

13. E. O. Fischer and H. Werner, Metal π -Complexes [translated from German by Express Translation Service], Elsevier, New York (1966) [Russian translation by Mir, Moscow (1968), p. 128].
14. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. Toops, Jr., Organic Solvents: Physical Properties and Methods of Purification, John Wiley, New York (1955) [Russian translation by Mir, Moscow (1958), p. 91].

EFFECT OF MODIFYING ADDITIVES ON THE SELECTIVITY OF TRANSFORMATION
OF METHANOL INTO AROMATIC HYDROCARBONS OR LOWER OLEFINS IN THE PRESENCE
OF PENTASILS

T. V. Vasina, S. A. Isaev,
A. V. Preobrazhenskii, N. N. Rostanin,
L. D. Konoval'chikov, B. K. Nefedov,
and O. V. Bragin

UDC 541.128.34:549.67:542.97:546.261

The development of new catalytic systems based on high-silicon zeolites (HS) for preparation of lower olefins and aromatic hydrocarbons (AH) from nonpetroleum raw material is currently an urgent problem. Pentasils ZHS, ZHM, Ultrasil, and ZSM in the decationized form exhibit relatively high activity in transformations of methanol into hydrocarbons [1-3]. However, zeolites in the H form are not very stable and are insufficiently selective. Modification with different additives is one of the methods of increasing the activity and stability and regulating the selectivity of catalysts of conversion of methanol [4-7]. It was previously shown [6] that the nature and amount of the matrix (Al_2O_3 , SiO_2 , MgO) has a significant effect on the catalytic properties of HS zeolites in transformations of methanol. In particular, it was found that the 70% HZHM + 30% Al_2O_3 composite is optimum for conversion of methanol into hydrocarbons.

The effect of the nature and amount of modifying additives and the conditions of preliminary treatment and conducting the experiments on the activity and selectivity of action of catalysts prepared from the 70% HZHM + 30% Al_2O_3 zeolite-containing composite was investigated in the present study. Metal oxides (cobalt oxide, mixture of chromium and zinc oxides) which promote the formation of AH from CO and H_2 [1] and phosphoric acid, which increases the selectivity of formation of C_2 - C_4 olefins from methanol, were selected as the modifying additives.

EXPERIMENTAL

A composite consisting of 70% HZHM and 30% γ - Al_2O_3 (base) was used for preparing the modified zeolite-containing systems. Modification was conducted by impregnating the base with solutions of Co, Zn, and Cr nitrates and phosphoric acid as in [6]. The following samples of catalysts were thus prepared and tested in conversion of methanol: CT-1-base, CT-2-TC-4, corresponding to 0.5, 5.0, 10.0 Co_2O_3 /base, Ct-5-Cf-9 contain zinc and chromium oxides applied to the base: Ct-5 (2% ZnO and 2% Cr_2O_3), subsequently Ct-6 (2 and 10), Ct-7 (5 and 2), Ct-8 (5 and 5), Ct-9 (5 and 10). Samples Ct-10-Ct-12 with 5, 10, and 20% P_2O_5 /base.

The studies were conducted in a flow-type setup and in a pulsed microreactor [7]. The catalyst load was 2.5 and 5.0 cm^3 (flow reactor) and 500 mg (pulsed reactor); the volume flow rate of CH_3OH varied from 1.4 to 8.4 h^{-1} ; the size of the sample in the pulsed mode was 10 μl . The experiments were conducted at 250-500°C and atmospheric pressure. The products of the reaction were analyzed by GLC.

To determine the optimum conditions of activation of the modified zeolite catalysts, the effect of the conditions of preliminary heat treatment was studied on the example of Ct-2, 3, and 6: in a reducing medium (H_2 , 500°C, 5 h: method I), in a redox medium (successively air, 520°C, 5 h, then H_2 , 500°C, 3 h: method II), and in an oxidizing medium (air, 520°C, 5 h: method III) on the activity and selectivity of their effect in transformations of methanol.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 12, pp. 2666-2670, December, 1987. Original article submitted April 1, 1986.

