

than the nonpromoted catalyst and the sample containing lithium. Metallic iron is the active component of these catalysts.

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CONVERSION OF METHANOL INTO HYDROCARBONS IN THE PRESENCE OF MODIFIED HIGH-SILICON ZEOLITE CATALYSTS

T. V. Vasina, E. G. Khelkovskaya-Sergeeva, N. N. Rostanin,
L. D. Konoval'chikov, B. K. Nefedov, and O. V. Bragin

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High-silicon (HS) zeolites in the H-form, active in the conversion of methanol into hydrocarbons [1], are insufficiently stable catalysts and require additional modification [2-5].

The properties of a series of zeolite-containing catalysts for synthesis of hydrocarbons from methanol, containing different modifying additives (B, Al, REE, Pt) and binder components as the matrix (Al_2O_3 , SiO_2 , $\text{Al}_2\text{O}_3 + \text{SiO}_2$, MgO) were studied in the present article. The effect of the nature and method of introducing the modifier and the zeolite/matrix ratio on the catalytic properties of the HS zeolite system were studied.

EXPERIMENTAL

All of the catalysts studied contained HS TsVM zeolite as the active component [6]. After decationizing NaTsVM twice with a solution of NH_4Cl , the concentration of Na_2O was 0.06%; $\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$.

The catalysts with a binder (samples I-VIII, Fig. 1) were prepared as follows: the calculated amount of Al_2O_3 (or SiO_2 , $\text{Al}_2\text{O}_3 + \text{SiO}_2$, MgO) were suspended in distilled water at -20°C , and the zeolite was added and stirred for 30 min, dried at 130°C , and molded.

The modified catalysts were prepared from the HS zeolite systems with a binder either by impregnation with salts of the corresponding metals (samples IX-XI) or by exchange of NH_4^+ for the metal (samples XIV-XVII); XII and XIII were prepared by application of the modified to the matrix (Al_2O_3 , $\text{Al}_2\text{O}_3 + \text{SiO}_2$) and treated as described above (Table 1).

The catalytic studies were conducted in a flow-type setup at 0.1 MPa [7]. The weighed portions of the catalysts were 5.5 g (10 cm^3). Before beginning the series of experiments, the catalysts were calcined at 550°C in a current of air for 5 h with 2 h between experiments. The duration of the experiments was 3 h.

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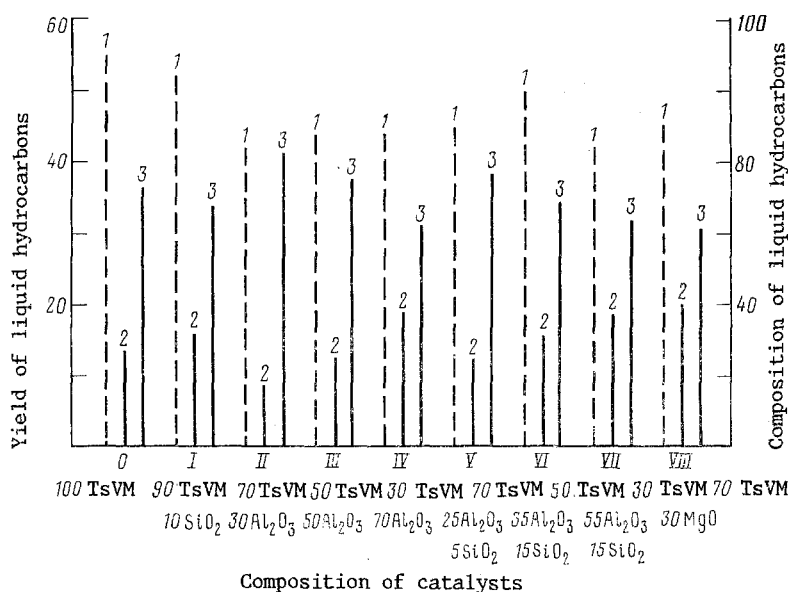


Fig. 1. Effect of the amount and nature of the binder component on the catalytic properties of zeolite-containing catalysts in conversion of methanol: 1) yield of liquid hydrocarbons; 2) concentration of aliphatic hydrocarbons of C₄-C₁₀ composition; 3) concentration of aromatic hydrocarbons of C₆-C₁₁ composition.

