PATHS OF METHANOL CONVERSION TO HYDROCARBONS ON HIGH-SILICA ZEOLITES

T. V. Vasina, E. G. Khelkovskaya-Sergeeva, B. K. Nefedov, and O. V. Bragin

The problem of methanol conversion to hydrocarbons in the presence of high-silica zeolites has been discussed extensively in recent years [1-8]. One of the important aspects of this problem is the mechanism through which C-C bonds are formed from  $C_1$  fragments in the first stage of conversion of methanol and dimethyl ether. This question still remains unresolved, and various investigators have given different interpretations [1, 3, 7, 8]. Another open question concerns the growth of the carbon chain.

In the present work, with the aim of determining the general relationships and nature of the individual stages, we have investigated, under comparable conditions, the conversion of  $CH_3OH$  and possible intermediates in its conversion ( $CH_3OCH_3$  and  $C_2H_4$ ) in the presence of Soviet-produced high-silica zeolites differing in composition and conditions of preparation.

### EXPERIMENTAL

The studies were performed in a continuous-flow catalytic unit [9]. The catalysts were zeolites synthesized from alumina-silica gels or silica sols with added boron compounds by crystallization under hydrothermal conditions [10, 11]. The type TsVK [high-silica] zeolites and the boron-containing silicate (BS)\* were obtained by the use of a tetrabutylammonium base; the TsVM was synthesized without the use of any organic compounds, by means of a modification of the procedure given in [12]. The following Na forms were obtained: TsVK-1 with  $SiO_2/Al_2O_3 = 71$ , TsVM with  $SiO_2/Al_2O_3 = 35$ , and BS with  $SiO_2/B_2O_3 = 87$ . In the catalytic experiments, the zeolites were used in decationized form (Na<sub>2</sub>O content < 0.1%); these were prepared by two treatments of the corresponding Na form with an NH<sub>4</sub>Cl solution at 70°C, with drying and calcining between treatments. The catalyst charge in the experiments was 2.5 ml (1.6 g) or 5.0 ml (3.2 g) of the 1-2 mm fraction. The feed rates were 0.013 mole/h for  $CH_3OCH_3^+$  and  $C_2H_4$ , and 0.055 mole/h for  $CH_3OH$ . Before starting an experiment, the catalyst was calcined in a flow of air for 5 h at 550°C; between experiments, it was calcined for 2 h. In the middle and at the end of a series, control experiments were performed; these indicated that the zeolites maintained their initial activity and selectivity up to the end of the series. The individual compounds  $CH_3OH$  and  $C_2H_4$  were used as initial reactants (purity ~99% by GLC analysis). The dimethyl ether that was used had saturated hydrocarbons as impurities: C3 2%, C4 11%, and C5 2%. The gaseous and liquid products from the reaction were analyzed separately by GLC under conditions that have been described in [9].

## DISCUSSION OF RESULTS

Previous articles [2, 13-15] have discussed the possibility that methanol conversion to hydrocarbons may proceed in accordance with the scheme

 $2CH_{3}OH \Rightarrow H_{3}COCH_{3} \rightarrow C_{2}-C_{5} \text{ (olefins)} \Rightarrow \begin{cases} \text{saturated,} \\ \text{aromatic,} \\ \text{olefinic hydrocarbons} \end{cases}$ 

\*The BS contains  $\sim 0.15 \text{ Al}_2 O_3$  [unit of measure not given in Russian original - Translator]. +Space velocities 100, 102, and  $65h^{-1}$  for H-TsVK-1, H-TsVM, and H-BS, respectively.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2435-2442, November, 1985. Original article submitted July 25, 1984.



Fig. 1. Yield of gaseous hydrocarbons as a function of temperature in conversion of methanol on H-TsVK: 1) dimethyl ether; 2)  $C_2H_4$ ; 3)  $C_2H_6$ ; 4)  $C_3H_6$ ; 5)  $C_3H_8$ ; 6)  $\Sigma C_4$ .

In [16, 17], doubt was expressed as to the intermediate formation of dimethyl ether; in [14, 18], two parallel paths of olefin formation were considered,

$$\begin{array}{c} 2CH_{3}OH \xrightarrow{} H_{3}COCH_{3} + H_{2}O \\ \downarrow \rightarrow \text{olefins} \leftarrow \downarrow \end{array}$$

We have investigated catalytic conversions of methanol, dimethyl ether, and ethylene under comparable conditions in the 225-500°C interval, in the presence of a series of Sovietproduced zeolites of the Pentasil type: TsVK, TsVM, and BS. As can be seen from Fig. 1 and Table 1, on the zeolites, which differed in composition and nature, in the experiments at relatively low temperatures (250-300°C), the sole product of  $CH_3OH$  conversion is  $CH_3OCH_3$ .\* A gradual increase in the temperature leads to the appearance of olefins, in the reaction products, mostly in the  $C_2-C_4$  range; this is accompanied by a decrease in the concentration of  $CH_3OCH_3$  and, simultaneously, by the formation of considerable quantities (up to 57%) of liquid aliphatic hydrocarbons (A1) and aromatic hydrocarbons (Ar) (Table 1).