TABLE 1. Conditions of Preliminary Treatment and Activity of Catalysts in Conversion of Methanol at 450°C (Pulsed Method)

Catalyst	Method of activation	Σ - Yield of products of the reaction, %	Yield of hydrocarb., % for methanol delivered			
			CH ₄	C ₂ -C ₄	C ₄ -C ₆	Σ AH C ₆ -C ₈
Ct-2	I	31	1,6	18,2	1,4	9,8
	II	50	2,0	33,3	2,0	12,7
	III	40	-	40,0	-	-
Ct-3	I	59	1,1	24,5	5,4	28,0
	II	64	2,4	32,0	9,4	20,2
	III	40	-	40,0	-	-
Ct-6	I	38	2,1	17,6	1,1	17,2
	II	60	3,0	30,4	2,1	24,5
	III	30	1,9	13,8	1,5	12,8

TABLE 2. Conversion of Methanol on Modified HS Zeolites

Catalyst	T., °C	Yield of C ₁ -C ₄ gaseous products, %	Comp. of liq. hydrocarb., %		Comp. of gas, %		
			Σ AlH C ₅ -C ₁₁	Σ AH C ₆ -C ₁₁	Σ C ₂ -C ₄ olefins	Σ C ₁ -C ₅ alkanes	DME
Ct-1	300	74,1	47,0	53,0	33,2	19,0	47,8
	360	33,6	43,7	56,3	24,6	73,1	2,3
	500	61,1	10,3	89,7	32,4	63,9	3,7
Ct-2	250	-	-	-	0,5	0,3	99,2
	300	87,9	45,1	54,9	16,4	5,0	78,6
	360	33,4	46,9	53,1	28,4	66,9	4,7
Ct-3	500	58,6	11,9	88,1	36,4	55,5	8,1
	250	-	-	-	-	-	100,0
	300	83,5	37,2	62,8	17,0	15,8	67,2
Ct-4	360	46,3	61,2	38,8	50,0	40,8	9,2
	500	78,8	6,1	93,9	47,2	52,8	-
	300	-	-	-	5,8	-	94,2
Ct-5	360	45,5	51,6	48,4	47,2	41,8	1,1
	500	-	-	-	Primary CO and CO ₂		-
	300	12,7	-	-	9,3	3,1	87,6
Ct-8	360	41,3	51,4	48,8	41,2	58,8	-
	500	60,6	5,8	94,2	5,6	94,4	-
	300	-	-	-	29,6	12,3	58,1
Ct-10	360	66,0	37,0	63,0	52,6	38,5	9,0
	500	62,0	3,7	96,3	35,8	64,2	-
	250	-	-	-	5,0	3,0	92,0
Ct-11	300	79,3	44,1	55,9	33,6	17,5	48,9
	360	57,9	40,8	59,2	35,4	63,5	1,1
	500	65,1	9,3	90,7	29,1	69,5	1,4
Ct-12	300	-	-	-	12,3	0,1	87,6
	360	57,1	54,9	45,1	70,4	27,4	2,2
	500	69,7	22,2	77,8	71,3	28,7	-
Ct-12	300	-	-	-	10,0	2,3	87,7
	360	61,0	57,7	42,3	56,4	16,2	27,4
	500*	84,6	-	-	67,4	32,6	-

*The activity of the catalyst decreases rapidly.

RESULTS AND DISCUSSION

The effect of the conditions of preliminary treatment of the catalysts modified with metal oxides on the activity and selectivity in conversion of methanol was investigated in the first stage of the study. As Table 1 shows, redox treatment was optimum for all systems studied, and the subsequent studies were thus conducted on catalysts previously treated with method II.

Based on the concepts of the possible mechanisms of transformation of methanol into hydrocarbons on unmodified pentasil [1], it could be predicted that the addition of different modifying additives to the zeolite would affect the rate of formation and consumption of the intermediate products of conversion of CH₃OH and consequently the selectivity of the reaction differently [8, 9].

