CONCLUSIONS

1. Catalytic systems based on TsVM high-silica zeolites are active catalysts of ethylene and ethane aromatization. The yields of aromatic hydrocarbons from ethylene on the H form of the TsVM are as high as 75%. The catalyst activity increases in the series Na-TsVM (I) \ll HNa-TsVM (II) < H-TsVM (III), apparently governed by their acidic function; the catalysts II and III are active in the aromatization of ethane.

2. The introduction of a dehydrogenating component into the H form of the TsVM, in particular platinum, increases the yield of aromatic hydrocarbons from ethane to 20%.

3. The aromatization of ethane in the presence of the bifunctional system M/H-TsVM (M = Pt, Pd, Rh) is influenced substantially by preliminary high-temperature treatment of the catalyst (air alone, air and hydrogen, or hydrogen alone).

4. In the course of ethane and ethylene conversions, the catalytic system M/H-TsVM "evolves," with an increase in the yield of aromatic hydrocarbons.

LITERATURE CITED

- 1. O. V. Bragin, A. V. Preobrazhenskii, and A. L. Liberman, Izv. Akad. Nauk SSSR, Ser. Khim., 1670, 2751 (1974).
- 2. J. R. Anderson, K. Foger, T. Mole, R. A. Rajadhyaksha, and J. V. Sanders, J. Catal., 58, 114 (1978).
- O. V. Bragin, T. V. Vasina, B. K. Nefedov, V. N. Lutovinova, A. V. Preobrazhenskii, N. V. Palishkina, T. V. Alekseeva, and Kh. M. Minachev, Second All-Union Conference on the Application of Zeolites in Catalysis [in Russian], Moscow (1981), p. 211.
- 4. D. A. Kondrat'ev, A. A. Dergachev, B. K. Bondarenko, T. B. Borovinskaya, B. K. Nefedov, Yu. S. Khodakov, R. V. Dmitriev, T. V. Alekseeva, and Kh. M. Minachev, Second All-Union Conference on the Application of Zeolites in Catalysis [in Russian], Moscow (1981), p. 207.
- 5. U.S. Pat. 3,775,501 (1973).
- 6. U.S. Pat. 4,120,910 (1978).
- 7. U.S. Pat. 4,157,293 (1979).
- 8. O. V. Bragin, T. V. Vasina, Ya. I. Isakov, B. K. Nefedov, A. V. Preobrazhenskii, N. V. Palishkina, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 954 (1982).
- 9. W. J. Reagan, A. W. Chester, and G. T. Kerr, J. Catal., 69, 89 (1981).
- 10. O. V. Bragin, E. S. Shpiro, A. V. Preobrazhenskii, T. V. Vasina, G. V. Antoshin, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 1256 (1980).

CONVERSION OF ISOBUTYLENE ON DECATIONIZED

SUPERHIGH-SILICA ZEOLITE MODIFIED WITH

ADDED VANADIUM

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UDC 542.97:547.313.4

The introduction of vanadium into superhigh-silica zeolite Na-SHSZ leads to p-xylene (PX) enrichment of the products from the conversion of C_2 - C_4 olefins [1]. Here we are reporting on a study of the influence of the additive concentration on the catalytic properties of the more active decationized form of this type of zeolite (H-SHSZ) in conversions of isobutylene (IB) at 320-580°C.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2009-2014, September, 1983. Original article submitted November 16, 1982.

0568-5230/83/3209-1814\$07.50 © 1984 Plenum Publishing Corporation



Fig. 1. IB conversion (1), yield of aromatic hydrocarbons (2), and yield of C_8 alkylbenzenes (3) as functions of V concentration in catalyst, at 320°C (a) and 500°C (b).