Using the same samples of zeolite, we studied the conversions of CH<sub>3</sub>OCH<sub>3</sub> under similar temperature conditions. As can be seen from Fig. 2 and Table 2, CH<sub>3</sub>OCH<sub>3</sub> conversion begins at 225-260°C, i.e., in the temperature region of its formation from CH<sub>3</sub>OH. As the temperature is raised, the CH<sub>3</sub>OCH<sub>3</sub> is consumed rapidly, within the simultaneous formation of hydrocarbon components. We should also note the considerable primary increase in the yield of ethylene in the gaseous products from the conversion of methanol and dimethyl ether at relatively low temperatures (250-275°C). This is particularly striking in the conversion of methanol (Fig. 1); when using dimethyl ether as the feed, the primary ethylene that has been formed is partly dimerized to C4 hydrocarbons (Fig. 2). The coinciding regions of temperature for the formation and consumption of dimethyl ether, the character of the temperature dependence of consumption of the original  $CH_3OH$  and  $CH_3OCH_3$  (Figs. 1 and 2), and the identity of products from CH<sub>3</sub>OH and CH<sub>3</sub>OCH<sub>3</sub> conversion in terms of composition and distribution (Tables 1 and 2) regardless of the type of zeolite; this indicates that the dimethyl ether formed as a primary product from methanol is an intermediate product in a staged conversion of CH<sub>3</sub>OH to hydrocarbons. As a result, we usually obtain from CH<sub>3</sub>OH and CH<sub>3</sub>OCH<sub>3</sub> a wide variety of identical-composition  $C_2-C_{11}$  aliphatic hydrocarbons (including highly branched hydrocarbons) and  $C_6-C_{12}$  aromatic hydrocarbons.

Comparative data on the conversion of ethylene in the presence of these same high-silica zeolites (Figs. 3 and 4 and Table 3) indicate identity of the products from conversion of  $CH_3OCH_3$  and  $C_2H_4$ . The relationships and the distributions of the gaseous and liquid hydrocarbons are also very similar, over a wide range of temperatures. At relatively low temperatures (225-300°C), we observe sharp decreases in the concentration of  $CH_3OCH_3$  or  $C_2H_4$ .

\*As in Russian original; the data in Fig. 1 and Table 1 indicate that this statement is correct only for a temperature of  $250^{\circ}$ C - Translator.

TABLE 1. Products of Methanol Conversion (space velocity 0.8  $\rm h^{-1})$ 

		Yield of		Composi	tion of	liquid pr	coducts, %		Gas o	composition,	%	
40110400	5 F	products	INTETANION		₩	ų	wh bue IA					-
valatyse	, .		%	ה קייי קייי	C <sub>6</sub> —C <sub>7</sub>	Gs	C <sub>9+</sub>	CH	C2H4/C2H6	C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>	, גני	CH <sub>s</sub> OCH <sub>s</sub>
H-TsVK-1	250	0										~100
	275	24	06	51	. 🕶	12	36	' t	18/	10/8	8	52
	300	49	98	60	2	12	26	1	20/1	5/13	6	51
	380	43	- 100	49	6	22	20	1	10/2	12/33	42	L
	500	33	100	22	25	35	18	23	16/4	32/21	24	I,
M-TsVM	250	0	92		· .			I.	1/1	-/-	1	98
	300	18	95	41	າບ	15	39	Ţ	18/1	12/3	4	. 61
	360	46	97	32	22	30	16	7	2/1	2/53	37	, eo
	200	32	100	17	14	- 48	21	7	15/6	12/37	12	6
H-BS	250	0	74					•				$\sim 100$
	300	0	84	·	•.							$\sim 100$
	325	21	83	64	4	12	23	ļ	-/9	8/1	4	. 81
	350	<b>44</b>	95	73	7	10	15.		21/-	30/5	19	24
	380	57	67	75	က	6	13	~	23/	40/6	33	9
	500	22	100	53	12	23	12		13/1	51/3	29	1

\*Remainder  $CO + CO_2$ .