The results of the tests of Ct-1-Ct-5, and 8 in the flow-type setup showed that they all exhibit high activity in conversion of methanol into hydrocarbons. In the 340-380°C range, the degree of conversion of methanol attains ~100% for all of the catalysts studied and a maximum is observed in the formation of liquid hydrocarbons; approximately the same amounts of aliphatic hydrocarbons (AlH) and AH are obtained. When the temperature of the reaction is

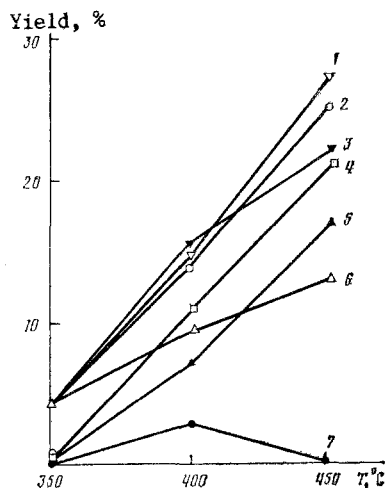


Fig. 1. Dependence of the yield of aromatic hydrocarbons (C_6-C_8) in conversion of CH_3OH on the temperature of the reaction and composition of the catalyst: 1) Ct-7; 2) Ct-8; 3) Ct-6; 4) Ct-9; 5) Ct-3; 6) Ct-1; 7) Ct-4.

increased ($>380^\circ C$), the contribution of cracking processes increases and the total yield of liquid hydrocarbons decreases markedly. The redistribution of hydrogen simultaneously intensified, and the concentration of AH in the products of the reaction increases significantly ($\geq 90\%$) (Table 2).

The addition of certain amounts of Co or Zn + Cr oxides to the HS zeolite system significantly affects both the overall activity of the catalyst and the selectivity of its action. Higher yields of liquid hydrocarbons are obtained on Ct-1 with relatively low concentrations of oxides in the catalyst; for the samples containing $>5\%$ oxides, the yield of liquid products decreases slightly and the selectivity of the catalyst changes significantly (see Table 2). It can be hypothesized that this is due to a decrease in the concentration of acid centers in the zeolite responsible for oligomerization and aromatization and partial blockade of its pores by the modifying additive. This results in a change in the rate of diffusion of molecules of the reagent and products of the reaction in the pores of the zeolite [10]. It is also possible that the decrease in the yield of liquid hydrocarbons is also due to acceleration of cracking of the oligomers formed when the concentration of metal oxides in the catalyst increases.

The antibatic dependence between the amount of added modifier and the yield of liquid hydrocarbons observed in most cases is particularly significantly manifested on Co-containing HS zeolites; the temperature of the reaction has the determining effect on their selectivity. When the concentration of Co_2O_3 is increased from 0.5 to 10%, the yield of liquid hydrocarbons at $300^\circ C$ decreases from 16% to 0 and DME is the basic product of the reaction; at $500^\circ C$, the yield of liquid hydrocarbons (Ct-2, 4) also decreases sharply from 41% to 0. In the last case, total oxidation of the methanol to CO, CO_2 , and H_2O takes place. At moderate temperatures ($340-380^\circ C$), the effect of Co-containing HS zeolites is directed toward formation of ALH and AH (see Table 2). A significant decrease in the yield of liquid hydrocarbons from 59 to 34% with an increase in the concentration of the metal oxides (Ct-5, Ct-8) is also observed for the catalysts modified with Zn and Cr compounds; the concentration of olefins in the gaseous products of the reaction simultaneously increases.

The specific effect of Co oxide in comparison to the Zn + Cr oxide mixture on the selectivity of conversion of methanol should also be noted. In the presence of Ct-4 and Ct-8 containing the same amount of the different metal oxides, significant differences are observed in their selectivity: at $300^\circ C$, dehydration of methanol to DME primarily takes place in the case of the Co-containing sample, while up to 42% C_2-C_5 ALH is formed on the Zn-Cr sample in these conditions. The differences in the effect of these catalysts at a higher temperature are especially important. At $500^\circ C$, hydrocarbons are not formed in general and only oxidation of methanol takes place on Ct-4, while it is transformed into hydrocarbons with 100% conversion on Ct-8 (see Table 2).