EXPERIMENTAL

The H-SHSZ samples used in this work were synthesized by procedures given in [2] $(SiO_2/Al_2O_3 \text{ ratio} 60.3, Na_2O \text{ content} < 0.1\%)$, and were modified by additions of V. The catalysts were prepared by impregnating the zeolite with a VOSO₄ solution by procedures given in [3]. The content of V in the catalysts was determined by atomic absorption spectrophotometry. The valence state of the vanadium was investigated by EPR. The concentration of hydroxyl groups was measured by an isotope exchange method [4]. The samples were vacuum-baked at 500°C.

Before use in the experiments, the catalysts (~ 2 cm^3) were successively treated at 500°C with air (10 liters/h, 3 h) and He (1 liter/h, 1 h). The procedures used in conducting the experiments and in the GLC analysis have been described in [5]. The IB, ~ 99% purity, was fed to the reactor at a space velocity of 500 h⁻¹.

DISCUSSION OF RESULTS

The influence of the V additive concentration on the catalytic properties of the H-SHSZ was investigated under conditions giving the maximum yield of liquid catalysate from the IB (320°C), and also under conditions most favorable for the formation of aromatic hydrocarbons (500°C) [2].

At both temperatures, both with and without added V, the products from the conversion of the IB contained C_2 - C_5 gaseous olefins and paraffins, along with C_6 - C_{10} aliphatic and aromatic hydrocarbons. The IB conversion was close to 100% in all experiments, so that the selectivity of the reaction could be evaluated from the yield of one group of hydrocarbons or another.

The experiments at 320°C showed (Fig. 1a) that the selectivity of the reaction with respect to the formation of aromatic hydrocarbons depends on the concentration of V. Thus, the introduction of 0.3% V into the zeolite gives a sharp increase of the total yield of aromatic hydrocarbons (from 25% to 40%, curve 2) and of the yield of C₈ alkylbenzenes (from 10% to 20%, curve 3). As the V concentration in the catalyst is increased from 0.3% to 10.3%, the yield of aromatic reaction products drops to zero. Regardless of the concentration of V introduced into the zeolite, the total yield of liquid catalysate remains constant (~ 84-86%). At this temperature and in this range of V concentrations, the yield of gaseous products is 10-12%.

At 500°C, these relationships are different in nature (Fig. 1b). In the range of V concentration from 0.3% to 1.3%, the total yield of aromatic hydrocarbons increases slightly; when the additive content is further increased to 10.3%, the yield of aromatic hydrocarbons drops off to approximately the original level. The yield of C₈ alkylbenzenes, which is 12% for the unmodified catalyst, increases to $\sim 20\%$ as the V content is raised to 2.8% and then remains constant. Regardless of the quantity of V in the catalyst, the content of aliphatic hydrocarbons in the liquid catalysate is quite low (1-6%). The yield of gaseous products at this temperature is 50-55%.

The conversions of IB on V/H-SHSZ, the same as on V/Na-SHSZ [1], are characterized by the formation of PX in quantities greater than its equilibrium concentration in the C_8 -alkylbenzene fraction. With increasing content of V, the quantity of PX in the fraction increases (Table 1). This effect is most pronounced at 320°C, where the dehydrocyclization takes place to a smaller degree: In the case of the unmodified zeolite, the quantity

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TABLE 1.