		 	Yield of	Compositi	on of li	iquid pro	oducts, %		Gas o	composition,	*+	
Catalyst	r, °c	Conver- sion. %	liquid hydro- carbons rela-	ر ب	Ā	ม	Al and Ar					
			tive to feed,	6) 1) 1)	C₁−C,	ບຶ	ten ten	CH,	C2H4/C5H6	C,He/C,Ha	บั	CII,OCH,
H-TsVK-1	225	60	0					1.	1/-	2/7	26	60
	250	8	16	71		9	20	1	13/1	4/21	34	24
	300	100%	67	41	6	. 16	37	í	1/2	1/45	50	1
	350	100	88	22	22	29	27	1	-/2	1/52	43	!
	380	100	38	17	34	24	25	2	1/3	1/59	50	I
	200 ·	100	22	er	43	25	29	11	5/13	6/52	11	l
H-TsVM	250	0	0					_	Gas compos	sition close	to orig	Inal
	275	09	6	52	5	14	29	£	-/5	4/6	19	65
	300	<b>8</b> 6	40	46	S	15	34	2	8/3	3/39	38	ũ
	380	100	30	14	23	32	31	61	1/3	1/65	27	*
	200	100	40.	1	47	20	32	22	4/22	4/39	4	1
H-BS	250	0	0						Gas compos	sition close	to orig	inal
	280	42	15	43 #	œ	12	37	1	.5/−	3/5	20	64
	300	6	45	71	۰. ۲	8	20	ŝ	29/1	7/20	27	6
	320	100	64	68	67	8	22	2	$19/2^{-1}$	7/23	41	l
	380	100	48	52	10	18	20	-	5/2	12/28	65	.1
	500	100	28	19	33	36	12	7	13/6	24/24	28	1

TABLE 2. Products of Dimethyl Ether Conversion

\*For feed composition, see Experimental section. +Remainder CO + CO2. ‡Content understated because of incomplete separation of higher-molecular-weight Al from Ar.



Fig. 2. Yield of gaseous hydrocarbons as a function of temperature in conversion of dimethyl ether on H-TsVK: 1) dimethyl ether; 2)  $C_2H_4$ ; 3)  $C_2H_6$ ; 4)  $C_3H_6$ ; 5)  $C_3H_8$ ; 6)  $\Sigma C_4$ .

Fig. 3. Dependence of gaseous hydrocarbon yield on temperature in conversion of ethylene on H-TsVK: 1)  $C_2H_4$ ; 2)  $C_2H_6$ ; 3)  $C_3H_6$ ; 4)  $C_3H_8$ ; 5)  $\Sigma C_4$ .

(see Figs. 2 and 3), with the simultaneous formation of considerable amounts of  $C_2C_{11}$  aliphatic hydrocarbons, including molecules with an odd number of C atoms. These results indicate that under relatively mild conditions of catalysis, in the initial stages of the process on high-silica zeolites, the initially formed low-molecular-weight unsaturated  $C_1$ - $C_2$  fragments are subject to linear oligomerization. Indeed, in the conversions of CH<sub>3</sub>OCH<sub>3</sub> and  $C_2H_2$  on the different high-silica zeolites, the gaseous products from the reaction (225-300°C) contain up to 50%  $C_4$  hydrocarbons, and also considerable quantities of ethylene in the conversion of CH<sub>3</sub>OH (Fig. 1 and Tables 1-3). Here, the gas contains a large amount of  $C_3$  hydrocarbons and very little CH<sub>4</sub> (<2%).

The formation of molecules with an odd number of C atoms  $(2n + 1) \ge 3$  (up to C<sub>11</sub>), particularly in the initial stages of the reaction, can serve as an indication of the intermediate formation of C<sub>1</sub> species participating in the growth of the hydrocarbon chain. These may be carbene radicals, obtained by  $\alpha$ -elimination in accordance with the scheme [2, 17]



Subsequently, under the actual conditions of catalysis on the acidic centers of high-silica zeolites, the carbenes apparently dimerize and also may alkylate the methanol and/or dimethyl ether, extending the carbon chain and forming hydrocarbons with higher molecular weights [1]. In the overall network of conversions of  $CH_3OH$  to hydrocarbons, disproportionation reactions are also possible, or, for example, alkylation of low-molecular-weight hydrocarbons by fragments of the methanol or dimethyl ether, resulting in growth of the carbon chain and the formation of straight-chain and branched-chain hydrocarbons. Actually, the products from the conversion of methanol and dimethyl ether on high-silica zeolites contain primarily branched-chain  $C_4-C_{11}$  aliphatic hydrocarbons. The small quantities of  $CH_4$  (<2%) in the products from  $CH_3OH$  conversion over a broad range of temperatures and on various catalysts indicates a low probability of primary formation of the <sup>+</sup>CH<sub>3</sub> ion from  $CH_3OH$  in its conversion on high-silica zeolites.