The study of conversion of methanol in the conditions of the pulsed method permitted observing the effect of the catalytic system when the effect of side reactions was significantly

smaller than in the conditions of the flow-type method. The yield of AH on pentasils modified with metal oxides is 1.5-2 times higher than on the base (Fig. 1). Ct-4 was an exception. As noted above, the occurrence of oxidative processes is characteristic of this catalyst. In the case of the flow method, the mono- and dialkylbenzenes obtained partially undergo deeper conversions due to the longer contact time, with the formation of polyalkylbenzenes which are difficult to desorb from the canals of the zeolite. In addition, side and secondary reactions (cracking, polymerization, coke formation) take place more intensively with a longer contact time. All of this results in a decrease in the yield of AH in the liquid products of the reaction. It was thus found that modification of the HS zeolite system (HZHM + Al₂O₃) with Co oxide or a mixture of Zn + Cr oxides significantly increases the aromatizing activity of the catalyst (Table 2 and Fig. 1).

The addition of P₂O₅ has a very different effect on the catalytic properties of the starting HS zeolite system in conversion of methanol. Treatment of ZSM-5 with trimethylphosphine increases the selectivity of the catalyst with respect to formation of C₂-C₄ olefins [8]. In the presence of phosphorus-containing catalysts prepared by modification of Ct-1 with phosphoric acid, the yield of C₂-C₄ olefins increases significantly, and in some conditions, the process of their formation becomes predominant. The promoting effect of P₂O₅ on formation of C₂-C₄ olefins with a >5% concentration of P₂O₅ in the catalyst is particularly marked (see Table 2). C₂-C₄ olefins (up to 71%) predominate in the gaseous products of the reaction on Ct-1 at 360-500°C. In similar experimental conditions, the concentration of C₂-C₄ olefins in the gas formed is ~2 times lower and equals 29-35% on Ct-1 and Ct-10. Increasing the amount of P₂O₅ in the catalyst to 20% (Ct-12) results in a decrease in the overall activity and a slight decrease in the selectivity for C₂-C₄ olefins; DME appears in significant amounts in the products of the reaction. It should also be noted that Ct-12 is unstable and rapidly loses its initial activity.

Ct-11 is thus the most efficient catalyst of conversion of methanol into C₂-C₄ olefins among the systems studied: the concentration of olefins in the gaseous products of the reaction on this catalyst attains 71% (yield of 46% for the CH₃OH delivered). Increasing the contact time by six times permitted significantly increasing the selectivity of the reaction for C₂-C₄ olefins. When the volume flow rate of methanol was changed from 1.4 to 8.4 h⁻¹ in the presence of Ct-11 at 500°C, the yield of olefins attained 74% (the concentration of olefins in the gas increased to 84%); AH were almost not formed. In the same experimental conditions, the yield of C₂-C₄ olefins on Ct-1 was only 38% (50% concentration of olefins in the gas). Similar features were also obtained at 380°C. However, it should be noted that with a relatively high volume flow rate of methanol (8.4 h⁻¹), the catalyst only remains active for the first hour and DME then appears in the products of the reaction, which indicates partial deactivation of the catalyst.

CONCLUSIONS

1. Modification of the 70% HZHM + 30% Al₂O₃ HS zeolite composite with Co or Zn + Cr oxides (from 5 to 15%) increases the aromatizing activity of the catalysts in conversion of methanol by 1.5-2 times.

2. The 10% P₂O₅/70% HZHM + 30% Al₂O₃ catalytic system is efficient in selective transformation of methanol into C₂-C₄ olefins (yield >70%).

3. The conditions of their preliminary activation have a significant effect on the catalytic activity of Co- and Zn + Cr-containing zeolite systems; successive air-hydrogen treatment was optimum for these systems.

LITERATURE CITED

1. C. D. Chang, Catal. Rev.-Sci. Eng., 25, 1 (1983).
2. Kh. M. Minachev and D. A. Kondrat'ev, Usp. Khim., 52, 1921 (1983).
3. T. V. Vasina, E. G. Khelkovskaya-Sergeeva, B. K. Nefedov, and O. D. Bragin, Izv. Akad. Nauk SSSR, Ser. Khim., 2435 (1985).
4. L. G. Agabalyan, N. S. Khashagul'gova, and I. I. Yaroshenko, Proceedings of the 3rd All-Union Conference on the Use of Zeolites in Catalysis [in Russian], Nauka, Moscow (1985), p. 82.
5. T. Ihui, E. Araki, T. Sezume, et al., Reakt. Kinet. Catal. Lett., 18, 1 (1981).
6. T. V. Vasina, E. G. Khelkovskaya-Sergeeva, N. N. Rostanin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1487 (1986).

