO_2/Al_2O_3 = 33$ has a higher aromatizing activity in ethylene conversion than does the H-TsVK-1. With either catalyst, as the temperature is increased, the selectivity of benzene and toluene formation increases.

2. The catalytic activity of the Na and H forms of these zeolites in reactions of ethylene oligomerization and aromatization is consistent with the spectral data obtained by IR spectroscopy in diffuse-scattered light. 3. The Na-TsVM and Na-TsVK-1 zeolites, which are practically inactive in ethylene oligomerization and aromatization, manifest high activities in the isomerization and disproportionation of 1-hexene.

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BEHAVIOR OF COPPER-RUTHENIUM CATALYSTS IN ENANTIOSELECTIVE HYDROGENATION

T. I. Kuznetsova, A. A. Vedenyapin, and E. I. Klabunovskii UDC 541,128:542,941

In skeletal copper-ruthenium catalysts for enantioselective hydrogenation, the active component is the Ru [1], but its properties in these catalysts are much different from the properties that it manifests in an individual Ru catalyst. In this connection, we have investigated analogous Cu-Ru catalysts supported on aerosil (SCRC), modified with R,R-tartaric acid (TA), in the liquid-phase hydrogenation of ethyl acetoacetate (EAA).

EXPER IMENTAL

The catalysts were prepared by impregnating aerosil (produced by the Kalush Combine, Grade A-300) with aqueous solutions of Cu and Ru chlorides, after which the wet mass was dried and then reduced for 3 h in a stream of H_2 + He. The series A catalysts contained a constant total quantity of metal (10% of catalyst weight) and different Ru:Cu weight ratios (1:9, 2:8, 3:7, 4:6, 5:5, and 10:0). The series B catalysts, with a constant Ru:Cu weight ratio of 1:4, differed in total content of metal (5, 10, 15, 20, 40, and 80% by weight). In the series C catalysts, with an Ru content of 1% by weight, the Cu content was varied from 0 to 14% (at.). The series A and B catalysts were reduced at 450°C, the series C at 500°C, The reduced catalysts were held while mixing for 1 h in a thermostatted (50°) cell with a 0.5% aqueous solution of TA (100 ml of solution per 0.5 g of catalyst). The hydrogenation of the EAA (5 ml per 0.5 g of catalyst) was performed at 90° and 100 atm without any solvent and in ethanol solution (1:1). The catalysate, after removal of the catalyst and distillation, was analyzed by GLC (Khrom-31 instrument, packed glass column, length 3 m, PEG/Chromaton-AW-CMDS, 80°) and spectropolarimetrically (Spektropol-1).

DISCUSSION OF RESULTS

The hydrogenation of EAA on the series A SCRCs modified at pH proceeds at a rather high rate, both in ethanol solution and without solvent, although in ethanol the hydrogenation rate (v) is about 30% higher. With increasing content of Ru in the SCRC, the activity in-

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