noted that if the isobutylene is diluted with increasing amounts of air, the activity of this catalyst decreases continuously as the ratio of air to isobutylene is increased from 1/10 to 1/5; and at a 1:1 ratio, the oligomerization is completely suppressed. The poisoning is reversible; after the air feed is stopped, the activity is restored. Hence we can ascribe the catalyst deactivation to competitive adsorption of isobutylene, oxygen, and possible oxidation products.

CONCLUSIONS

1. A study has been made of the activity of rhenium oxides (ReO_2 , ReO_3 , and Re_2O_7) and supported alumina-rhenium catalysts (5-40% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$) in isobutylene oligomerization.

2. The highest activity is manifested after calcining the catalysts in air at 400°C; treatment with nitrogen lowers the activity, and calcination in hydrogen deactivates the catalysts.

3. The activity of these catalysts is due to rhenium in the highest degree of oxidation (VII). It is suggested that the oligomerization proceeds through an acidic mechanism.

LITERATURE CITED

- 1. Yu. S. Khodakov, K. Anders, A. N. Subbotin, V. S. Nakhshunov, R. Fel'dgauz, Z. Novak, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 1724 (1981).
- 2. S. Tribalat, M. L. Jungfleisch, and D. Delafrosse, C. R. Acad. Sci., 259, 2109 (1964).
- 3. Yu. E. Ratner, Yu. V. Tsvetkov, and L. G. Berezkina, Zh. Neorg. Khim., 13, 1516 (1968).
- 4. Inorganic Syntheses [Russian translation], IL, Moscow (1952), Vol. 3, p. 174.
- 5. R. Johne and D. Severin, Chem. Ing. Techn., 37, 57 (1965).
- 6. E. S. Spiro, V. I. Avaev, G. V. Antoshin, M. A. Ryashentseva, and Kh. M. Minachev, J. Catal., 55, 402 (1978).
- 7. R. V. Dmitriev, V. I. Avaev, M. A. Ryashentseva, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 2448 (1977).

AROMATIZATION OF ETHANE ON METAL -

ZEOLITE CATALYSIS

O. V. Bragin, T. V. Vasina, Ya. I. Isakov, N. V. Palishkina, A. V. Preobrazhenskii, B. K. Nefedov, and Kh. M. Minachey

UDC 542.97:547.212

The dehydrocyclooligomerization of ethane to benzene and other aromatic hydrocarbons (AH), which was described for the first time in [1] in the example of catalysts M/Al_2O_3 (M = Pt, Pd, Ir, Rh, Ru), is of considerable interest from the standpoint of obtaining valuable products from inexpensive and readily available raw materials.

Effective catalytic systems for the conversion of C_2H_6 to AH can be obtained on the basis of high-silica zeolites, which are active in the aromatization of lower olefins and are used as components of catalysts for the conversion of C_1-C_5 n-alkanes to AH [2-8]. Here we are reporting on an investigation of the behavior of catalysts prepared from TsVM zeolite in the conversion of ethane and (for comparison) in the conversion of ethylene. Particular attention has been given to metal-containing systems (M/H-TsVM), which have hydrogenating-dehydrogenating and acidic functions.

EXPERIMENTAL

The catalysts were prepared from Na-TsVM zeolite, synthesized by the new process technology without the use of any organic components, this zeolite having the following characteristics: SiO_2/Al_2O_3 mole ratio

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, Vol. 9, pp. 2002-2009, September, 1983. Original article submitted November 12, 1982.

Sample				Yield of	Comp. of lic	ucts, % *	Gas e	composition,	h t	
number	Catalyst	Feedstock	T., °C	liquid cata- lysate, %	AH Cs—Cs	Cs-Cl2	CH4	C ₂ H,	C_2H_6	ΣC ₃ , C ₄
I	Na- TsVM	Ethane	600		1		2.5	7.5	06	Trace
		Ethylene	200	0	1	ł	Trace	96,5	1,5	01
		Ŧ	600	Trace	١	1	r	94,5	1,5	4
п	HNa-TsVM	Ethane	600	10	16	6	17	4	79	Trace
		Ethylene	600	60	67	33	12	9	22	60
III	H- TsVM	Ethane	600	10	95	ŋ	က	1	96	Trace
		Ethylene	200	75	55	45	33	en	- 48	46
	linhatio hudro	em suoqueo	rna datante	ر م						
† Here and	Tin Tahle 2 fi	be data ref	ar to the r	omnocitio	n of the h	يصطع ومصطمع	Hort of t		nnodinato	tin oddi
		TAT mmm ATT		OTATOOCITHO		TOO TROOTR	ה דר חדוים ד	in gascone	enonnord .	-Inne III)

TABLE 1. Catalytic Conversions of Ethane and Ethylene on TsVM Type Zeolites (flow system, feedstock space ⊳ I