Conver-	1	B	T	n of liqui aromatic carl Cs	d catalys: hydro- oons C ₉ C ₁₀	aliphatic hydro- carbons	DX Comb	e of C _g zene fra MX	-alkylb iction, ⁶ OX	EB EB	T,°C	Cor	np. of fract MX	C ₈ -alkylb ion, 96 OX	enzene EB
97,7 14,2 44,6 33,2	14,2 44,6 33,2	44,6 33,2	33,2		7,0	1,0	17,9	50,2	22,1	9,8	320	30,8	48,1	8,6	12.5
97,0 14,1 40,1 37,2	14,1 40,1 37,2	40,1 37,2	37,2		7,8	0,8	22,1	50,1	20,1	7,7	320	44,5	34,0	7,3	14,2
97,0 9,9 40,4 39,1	9,9 40,4 39,1	40,4 39,1	39,1		0'0	1,6	24,6	47,3	20,6	7,5	320	43,1	37,2	6,0	13,7
98,1 9,2 37,6 43,4	9,2 37,6 43,4	37,6 43,4	43,4		8,5	1,3	25,3	47,5	20,0	7,2	320	49,3	30,7	6.9	13,1
97,5 8,0 41,6 40,5	8,0 41,6 40,5	41,6 40,5	40,5	_	5,9	4,0	33,7	42,3	13.9	10,1	320	61,8	21,6	7,0	9.6
98,7 8,1 39,2 44,9	8,1 39,2 44,9	39,2 44,9	44,9		4,8	3,0	40.5	41,4	8,5	9,6	320	57,5	25,5	6,4	10,6
96,3 8,0 38,4 42,6	8,0 38,4 42,6	38,4 42,6	42,6		5.0	6,0	47,5	33,0	9,4	10,1	320	1	1	1	1

TABLE 2. Effect of Process Temperature on Compositions of Liquid Catalysate and C_8 Alkylbenzenes in Aromatization of IB on 2.8% V/H-SHSZ Catalyst

		Vield on IB f	निवर्त वि		Compc	sition of liq	uid catalysate	2, %		زر ما اسر ا		B
T °C	Conversion.		of			aromatic h	vdrocarbons		comp. u	I U8-AIKYI	Delizene Irac	uon, %
	ц,	liauid	aromatio	c	E			alinhatic				
	9	catalysate	hydrocarbon	a - %		G	Cs-Cia	hydrocarbons	PX	MX	ХО	EB
320	94,8	85,5	14,8	0,3	3,6	8,2	5,3	82,6	61.8	21.6	7.0	9.6
380	98,8	77,0	56,8	1.5	20,8	36,5	15,0	26,2	57.4	23.8	5,5	13.3
420	94,6	57,6	52,9	3,9	40,8	43,0	3,1	9,2	36.7	44.9	10.7	7.7
500	97,5	50,4	48,4	8,0	41,6	40,5	5,9	4,0	33,7	42,3	13,9	10.1
550	97,4	46,6	46,1	14,0	50,0	32,0	3,0	1,0	40,2	40.8	11,7	7.3
580	1, 10, 7	48,8	48,5	14,1	50,5	32,1	2,7	0,6	39,6	43,7	10.7	6.0

TABLE 3.	Kinetic	Diameters	of	Aromatic
Hydrocarb	on Mole	cules		

Hydrocarbon	Kinetic diameter, Å	Hydrocarbon	Kinetic diameter, Å
Toluene p-Xylene m-Xylene	5,8 5,8 6,8	o-Xylene m-Ethyltoluene Trimethylben- zene	6,8 7,6 7,5

of PX in this fraction (~ 31%) is greater than the equilibrium concentration of this isomer (23.8% [6]); and with V contents of 2.8% and 5.7% in the H-SHSZ, the PX concentration is ~ 60%. In contrast, under the conditions of preferential aromatization (500°C), the contents of PX in the C₈-alkylbenzene fraction are 18%, 34%, and 40% for catalysts containing 0, 2.8%, and 5.7% V, respectively.

Thus, the distribution of isomeric xylenes in the products from the conversion of IB on V/H-SHSZ depends not only on the concentration of V but also on the reaction temperature. Experiments with the 2.8% V/H-SHSZ catalyst showed (Table 2) that when the temperature is increased from 320° to 420°C, the relative amount of PX in the C₈ aromatic products decreases; in the 420-580 °C region, the temperature has practically no effect on the distribution of isomeric xylenes.