TABLE 1. Composition and Conditions of Preparation of Modified HS Zeolite Systems

Catalyst No.	Modifying additives, *%	Composition of base, %			Method of adding modifying additive
		H-TsVM	Matrix		
			Al ₂ O ₃	SiO ₂	
IX	5 Ce, La	50	35	15	Impregnation of base with Ce and La compounds
X	5 REE	50	35	15	
XI	5 REE	50	35	15	Impregnation of base (granules) with REE compounds
XII	5 Ce, La	50	35	15	Impregnation of base (crushed) with REE compounds
XIII	5 REE	50	35	15	
XIV	0.5 Pt	50	35	15	Impregnation of Al ₂ O ₃ with Ce and La compounds
XV	5 Ce, 5 Al	70	30	—	Impregnation of matrix with REE compounds
XVI	5 Ce	70	30	—	Addition of modifier by exchange method
XVII	5 Al	70	30	—	»
XVIII	5 B	50	35	15	»
XIX	5 B	50	50	—	Modification of matrix with B compounds
XX	2 B	70	30	—	»

*On conversion to oxides, except for Pt.

The activity of the catalysts was studied at 360-380°C, $v = 2 \text{ h}^{-1}$, and evaluated by the yield of liquid hydrocarbons. The yields are reported in conversion to the hydrocarbon part of the methanol molecule. The products of the reaction were analyzed by GLC.

DISCUSSION OF RESULTS

The catalytic properties of two series of HS zeolite systems were studied: series 1: catalysts with a different matrix/HTsVM ratio (Table 2 and Fig. 1), series 2: the catalysts in series 1 modified with additives (Tables 1 and 3).

The data in Table 2 and Fig. 1 indicate that the initial form of HTsVM exhibits the highest activity in the formation of liquid hydrocarbons from methanol. The addition of a binder

TABLE 2. Results of Conversion of Methanol on HS Zeolite Catalysts Containing a Binder Base (360-380°C, space velocity 2 h⁻¹)

Catalyst No.	Yield of liquid hydrocarbons*	Composition of liquid hydrocarbons			Composition of gas, %				
		AlH [†] C ₉ -C ₁₀	AH		CH ₄	C ₂ H ₄ /C ₂ H ₆	C ₃ H ₆ /C ₃ H ₈	ΣC ₄	DME
			C ₆ -C ₈	C ₉ -C ₁₁					
0	55	27	56	17	1	1/2	3/56	37	--
I	52	32	56	12	3	2/2	3/41	49	--
II	42	17	70	13	1	2/2	4/46	45	--
III	44	25	50	25	2	8,5/1	12/28	46	2,5
IV	44,5	37	37	26	3	19/1	20/12	37,5	7,5
V	45	24	62	14	2	2/2	3,5/45	43	2,5
VI	50	31	45	24	3	4,5/1,5	9/31	51	--
VII	42	36,5	31	32,5	2,5	16/0,5	25/12	43	1
VIII	45	38,5	53,5	8	2	5/1	11/28	50	2

*Yield after 3 h, the remainder are gaseous products (90-100% conversion).

†The presence of small amounts of hydrocarbons of C composition is possible.

component in the form of Al₂O₃, SiO₂, Al₂O₃ + SiO₂, or MgO to the zeolite in the conditions studied does not significantly affect the total conversion of methanol, but the yield of the liquid hydrocarbon fraction on the samples with a binder decreases from 55% (HTsVM) to 42-50%. There were also differences in the selectivity of action with respect to the formation of aliphatic (AlH) and aromatic (AH) hydrocarbons among the catalysts in series 1. The highest aromatizing capacity was observed on the H-form of TsVM and on samples containing ≥50% TsVM (see Fig. 1, samples II and III). An increase in the amount of Al₂O₃ in the system or a change in the nature of the matrix (SiO₂ + Al₂O₃, MgO) resulted in a decrease in the concentration of AH in the catalyzate and a change in their composition: in the presence of catalysts containing HTsVM ≤ 50%, the selectivity with respect to the formation of high molecular weight AH was slightly higher. This finding is apparently due to the effect of the catalytic action of Al₂O₃ on the selectivity of the aromatization process [8].