• tion to $C_n {\rm H}_m$, the products contained ${\rm H}_2)$. TABLE 2. Catalytic Conversions of Ethane and Ethylene on Metal-Zeolite Catalysts (flow system, feedstock space velocity 120 h⁻¹, catalyst treated by method A)

2		<i>.</i>	-	·						
Sample				Yield of liquid cata-	Comp. of li tion prod	quid reac- ucts, %	5	as compositi	on, %	
number	Catalyst	Feedstock	T, °C	lysate, ϕ_{0}	AH cscs	AH c9-C12	CH,	C_2H_4	G_2H_6	ΣC ₃ , C,
IV	0,5% Pt/Na- TsVM	Ethane	600 *	Trace	1 1	11	6,5 38	11,5 16	82 46	Trace
Λ	0,2% Pt/H-TsVM	2	500 550	12.5	90 93	10	12,5 22	8,5	79,5 68	5,5 2
		Ethylene	600 * 600 *	564200 564200	999 95 95	3+420 3+420	$\frac{35}{26}$	r∞∞√	$53 \\ 62 \\ 62 \\ 62 \\ 62 \\ 62 \\ 62 \\ 62 \\ 6$	5 14 Trace
Ν	0,5% Pt/H- TsVM	Ethane	500 550 600	120 202 202	74 86 83	26 14	$^{18}_{19}$	4 12 20	75 68 78	Trace "
		Ethylene	800 * 500 *	1 7 40	78 54	22 46	35 38 37 38	22 25	57 62	°,5
ΝI	1%Pt/H-TsVM	Ethane	500 550 600	0 10 17,5	- 83	13	040	400	96 89	1 Trace
ΝIII	0,5% Rh/H- TsVM	1	500 600 500 *	$^{10}_{2,5}$	£311	1 - 15	29 29	014 -	92 67 89	Trace
	-	Ethylene	450	33	. 12	29	25	ന	37	35
XI	0,5% Pd/H- TsVM	Ethane	600 800	2,5 12,5	54	40	12	897 22	85 90	Trace
		ruyiene	500	26	1.9	33	65	n	42	18

* Catalyst treated by method B.



Fig. 1. Influence of conditions of pretreating metal-zeolite catalysts on yield of aromatic hydrocarbons from ethane, in flow system at 600° C. Treatments: 1) air (method A); 2) air-hydrogen (method B); 3) hydrogen (method C).

Fig. 2. "Evolution" of Pt/H-TsVM catalysts in aromatization of ethane and ethylene under conditions of pulse method at 550°C. Graph a is for ethane: 1, 2) Pt/H-TsVM and Pd/H-TsVM treated by method A; 3, 4) same, method B. Graph b is for ethylene: 1-3) Pt/H-TsVM, Pd/H-TsVM, and H-TsVM treated by method A.

33.3; Na₂O content 3%, Fe₂O₃ 0.12%; purity of phase composition ~100%; sorption capacity for H₂O 0.08 cm³/g, for C₆H₆ 0.12 cm³/g. Samples of HNa-TsVM (1.7% Na₂O, degree of exchange of Na⁺ ~ 43%) and H-TsVM with a residual content of Na₂O < 0.1% were obtained by ion exchange with an aqueous NH₄NO₃ solution and subsequent heating of the NH₄ zeolite in a stream of air; metal-containing catalysts were obtained by treatment of Na-TsVM and NH₄-TsVM with the calculated quantity of a solution of the salt of the particular metal, under conditions of ion exchange and impregnation. The powdered preparations were dried and pressed without any added binder; the pellets were crushed, and 1-2 mm granules were taken for test.

Before use, the catalysts were heated for 5 h at 550°C in a stream of air (method A). After use in an experiment, the catalyst was regenerated by treatment with air for 2.5-3 h at the same temperature. In a number of cases, reduced forms of the metal zeolite systems were investigated; these were obtained by H_2 treatment at 500°C after calcining in air for 5 h at 550°C (method B), or the catalysts were obtained by treatment of the original specimens in a stream of H_2 only, 5 h at 500°C, before the start of a series of experiments and also between the experiments (method C). Cylinder-grade ethane and ethylene were used as the starting materials, with purities > 99%.

The experiments were performed at 400-600°C in flow and pulse units at atmospheric pressure, following procedures given in [1]. The catalyst charge was $1.7-1.8 \text{ g} (2.5 \text{ cm}^3)$ in the flow reactor, and 100 or 500 mg in the pulse reactor. The C_2H_6 or C_2H_4 feed rate was 300 ml/h; pulse volume 0.1 or 4 ml; carrier gas (He) flow rate 1200 ml/h. The liquid and gaseous products were analyzed separately by GLC [1].

