CONCLUSIONS

1. The unpaired electron in methyl 2-thiophenecarboxylate anion-radicals is mainly located in the thiophene ring.

2. The one-electron reduction product of an aromatic acid ester reacts with C-phenyl-N-tert-butylnitrone with transfer of the methyl radical.

LITERATURECCITED

- 1. V. P. Gul'tyai, T. Ya. Rubinskaya, and L. M. Korotaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1677 (1982).
- 2. I. M. Sosonkin and A. N. Domarev, Zh. Prikl. Khim., 44, 950 (1971).
- 3. P. M. Sosonkin, V. N. Belevskii, G. N. Strogov, A. N. Domarev, and S. P. Yarkov, Zh. Org. Khim., 18, 1504 (1982).
- 4. L. M. Baider, G. Ya. Liberman, and M. G. Fleisher, Abstracts of Papers of Fourth All-Union Conference on Application of Computers in Molecular Spectroscopy [in Russian], Novosibirsk (1977), p. 228.
- 5. E. G. Janzen and B. J. Blackburn, J. Am. Chem. Soc., 91, 4481 (1969).
- 6. E. G. Janzen and C. A. Evans, J. Am. Chem. Soc., 97, 205 (1975).
- 7. V. E. Zubarev, V. N. Belevskii, and L. T. Bugaenko, Vestn. Mosk. Univ., Ser. Khim., 295 (1975).
- 8. V. N. Belevskii, Khim. Vysok. Energ., 15, 3 (1981).

TRANSFORMATIONS OF PIPERYLENE ON ULTRAHIGH SILICA ZEOLITES

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Ultrahigh silica zeolites (UHSZ) are efficient catalysts for the aromatization of either the lower olefins [1-6] or a mixture of olefins and dienes [7] to give predominantly toluene and xylenes. The transformations of individual dienes on catalysts of this type have not been studied up to now. On the other hand, the aromatization of the lower dienes, and specifically butadiene and piperylene, proceeds successfully either on Al_2O_3 [8, 9] or mordenites that contain a transition metal ion [10]. Consequently, it seemed of interest to study the aromatization of piperylene on an UHSZ and compare its transformations on this catalyst with the existing data of aromatization on Al_2O_3 [8].

EXPERIMENTAL

The transformations of piperylene were studied on a domestic UHSZ of the HMZ type, which was prepared by the crystallization at 130°C of alkaline aluminosilicate mixtures that lacked an organic additive. The thus obtained zeolite as the Na form was subjected to ion exchange to give various forms of the zeolite, containing ~3% of the exchange cation. The washed and dried catalyst was pelleted, ground, and the 0.5-1.0 mm fraction was taken and ignited for 2 h in an air stream at 600°C.

The experiments were run on equipment of the flow type with 2.5-15 cm³ of the catalyst at 400-500°C and piperylene space velocities of 0.5-6.0 h⁻¹, with collection of the liquid and gaseous portions of the catalyzate. In some cases the piperylene was passed with a diluent (N₂, etc.) at a piperylene:diluent mole ratio = 1:5 or 1:10. After each experiment,

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Composition of reaction products	HMZ-M*		HMZ-M*, 1:10 dilution		HMZ-Mg		$\begin{array}{c} \mathrm{Al_2O_3} \underset{[8]}{\longrightarrow} \mathrm{K_2O} \end{array}$	
A liphatic hydrocarbons	35,9		55,3		53,1		43,8	
Methane		4,4		0,4		0,4	h)	
Ethylene		3,1		8,0		4,3]	
Ethane		4,5	{	0,1		0,1	11	1,1
Propylene		3,6		19,2		10,4		
Propane		9,6		2,3		1,8		
Butane + butenes		8,6	1	18.6		19,5)	
C_5		2,0		3,4		10,5		41,6
C ₆		0,1		1,5		4,3	ŀ	1,1
C_7	1	-		0,9		1,3		
C ₈				0,9		$_{0,5}$		
Alkenvlcvclohexenes	-		-		-		8,6	
Aromatic hydrocarbons	64,1		44,7		46,9		47,6	
Benzene		6.5		1,5		4,6		3,6
Toluene		34.9		13,2		16, 4		5,1
Aromatic Cg	16.4	,	18.0		17.5		-5,4	
Ethylbenzene		1.4		3.0		3,0		1,1
m-, p-Xylenes		11.6		12.6		11,9		2,3
o-Xylene		3.4		2.4		2.6		2.0
Aromatic C9	3.5	- , -	9.4		6.7		1,4	
Propylbenzene	-,-	0.1		0.2		~~~		
1,3- and 1,4-Methylethylbenzene		1.4		4.6		3.8	1	1.4
Mesitylene		0.4	1					
Pseudocumene		16		4.6		2.9		
Alkylaromatic C_{10}	2,8	1,0	2,6	2,0	1,7		32.1	

TABLE 1. Transformations of Piperylene on UHSZ (500°C, 1 h, space velocity based on liquid piperylene = $1 h^{-1}$)

*M = Group VIII element, see [7].

lasting 1-2 h, the catalyst was regenerated at 550° C by the passage of a steam-air mixture at a flow rate of 6 liters/h.