7. O. V. Bragin, A. V. Preobrazhenskii, and A. L. Liberman, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2751 (1974).
8. W. W. Kaeding and S. A. Butter, *J. Catal.*, **61**, 155 (1980).
9. V. N. Romannikov and K. G. Ione, *Proceedings of the 3rd All-Union Conference on the Use of Zeolites in Catalysis [in Russian]*, Nauka, Moscow (1985), p. 87.
10. P. B. Weisz, *Pure Appl. Chem.*, **52**, 2103 (1980).

AMALGAM REDUCTION OF NITROGEN IN THE SYSTEM Ti(III)—Mo(III)—PYROCATECHOL
IN AQUEOUS SOLUTIONS

G. N. Petrova, O. N. Efimov,
and N. T. Denisov

UDC 541.138.3:546.17:541.128:541.49:
547.565.2:546.823:546.773

In molybdenum-containing catalytic systems that reduce N_2 under mild conditions to hydrazine and ammonia, titanium acts as the reducing agent, and molybdenum catalyzes the reduction of N_2 [1]. The yield of the nitrification products is increased in these systems when an Na amalgam is introduced as an additional source of electrons. These systems act in methanol in the presence of small amounts of water, which acts as a proton donor. In light of the above it was important to find Mo(III) complexes capable of catalyzing the reduction of N_2 in aqueous solutions. For this purpose we used the system Ti(III)—Mo(III)—pyrocatechol (PC), which catalyzes the electrochemical reduction of compounds with short bonds (CO , C_2H_2 , CN^- , CH_3CN) in water [3]. A preliminary communication was published in [4]. In this paper we present detailed results of the study.

EXPERIMENTAL

The system was prepared from aqueous solutions of Na_2MoO_4 , $Ti_2(SO_4)_3$, and pyrocatechol with subsequent reduction at a mercury cathode at a current density of $3.5 \text{ mA}/\Omega^2$ as described in [3]. During the course of the electrolysis, the pH of the solution rose from 2.5–3.0 to 6.7–7.0. Under a flow of Ar, 6 ml of the reduced solution was introduced into one compartment of a three-part vessel [5]. To the other compartments, 2.2 ml of an Na amalgam and 2 ml of aqueous H_2SO_4 (1:1) were added. In preliminary experiments it was shown that the yield of N_2H_4 and NH_3 was practically independent of the Na concentration in the amalgam at $C_{Na}^0 > 1.75$ mole/liter. The experiments were performed with concentrated amalgam, $C_{Na}^0 = 3.5$ mole/liter. The filled vessel was placed in an autoclave and N_2 was passed through it three times at pressures up to 2–2.5 MPa with subsequent removal of the pressure. After this, the required pressure of N_2 was created in the autoclave and the autoclave was turned to a position allowing the amalgam to mix with the reduced solution. The autoclave was agitated in a rocker at a frequency of 170–190 cycle/min, during which time the yield of NH_3 reached a constant value and did not depend on further increases in the rate of rocking.

The reaction was halted, and the autoclave was rotated to a position allowing H_2SO_4 to be added to the reaction mixture, leading to acidification of the solution and the rapid decomposition of the amalgam.

In determining hydrazine, 5 ml of the solution from the reaction vessel was poured into 2 ml of conc. HCl. The solution, which had turned colorless, was analyzed spectrophotometrically by reacting it with p-dimethylaminobenzaldehyde [6].

To trap the NH_3 , the gas from the autoclave was passed slowly through a trap with 0.1 N H_2SO_4 . The solutions from the three-part vessel and the trap were combined, evaporated to dryness, and the NH_3 in the distillate was determined by a phenolphthaleimide method [7]. The amount of NH_3 which forms under the given conditions from the decomposition of N_2H_4 did not exceed 5% of the total amount of NH_3 and was corrected for in the calculations.

The kinetics of the decomposition of amalgam in the presence of the catalytic system was studied by following the evolution of hydrogen after shaking the reaction vessel on the rocker.

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Division.
Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 12, pp. 2670–2674,
December, 1987. Original article submitted April 21, 1986.