DISCUSSION OF RESULTS

Data on the activity and selectivity of the catalysts are summarized in Tables 1 and 2. Of particular interest are the results obtained in the presence of the H-TsVM (sample III), on which, without any additional introduction of dehydrogenating components, up to 10% AH was formed from ethane, approximately 95% of the AH having the composition C_6 - C_8 . The H-TsVM was also the most active in the aromatization of ethylene: The AH yield on this catalyst at 500°C amounted to 75% (Table 1).

Next, in the example of conversions of ethane [8] and ethylene, it is interesting to follow the catalytic activity of zeolites with acidities that vary in the following order: Na-TsVM (I) \ll HNa-TsVM (II) < H-TsVM (III).

Sample I did not manifest any appreciable activity in these reactions; even when the temperature was raised to 600°C, the reaction products contained practically no AH, and only small amounts of C_1-C_4 hydrocarbons were obtained (Table 1). Judging from the composition of the three catalysts under consideration, we can assume that in the case of the Na-TsVM, the acid centers that are needed for manifestation of catalytic activity are indeed completely "neutralized" by Na ions.

The HNa-TsVM zeolite, for which a considerable part of the Na⁺ has been replaced by H⁺, manifested activity that is somewhat lower than that of sample III (but still fairly high) in the aromatization of ethylene; it differed but little from the H-TsVM in respect to ethane conversions. These results provide a convincing demonstration of the important role of protonic acid centers in catalytic conversions of C_2H_4 and C_2H_6 on TsVM zeolite. The mechanism of ethane aromatization in the presence of the catalysts H-TsVM and HNa-TsVM is not at all clear at the present time. We can assume that C_2H_6 is subjected to dehydrogenation on the Fe impurity centers that are present in small quantities in the zeolite (0.12% calculated as Fe₂O₃), thus forming ethylene that is subsequently converted to AH. This interpretation is supported by the fact that ethylene was present in the products from the reaction of C_2H_6 on all of the catalysts (Table 1), the ethylene concentration being relatively greater in the case of the Na-TsVM, which is inactive in conversions of C_2H_4 and C_2H_6 to AH.

However, we cannot eliminate the further possibility of a contribution of thermal dehydrogenation of ethane. It is probable that the stage of C_2H_4 formation from C_2H_6 is indeed the limiting stage in the aromatization of C_2H_6 , and this explains the identical activity of catalysts II and III in ethane conversion in spite of the fact that these two catalysts differ in acidity and in their effectiveness in C_2H_4 reactions.

An analysis of the data obtained on the H-TsVM and HNa-TsVM catalysts in the aromatization of C_2H_6 and C_2H_4 has led to the conclusion that the introduction of dehydrogenating components into the zeolites should tend to increase the activity of the catalysts in aromatization of ethane. With this in view, we tested a series of metal-containing catalysts, both monofunctional catalysts (0.5% Pt/Na-TsVM) and bifunctional catalysts based on H-TsVM, these bifunctional catalysts being designated M/H-TsVM (samples V, VI, and VII, containing 0.2%, 0.5%, and 1.0% Pt, respectively), and also Rh and Pd samples for comparison (0.5% metal). Here we were able to reveal the specific features of the action of each element as governed by its nature, in particular the nonidentical capability of the M^{n+} cations for changing their degree of oxidation in oxidation—reduction treatment, and also possible differences in the distribution of the metallic phase in the channels and on the surface of the zeolitic component of the catalyst.

As can be seen from Table 2, the introduction of Pt into the zeolite actually did give a considerable increase of dehydrogenating activity of the catalysts, as a result of which the corresponding samples manifested a considerably higher activity (by a factor of 1.5-2) in ethane aromatization in comparison with the H-TsVM (sample III). Along with this, in the case of ethylene, the activity of the metal-containing samples IV-IX has been lowered significantly (Table 2), possibly due to the more intense occurrence of hydrocarbon hydrogenation and hydrogenolysis reactions on the metal/zeolite systems.

Along with their dehydrogenating activity (up to 12% ethylene in the gaseous products from ethane), these catalysts also had considerably higher activities in the reaction of hydrocarbon hydrogenolysis to form CH_4 . Even though the total AH yield was reduced because of the drop in selectivity of the aromatization process as a result of the intense methane formation, the AH yield on samples V and VI amounted to 20% of the ethane passed through the system (Table 2). The conversion of ethane to AH was no lower when the Pt content was reduced from 1% to 0.2% in the Pt/H-TsVM catalysts.

In the case of the 0.5% Rh/H-TsVM, the maximum AH yield (10%) was obtained at 500°C, i.e., 100°C lower than on the H-TsVM (compare Tables 1 and 2). An increase of the temperature to 600°C led to a substantial drop of the AH yield (2.5%) along with more methane formation; the CH_4 content in the gaseous products rose to 29% (Table 2). This is probably related to a change in the dispersity and the distribution of the Rh particles in the zeolitic catalyst at high temperatures, as rhodium catalysts are usually less resistant to the effects of

high temperatures in comparison with (for example) the corresponding platinum catalysts. The Rh/H-TsVM also exhibited a sharper drop of activity with the passage of time.