The results that we have obtained can be explained by means of hypotheses previously advanced on limitation of the rates of the reactions on SHSZ by internal diffusion [1, 2, 7]. For example, as can be seen from the data we have already examined (Fig. 1a), the introduction of 0.3-0.5% V into the H-SHSZ leads to an increase of selectivity (at 320°C) of the conversion of IB to aromatic hydrocarbons, in particular C₈ alkylbenzenes. The only possible reasons for this are (a) a decrease of the effective diameter of the zeolite channels due to formation of V oxides in the channels in the course of the catalyst preparation, or (b) blockage of the mouths of the pores. Either of these forms of restriction can lower the rate of diffusion, into the gas phase, of the oligomers that are formed in the first stages of the reaction, thereby extending their residence time in the catalyst pores and increasing the probability that these oligomers will interact with aromatization centers. The introduction of larger quantities of V into the H-SHSZ (> 0.5%) is accompanied by a lowering of selectivity with respect to the formation of aromatic hydrocarbons. This may be due to the creation of additional structural limitations hindering the formation of large molecules of aromatic hydrocarbons in the zeolite channels. These limitations should be manifested more strongly when the molecules that are formed have greater kinetic diameters (Table 3) [8, 9]. The results that we obtained (Fig. 2) support this view: As the V concentration in the catalyst is increased from 0.5% to 5.7%, the yields of C_9-C_{10} aromatic hydrocarbons and m-xylene (MX) are lowered by factors of approximately 5, whereas the yields of toluene (T), ethylbenzene (EB), and PX are cut only in half. The degrees to which the yields of benzene (B) and o-xylene (OX) are reduced is difficult to evaluate because of the low contents of these products in the catalysates.

According to data we have already examined (Figs. 1a and 1b and Tables 1 and 2), at higher temperatures, the selectivity of aromatic hydrocarbon formation from the IB is less dependent on the V concentration than it is at 320°C. Also, when the temperature is increased, a decrease of selectivity with respect to PX formation is observed. In [7], examples of lower selectivities in a number of processes on zeolite catalysts at higher temperatures were taken as evidence that the reactions proceed in the "configurational" diffusion regime, i.e., under conditions such that the size of the reacting molecules is commensurate with the size of the zeolite channels. In contrast to the internal diffusion regime, in which the diffusion rate is less dependent on temperature than is the reaction rate, in the "configurational" diffusion region we find that an increase of temperature is accompanied by a sharp increase of the diffusion coefficients, and this may bring about a reduction of the process selectivity.

The selectivity of PX formation from IB can be evaluated from the ratio of concentrations of isomeric xylenes (PX/MX) in the reaction products. These data (Fig. 3) indicate that in the case of the unmodified zeolite, the distribution of xylenes corresponds to the equilibrium distribution, deviating slightly from equilibrium only at temperatures below 400°C. For the 2.8% V/H-SHSZ catalyst, the PZ/MX ratio is considerably greater than the equilibrium value (0.44) over the entire range of temperatures investigated. We can conclude that at low temperatures, on both the modified and the original H-SHSZ, the diffusion rates of PX and MX differ sub-stantially. As the temperature is increased, the difference between the diffusion rates of the two isomers decreases rapidly, and the selectivity with respect to PX formation drops off. Thus, the character of the curves in Fig. 3 indicates that the IB conversions take place in the "configurational diffusion" regime.



Fig. 2. Yields of aromatic products in conversion of IB (320°C) as functions of V concentration in catalyst: 1) T; 2) PX; 3) MX; 4) EB; 5) C_9-C_{10} aromatic hydrocarbons.

Fig. 3. Temperature dependence of ratio of PX and MX concentrations in IB conversion products (1, 2) and in OX conversion products (3): 1, 3) 2.8% V/H-SHSZ; 2) H-SHSZ.



Fig. 4. OX conversion and concentration of hydroxyl groups as functions of content of V in catalyst.

Indirect support for the hypothesis of the influence of diffusion on the variation of selectivity can be found in data obtained in experiments on the isomerization of OX in the presence of H-SHSZ and V/H-SHSZ (Fig. 4). An increase of the quantity of V introduced into the catalyst leads to a considerable drop of the OX conversion; at 250°C, the conversion drops from 56% in the case of the 0.3% V/H-SHSZ to 1.1% in the case of the 2.8% V/H-SHSZ. The catalyst containing 2.8% V shows appreciable activity only at 350-500°C (OX conversion 5.4% and 11.1% at these two respective temperatures).