On the whole, a comparison of the results obtained on the conversion of  $CH_3OH$ ,  $CH_3OCH_3$ , and  $C_2H_4$ , along with the observed relationships and the distribution of the individual components, particularly in the initial stages, indicates a similarity of the processes taking place in the conversion of these three substances, leading in the end to identical reaction products. We should first note the symbaticity in changes in the composition of individual

\*The increase in CH4 content at 500°C is apparently the result of dealkylation of alkylaromatic hydrocarbons and cracking of aliphatic hydrocarbons.



Fig. 4. Temperature dependence of conversion (1) of dimethyl ether (A) and ethylene (B), and temperature dependence of composition of liquid products obtained on H-TsVK (curve 2 for  $C_6-C_{12}$  aromatic hydrocarbons, curve 3 for  $C_4-C_{11}$  aliphatic hydrocarbons).

TABLE 3. Products of Ethylene Conversion (space velocity 120  $h^{-1})$ 

		Yield of	Con- ver-	Composition of liquid products, %				Gas composition, %			
Catalyst	°C	products	sion	A1	A	y	A1 and		С.н./	C.H./	
·		%		C <sub>4</sub> -C <sub>9</sub>	C <sub>6</sub> C <sub>7</sub>	C <sub>8</sub>	Ar Cr <sub>9+</sub>	CH4	$/C_2H_6$	/C <sub>3</sub> H <sub>8</sub>	ΣC4
H-TsVK-1	250 300 400 500	43 64 43 45	54 99 99 98	100 44 15 1	4 30 51	11 23 20	41 32 28	- - 1 12	81/1 3/3 1/8 3/25	4/1 1/40 2/55 4/48	13 52 33 6
H-TsVM	250 300 350 400 500	0 37 37 40 53	0 55 100 100 99	82 7 4 1	2 33 41 51	3 23 18 11	13 37 37 37 37	- - 2 33	100/-74/1 -/4 -/11 2/35	-/- 4/9 -/76 -/77 1/27	
H-BS	250 300 350 380 400 500	24 64 72 48 42 43	28 80 94 94 92 95	100 70 49 37 26 6	- 6 3 21 32 44	6 3 18 27 30	- 18 45 24 15 20	- - 1 4 22	95/1 56/4 22/7 12/8 14/16 10/34	-/1 17 5/22 2/20 3/31 7/21	3 23 44 57 32 6

# \*Remainder CO + $CO_2$ .

hydrocarbons formed from  $CH_3OCH_3$  and  $C_2H_4$  in the 225-500°C interval. At relatively low temperatures, we observe a maximum in the  $C_2H_4$  formation and predominance of  $C_2H_4$  and the products of  $CH_3OH$  conversion in comparison with  $C_3$  and  $C_4$  hydrocarbons (see Fig. 1 and Figs. 2-4). These results are evidence in favor of the formation of  $C_2H_4$  as one of the main intermediates in the conversion of  $CH_3OH$  to hydrocarbons. Certain differences that occur in the quantitative distribution of the hydrocarbons that are formed in the conversions of  $CH_3OH$ (Fig. 1 and Table 1) in comparison with  $CH_3OCH_3$  and  $C_2H_4$  (Figs. 2-4 and Tables 2 and 3) may be related to the influence of the relatively large quantities of water evolved in the process of methanol conversion. The  $H_2O$  molecules may block the acidic centers that are responsible for such stages of the process as oligomerization, dehydrocyclooligomerization, and others. According to [19], in the conversion of  $C_2H_4$  with added steam, the composition of the reaction products is shifted toward the formation of aliphatic hydrocarbons. Another source of the differences may be the substantial difference between the rate of feed of  $CH_3OH$  and the rate of passage of the gaseous reactants ( $CH_3OCH_3$  and  $C_2H_4$ ).

The data on the intermediate formation of ethylene are in good agreement with the results reported in [5], where it was shown that in the conversion of  $CH_3OCH_3$  on a modified ZSM-5 catalyst, the sole reaction product was ethylene. Subsequent conversion of the ethylene may proceed along the path of oligomerization, followed by  $C_5$  and  $C_6$ -dehydrocyclization to aromatic hydrocarbons, or along the path of alkylation of  $CH_3OH$  and  $CH_3OCH_3$  with the formation of homologues of ethylene. The predominance of one path or the other will depend primarily on the reaction conditions (temperature, contact time) and on the nature of the catalyst.