For the 0.5% Pd/H-TsVM (sample IX), we found a strong dependence of the catalytic activity on the pretreatment conditions. Thus, the highest activity in ethane aromatization at 600°C was shown by the Pd catalyst that had been pretreated first with air (5 h, 550°C) and then with H_2 (5 h, 500°C). The yield of AH on this sample was 12.5%. If the catalyst (a new charge of catalyst) was pretreated with air only or H_2 only, the AH yield at 600°C was no more than 2.5% (Fig. 1). So great a difference is apparently due to differences in the content and state of the Pd in the catalysts that are formed in the process of oxidative, oxidative/reductive, and only reductive treatment of the original metal-zeolite system.

This is consistent with the fact that the Pd/H-TsVM (IX), which after treatment with air had very little activity in C_2H_6 conversion, manifested a rather high activity (AH yield 56%, see Table 2) in the reaction of C_2H_4 , which does not require the presence of Pd⁰. Apparently this Pd-containing sample contains an adequate quantity of acidic centers for aromatization of ethylene.

In contrast to the palladium catalysts, the Pt catalysts were not as sensitive to pretreatment. On 0.5% Pt/H-TsVM that had been subjected to various pretreatments before use, the AH yield from ethane at 600°C varied only over the 15-20% range (Fig. 1).

These observations are in good agreement with the data of [9] on the influence of the atmosphere on the thermal decomposition of Pt and Pd amine complexes introduced into Y zeolites by cation exchange. It was established in [9] that upon decomposition of the complex Pt cations in an air atmosphere, and also in He, the Pt is converted to the metallic state (NH₃ as the reducing agent); the air is, in effect, an inert medium. In contrast, in the case of the Pd complexes, the Pt^{2+} is only partially reduced to the metal, and in the finished samples, the Pd is present mainly in the form of Pd^{2+} cations, such that it is necessary to reduce the zeolite with hydrogen to obtain metal-containing systems.

It can be assumed that the Pt or Pd amino complex cations introduced into the TsVM zeolite behave in a manner similar to the Pt(Pd) $(NH_3)_4^{2+}$ Y systems; thus, the above-described dependences of the Pd/H-TsVM and Pt/H-TsVM properties on the type of pretreatment have now found a rather convincing explanation. Here we must also take into account the influence of the temperature on the dispersity and localization of the metal particles that are formed.

A characteristic feature of the catalytic action of M/H-TsVM systems in the aromatization of C_2H_6 and C_2H_4 is their "evolution" during the course of the reaction, accompanied by an increase of the AH yield (in the flow system, with ethane feed, the maximum was usually reached in the second or third hour of operation of the catalyst; these yields are the values given in Table 1 and Fig. 1). This effect could be observed more distinctly in the pulsed regime in the case of the Pt and Pd catalysts that were preactivated in air or by successive treatment with air and H_2 (Fig. 2). It will be noted that the "evolution" shows up very graphically in ethylene conversions; in the case of ethane, the same qualitative relationship was observed (Fig. 2a). The experiments with C_2H_4 on H-TsVM showed that without the Pt or Pd, this evolution effect is not manifested (Fig. 2b, curve 3).

All of this strongly suggests that one of the reasons for the change of activity and selectivity of these catalysts in the course of operation is the action of the reaction mixture, leading to modification of the catalytic system as a result of changes in the valence and physical state of the transition element (reduction of M^{n+} to M^0 , aggregation and migration of M^0), possibly resulting in a different distribution of the metals in the channels and on the surface of the zeolite crystals. Another factor that we cannot ignore is the change in acidity of the aluminosilicate component (concentration of acidic centers and ratio of centers of different types). The contributions of the various individual factors must obviously depend on the nature of the metal and its content in the catalyst, on the degree of exchange of Na⁺ by Mⁿ⁺ in the zeolite, and on the reaction temperature.

Previously, in the example of the catalyst Rh/Al_2O_3 it was shown by means of XPS [10] that in the course of ethylene aromatization, a positive charge is generated on reduced Rh^0 particles, the magnitude of which increases symbatically with increasing catalytic activity. The subsequent drop of catalytic activity is accompanied by a return of the Rh to a state close to Rh^0 .

Attention is drawn to the fact that the AH yields in the 4-h experiments is very much dependent on the type of catalyst pretreatment (Fig. 1). This indicates that the action of the reaction mixture leads to different states of the same M/H-TsVM that has been activated under different conditions.

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

D. A. Kondrat'ev, T. B. Borovinskaya,
A. A. Dergachev, R. V. Dmitriev,
B. K. Nefedov, T. V. Alekseeva,
and Kh. M. Minachev

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