With increasing V concentration, the selectivity of the reaction with respect to PX formation increases. The PX/MX ratio for the 2.8% V/H-SHSZ is 1.1-1.2 (Fig. 3, line 3), which is 2.5-3.0 times the equilibrium value. In the isomerization of OX on the unmodified catalyst, the distribution of xylenes is no different from the equilibrium distribution.

It is known [10] that the catalytic activity of zeolites in the isomerization of alkylaromatic hydrocarbons is determined by the presence of acidic OH groups on the catalyst surface. A comparison of data on the conversion of OX on SHSZ containing various quantities of V with the results obtained in determinations of the OH group concentration shows (Fig. 4) that there is no correlation between the activity and acidity of the V/H-SHSZ. Hence we can assume that the inhibition of OX isomerization with increasing concentration of V introduced into the zeolite is more likely related to a change in the pore structure of the zeolite rather than to any change in acidic properties. It was of interest to determine the state in which the V exists in the zeolite. It was shown by ESR that for all of the oxidized and reduced forms of the catalysts that were investigated, containing V in amounts from 0.3% to 2.8%, the spectrum that was observed was characteristic for vanadium(IV) complexes having the vanadyl structure. The intensity of the ESR signal from the VO²⁺ was found to be independent of the quantity of V introduced into the zeolite. However, most of the V is in valence states that are not registered in the ESR spectrum, i.e., vanadium(III) and vanadium(V).

The ESR studies of the vanadium-modified SHSZ were carried out by V. A. Shvets and A. L. Tarasov, to whom the authors wish to express their appreciation.

CONCLUSIONS

1. The introduction of 0.3% vanadium into decationized SHSZ increases the overall yield of aromatic products in isobutylene conversion at 320° C by a factor of 1.5. This effect is considerably less pronounced at 500° C.

2. Increases of the vanadium concentration in the zeolite lead to higher contents of p-xylene in the C_{8} -alkylbenzene fraction.

LITERATURE CITED

- 1. Kh. M. Minachev, D. A. Kondrat'ev, A. A. Dergachev, T. B. Borovinskaya, T. N. Bondarenko, B. K. Nefedov, and T. V. Alekseeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1833 (1981).
- Kh. M. Minachev, D. A. Kondrat'ev, A. A. Dergachev, B. K. Nefedov, T. N. Bondarenko, T. V. Alekseeva, and T. B. Borovinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2509 (1980).
- 3. Kh. M. Minachev, D. A. Kondrat'ev, A. A. Dergachev, B. K. Nefedov, T. N. Bondarenko, T. V. Alekseeva, and T. B. Borovinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1304 (1981).
- 4. Kh. M. Minachev, R. V. Dmitriev, Ya. I. Isakov, and O. D. Bronnikov, Kinet. Katal., 12, 712 (1971).
- 5. D. A. Kondrat'ev, T. N. Bondarenko, A. A. Dergachev, and E. N. Sevost'yanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1068 (1976); 628 (1978).
- 6. A. A. Vvedenskii, Thermodynamic Calculations of Petrochemical Processes [in Russian], Gostoptekhizdat, Leningrad (1960), p. 320.
- 7. P. B. Weisz, Seventh International Congress on Catalysis, Tokyo (1980), Preprint P1.
- 8. J. R. Anderson, K. Foger, T. Mole, R. A. Rajadhyaksha, and J. V. Sanders, J. Catal., 58, 114 (1979).
- 9. J. R. Csicsery, J. Catal., 19, 394 (1970).
- 10. J. Ward, in: Zeolite Chemistry and Catalysis, J. A. Rabo (ed.), American Chemical Society, Washington, D.C. (1976).