The results we have obtained do provide a quite definite indication of the intermediate formation of  $CH_3OCH_3$  and  $C_2H_4$  in the overall chain of reactions taking place in the conversion of  $CH_3OH$  to aliphatic and aromatic hydrocarbons on Soviet-produced high-silica zeolites. Along with this, we find indirect evidence tht a bivalent species [: $CH_2$ ] participates in the formation of the C-C bond. The following facts support this hypothesis: the constant presence, in the products of  $CH_3OH$  conversion, of considerable quantities of hydrocarbons with an odd number of C atoms, even at low temperatures at which there will be very little cracking; the low contents of  $CH_4$  in the reaction products; the preferential formation of branched-chain hydrocarbons; and the presence of a complete set of polymethyl-substituted homologues of benzene.

## CONCLUSIONS

1. In the presence of a number of Soviet-produced zeolites of the Pentasil type (TsVK, TsVM, high-silica borosilicate), under comparable conditions (250-500°C), methanol, dimethyl ether, and ethylene undergo identical conversion, forming  $C_2-C_{11}$  aliphatic hydrocarbons and  $C_6-C_{12}$  aromatic hydrocarbons.

The experimental data that have been obtained in this study indicate that dimethyl ether and ethylene are the principal intermediates in the conversion of methanol to hydrocarbon on these catalysts.

#### LITERATURE CITED

- 1. C. D. Chang, Catal. Rev., 25, 1 (1983).
- 2. C. D. Chang and A. J. Silvestri, J. Catal., <u>47</u>, 249 (1977).
- 3. Kh. M. Minachev and D. A. Kondrat'ev, Usp. Khim., <u>52</u>, 1921 (1983).
- 4. P. Salvador and W. Kladnig, J. Chem. Soc., Faraday Trans. 1, 1153 (1977).
- 5. W. W. Kaeding and S. A. Butter, J. Catal., <u>61</u>, 155 (1980).
- 6. J. B. Nagy, J. P. Gilson, and E. G. Derouane, J. Mol. Catal., 5, 393 (1979).
- O. V. Bragin, T. V. Vasina, B. K. Nefedov, A. V. Preobrazhenskii (Preobrazhensky), N. V. Palishkina, T. V. Alekseeva, and Kh. M. Minachev, Proceedings of the 11th World Petroleum Congress, London (1983), Preprint PD9 (4).
- 8. G. V. Isagulyants, K. M. Gitis, Yu. G. Dubinskii, A. G. Timokhov, and V. N. Kornyshev, Izd. Akad. Nauk SSSR, Ser. Khim., 75 (1984).
- 9. O. V. Bragin, A. V. Preobrazhenskii, and A. L. Liberman, Izd. Akad. Nauk SSSR, Ser. Khim., 2751 (1974).
- 10. R. Chu, U. S. Pat. No. 3,709,975 (1973).
- 11. M. R. Klotz, Fr. Pat. No. 2, 367,701 (1978), Chem. Abstr., 89, P118480s (1978).
- V. Yu. Volkov, M. A. Kaliko, B. A. Lipkind, and V. V. Zadymov, Khim. Tekhnol. Topl. Masel, No. 6, 8 (1982).
- E. G. Derouane, J. B. Nagy, P. Dejaifve, J. H. C. van Hoof, B. P. Spekman, J. C. Vedrine, and C. Naccache, J. Catal., <u>53</u>, 40 (1978).
- 14. J. R. Anderson, K. Foger, T. Mole, R. A. Rajadhyaksha, and J. V. Sanders, J. Catal., 58, 114 (1978).
- O. V. Bragin, B. K. Nefedov, T. V. Vasina, V. N. Lutovinova, T. V. Alekseeva, A. V. Preobrazhenskii, and Kh. M. Minachev, Dokl. Akad. Nauk SSSR, <u>255</u>, 103 (1980).
- 16. N. S. Khashagul'gova, S. N. Khadzhiev, and A. A. Kubasov, Kinet. Katal., 24, 1261 (1983).
- 17. P. B. Venuto and P. S. Landis, J. Catal., <u>21</u>, 330 (1971).
- 18. S. Ceckiewicz, J. Chem. Soc., Faraday Trans. 1, 77, 269 (1981).
- P. Dejaifve, J. C. Vedrine, C. Naccache, and E. G. Derouane, Proceedings of the 7th Congress on Catalysis, Tokyo (1980), Preprint A-51.