The stability of the catalysts studied is also dependent on the matrix/HTsVM ratio, and this is especially marked with a 20-30°C decrease in the temperature of the reaction. Samples containing ≤50% HTsVM rapidly lose activity in the synthesis of liquid hydrocarbons, the yield decreased by 2-3 times in the third h of use of the catalyst, and significant amounts of dimethyl ether appear in the gas (see Table 2).

The nature and amount of the matrix thus significantly affect the catalytic properties of the HS zeolite system and determine its activity, selectivity, and stability to a significant degree. Systems containing <50% of the active components (HTsVM) are not very effective in this process.

Series 2: HS zeolite systems modified by additives of B, Al, REE, and Pt, were prepared to increase the selectivity and stability of the catalysts (Table 1). The samples of the catalysts in this series were also tested in the conversion of methanol in conditions of the optimum yield of liquid products. The catalysts modified with REE oxides behaved differently as a function of the method of application of the additives (see Table 3). All of the catalysts prepared by impregnation (samples IX-XI) were less active with respect to the formation of liquid hydrocarbons (Tables 1 and 3) than the initial zeolite/matrix system (sample VI, Table 2). The stability of these catalysts is low; in the third hour, the yield of liquid products decreased by 2-6 times. Samples XII and XIII (application of the modifier on Al₂O₃ and Al₂O₃ + SiO₂) were an exception. With respect to the selectivity of action, they are similar to VI and differ from the other impregnated samples (IX-XI): the products of the reaction obtained on XII and XIII (as on VI) contained more AH than for the other catalysts in this group. The presence of up to 45% dimethyl ether in the gaseous products of the reaction also indicates the low activity of IX-XI in the formation of liquid products.

The difference in the catalytic properties of XII and XIII could be due to the fact that the modified (Ce-La concentrate) was applied to the Al₂O₃ matrix and to Al₂O₃ + SiO₂ in the

TABLE 3. Results of Conversion of Methanol on Modified HS Zeolite Catalysts (360-380°C, space velocity 2 h⁻¹)

Catalyst No.	Conversion	Yield of liquid hydrocarbons %	Composition of liquid hydrocarbons			Composition of gas, %				
			AlH [†] C ₃ -C ₁₀	AH		CH ₄	C ₂ H ₄ /C ₂ H ₆	C ₃ H ₆ /C ₃ H ₈	ΣC ₄	DME
				C ₃ -C ₆	C ₇ -C ₁₁					
IX	94	17	42	34	24	0,5	20/-	19/1,5	14	45
X	94	30	46	34,5	19,5	1	28/-	19,5/6	23,5	12
XI	93	23	52	34	14	0,5	22,5/0,5	35/3,5	32	6
XII	100	47	31	37,5	31,5	2	6,5/1	13,5/24	53	-
XIII	100	42	23	55	22	1	4/2	9/31	53	-
XIV	96	39	42,5	38,5	16	0,5	11/-	11/3	18	56,5
XV	100	55	42	44	14	2	3/2	7/41	45	-
XVI	100	46	14	70	16	3	1/2	3/52	39	-
XVII	100	56	37	44	19	2	3/2	5/47	41	-
XVIII	86	43	55	34	11	1	19/0,5	21/2	27,5	29
XIX	100	50	40	48,5	11,5	4	4/1	8,5/34	46,5	4
XX	83	9	59	16	26	-	8/-	13/-	7	71

*Yield after 3 h; remainder: gaseous products.

†The presence of small amounts of hydrocarbons of C₄ composition is possible.

preparation of these samples, while the zeolite system with the binder underwent impregnation in the case of the other catalysts. The addition of the modifier by impregnation of the matrix and subsequent preparation of the HS zeolite/matrix composite is apparently better than impregnation of the finished composite. In the last case, the efficiency of modification can decrease as a result of neutralization of the active (primarily acid) sites in the HS zeolite, and possibly also due to the irregular distribution of the modifier.

Samples XV and XVI, in which REE were added by the exchange method, differ significantly in activity and selectivity from the catalysts prepared by the impregnation method. The yield of liquid hydrocarbons on XV and XVI was significantly higher than for impregnated samples IX-XI.