The composition of the reaction products was established via GLC, using a flame-ionization detector to analyze the gaseous products at $60-170^{\circ}$ C on a 1.5 m × 2.5 mm column packed with Poropak Q. The complete analysis of the liquid reaction products was run at 110°C on a stainless steel capillary column (50 m × 0.25 mm), wetted with Apiezon N. In addition, the low-boiling hydrocarbons (up to benzene inclusive) present in the liquid catalyzate were analyzed at ~20°C on another capillary column of the same type, which was wetted with triethylene glycol dibutyrate.

Piperylene that was at least 98.5% pure was obtained by the distillation of technical piperylene through a fractionating column with an efficiency of ~100 theoretical plates.

DISCUSSION OF RESULTS

As was shown experimentally, the Na form of the UHSZ has a low activity in the aromatization of piperylene. According to [3], replacing the Na⁺ by a transition metal ion leads to a substantial increase in the aromatization activity of the catalyst. When the experiments are run without dilution the amount of aromatic hydrocarbons in the reaction products reaches 64% (Table 1). Although the spectrum of these hydrocarbons is quite broad (from benzene to C_{10} arenes), more than half of the total aromatics (35%) is toluene. The amount of the remaining aromatic hydrocarbons decreases with increase in their molecular weight. The C3 and C4 hydrocarbons, chiefly paraffins, predominate in the aliphatic portion of the catalyzate. Running the experiments with dilution led to a decrease in the amount of aromatic hydrocarbons, with a simultaneous increase in the amount of C₈ and C₉ aromatics in them. If in the experiments without dilution the ratio of the arenes $C_7:C_8:C_9 = 10:4.7:1$, then with dilution this ratio changed to 3.4:4.7:2.5. The aliphatic portion of the reaction products also changes simultaneously. If the amount of olefins is small in the experiments run without dilution, then in the experiments run with dilution the aliphatic hydrocarbons analyzed at least 90% olefins. The UHSZ, containing the Mg²⁺ ion, is as inactive as the starting Na form of the zeolite. In this case, even without dilution, the amount of aromatic hydrocarbons in the reaction products did not exceed 47%, and the amount of C₈ aromatics predominated in them. Here the aliphatic portion of the catalyzate was also rich in olefins. As a whole, the impression is created that the less the catalyst activity or the lower the piperylene conversion, the lower is the amount of toluene in favor of the higher aromatic hydrocarbons and the greater is the amount of unsaturated hydrocarbons in the aliphatic portion of the catalyzate.



Fig. 1. Effect of contact time on amount of separate components in aromatic portion of catalyzate during aromatization of piperylene on HMZ (400°C, dilution 1:5, molar):
1) benzene; 2) toluene; 3) C₈ arenes;
4) C₉ arenes; 5) C₁₀ arenes; 6) total yield of aromatic hydrocarbons.

Similar rules (Fig. 1) were obtained when the contact time was varied. It proved that with increase in the contact time, i.e., with increase in the piperylene conversion, the amount of toluene increases, the amount of C_9 and C_{10} aromatics decreases, and the amount of C_8 changes slightly.

A comparison of the results, obtained in the present paper, with the data on the aromatization of piperylene on Al_2O_3 , containing an alkaline addition [8], reveals that the composition of the aromatic portion of the catalyzate is quite different on the UHSZ. From the data given in Table 1 it can be seen that toluene and xylenes are formed mainly on the UHSZ, and not C_{10} arenes, which predominate in the transformation products of piperylene on Al_2O_3 . At the same time the piperylene catalyzate, obtained in UHSZ, in composition is close to that of the catalyzate obtained by the aromatization of the lower olefins on UHSZ (see, for example, [3, 4]), although the total yield of aromatic hydrocarbons from piperylene under analogous conditions is substantially higher. This, on the one hand, testifies to the higher reactivity of piperylene when compared with olefins, and on the other hand it indicates the generality of the mechanism for the aromatization of various unsaturated hydrocarbons on these catalysts.

CONCLUSIONS

1. Piperylene in the presence of ultrahigh silica zeolites (UHSZ) at 500°C forms a mixture of aromatic (mainly toluene and xylenes) and aliphatic (mainly C_3H_8 and $C_4H_{1 o}$) hydrocarbons.

2. With increase in the piperylene conversion the amount of toluene increases, with a simultaneous decrease in the amount of C₉ aromatics in the composition of the aromatic hydrocarbons, and the amount of unsaturated hydrocarbons in the aliphatic portion of the catalyzate decreases.

3. It was shown that the composition of the aromatic hydrocarbons is different when piperylene is transformed on an UHSZ and Al_2O_3 .

LITERATURE CITED

- 1. E. N. Givens, C. J. Plank, and E. J. Rosinski, U. S. Patent 3,813,330 (1973).
- 2. E. N. Givens, C. J. Plank, and E. J. Rosinski, U. S. Patent 3,960,978 (1976).
- 3. O. V. Bragin, B. K. Nefedov, T. V. Vasina, T. V. Alekseeva, V. N. Lutovinova, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 2639 (1979).
- 4. Kh. M. Minachev, D. A. Kondrat'ev, B. K. Nefedov, T. N. Bondarenko, A. A. Dergachev, and T. V. Alekseeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2646 (1979).
- 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).

- 6. O. V. Bragin, B. K. Nefedov, T. V. Basina, V. N. Lutovinova, T. V. Alekseeva, A. V. Preobrazhenskii, and Kh. M. Minachev, Dokl. Akad. Nauk SSSR, <u>255</u>, 103 (1980).
- 7. W. O. Haag and T. J. Huang, U.S. Patent 4,097,367 (1978).
- 8. K. M. Gitis, V. I. Kadentsev, M. I. Rozengart, and O. I. Mokrinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 633 (1978).
- 9. M. A. Ryashentseva, Yu. A. Afanas'eva, and Kh. M. Minachev, USSR Patent 358,306; Byull. Izobret., No. 34, 78 (1972).
- 10. M. Hession and R. Senior, J. Catal., <u>44</u>, 163 (1976).

DEHYDROGENATION OF n-DECANE ON DEPOSITED

TECHETIUM CATALYSTS

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The catalytic properties of technetium were studied in the hydrogenation of benzene [1] and the transformation of cycloparaffins [2-5] and n-paraffins [4, 5]. The present paper is devoted to a study of alumina-technetium catalysts in the dehydrogenation of n-decane to monoolefins; up to now these catalysts have not been tested in the catalysts of the higher paraffinic hydrocarbons. A comparison was also made of the catalytic properties of technetium with those of other elements of the manganese subgroup in the same reaction.

EXPERIMENTAL

The catalysts, containing 0.08-4.20 at.% of Tc, Re or Mn, were prepared by impregnating γ -Al₂O₃ (0.5-1 mm fraction, specific surface area S = 160 m²/g) with aqueous solutions of the corresponding NH₄TcO₄, NH₄ReO₄ or Mn(OAc)₂·4H₂O. After 12 h the samples were dried for 2 h at 150°C and then reduced for 4 h in an H₂ stream (~6 liter/h) at 600°C. The specific surface area of the obtained samples is close to that of the starting γ -Al₂O₃ and was 130-140 m²/g (determined by the adsorption of air [6]).

The dehydrogenation of n-decane was run in a flow reactor made from stainless steel 12Kh18N10T under the conditions usually employed for this reaction, and specifically at 470 and 500°C, n-decane space velocities (v) = 10-40 h⁻¹, H₂ pressure (p_{H_2}) = 1.01-4.05 · 10⁵ Pa,

and molar dilution of n-decane with hydrogen $(\rho_{H_0}) = 8$.

The yield of the liquid catalyzate is close to 100%. The formed products were analyzed by GLC at 130°C (3 m \times 3mm steel column packed with 15% Carbowax 20 M deposited on Chezosorb AW-HMDS). From the chromatograms were calculated the total conversion (Σ), the yields of the mono- and diolefins, aromatic hydrocarbons, and the skeletal isomerization and cracking products, and also the selectivity in monoolefins (γ).

DISCUSSION OF RESULTS

Under the studied conditions, n-decane in the presence of $Tc-Al_2O_3$ is converted mainly to olefins (Table 1). With increase in the amount of TC from 0.08 to 4.2 at.% the dehydrogenating activity of the catalyst is nearly doubled. A similar effect of the Tc concentration is also observed in the dehydrogenation of cyclohexane [3]. The n-decane conversion increases mainly via an increased yield of monodlefins and cracking products. In addition, small amounts of diolefins, aromatic hydrocarbons, and skeletal isomerization products are formed.

An analysis of the function $\gamma - f(\Sigma)$ (Fig. 1) disclosed that not only the total activity of the catalyst increases with increase in the amount of Tc, but also the selectivity of forming olefins, which proved to be maximum for the sample with 2.8 at. % of Tc, and dropped

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