The method of addition of the modifying additive thus significantly affects the activity and selectivity of action of HS zeolite catalysts in conversion of methanol. The impregnation method worsens the catalytic properties of the samples in comparison to the initial unmodified system. Modification by exchange has a positive effect on the properties of the catalysts.

The catalysts modified with B₂O₃ (samples XVIII-XX) exhibit relatively high catalytic activity in the formation of liquid hydrocarbons, except for sample XX, which exhibits lower activity and stability. The yield of liquid hydrocarbons did not exceed 9% on the average. The gaseous products of the reaction contained 71% dimethyl ether; the conversion of methanol was also decreased in comparison to the initial conversion. This pronounced difference in the catalytic properties of XVIII and XIX with respect to XX is apparently due to the preliminary high-temperature steam treatment of the latter. As a result of this treatment, the active sites responsible for oligomerization and aromatization processes are probably eliminated. For all three samples, modification with B₂O₃ resulted in a marked increase in the concentration of AlH in the liquid products in comparison to the initial unmodified systems.

Addition of Pt to zeolite system (XIV) had a promoting effect on the formation of liquid hydrocarbons from methanol; the yield in the presence of XIV attained 62% at the beginning of the experiments (1st hour), i.e., it was much higher than for most of the catalysts studied. However, the stability of the Pt sample was low. The yield of liquid catalyzate decreased by 5-7 times in the third hour, and up to 85% dimethyl ether appeared in the gas. The rapid poisoning of the Pt-zeolite catalyst is apparently due to its coking.

Sample XV, simultaneously modified with Ce and Al compounds by the exchange method, exhibited elevated activity and stability in the formation of liquid hydrocarbons. The yield of liquid hydrocarbons was 55% and virtually did not change during the experiment. No dimethyl ether was found in the gaseous products, in contrast to most of the other catalysts (see Table 3). Two more samples containing Ce or Al (XVI and XVII) were prepared and tested to determine the modifying effect of Ce and Al individually. It was found that XVI modified

with Ce compounds was less active than the sample containing Ce-Al (XV); at the same time, XVII, modified with aluminum, exhibited elevated activity in the formation of liquid hydrocarbons from methanol (56%, see Table 3). The significant differences in the selectivity of Ce- and Al-containing catalysts should also be noted. In the presence of XVI, aromatization is the basic direction of conversion of methanol: the concentration of AH in the liquid catalyzate was 86% (70% of them were C₆-C₈AH). XV and XVII modified with aluminum compounds, as is the case of boron compounds [9], caused conversion of methanol in the direction of greater formation of AlH: 40% of the liquid hydrocarbons consisted of AlH (see Table 3). The observed effect of the catalytic action of Al could be due to the fact that in the modification of a zeolite system with Al compounds, the latter partially occupies cationic positions which alter the catalytic properties of the entire system.

The catalytic action of the modified HS zeolite in the conversion of methanol is thus dependent on both the nature of the modifier and the method of modification to a significant degree. Studied of a wide group of HS zeolite catalysts with a different concentration of zeolite in both the H and the cation-exchange forms showed that they have relatively high selectivity in the formation of liquid hydrocarbons but are rapidly deactivated due to intense coking. The data obtained in the present study permitted developing a method of modification which ensures a decrease in the acidity and a decrease in the rate of precipitation of coke. As a result, a catalyst which works for more than 500 h with no marked decrease in activity and ensures a 99-100% degree of conversion of methanol was developed.

CONCLUSIONS

1. The significant effect of the nature and method of addition of the modifying additive (boron, aluminum, rare-earth elements, platinum) on the properties of catalysts for conversion of methanol into hydrocarbons was demonstrated; catalysts prepared by the exchange method exhibited higher activity and stability.

2. The nature and amount of the matrix have a large effect on the catalytic properties of HS zeolite catalysts in transformations of methanol. The HTsVM/Al₂O₃ (HTsVM ≥ 50%) composite is best in the conditions studied.

3. An active and stable catalyst for conversion of methanol into hydrocarbons which worked for more than 500 h was developed based on the data obtained.

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