STUDY OF THE PROPERTIES OF PENTASIL-CONTAINING CATALYSTS IN REACTIONS OF TRANSFORMATION OF HYDROCARBONS.

3.* KINETICS OF AROMATIZATION OF PROPANE AND PROPYLENE ON H AND Zn FORMS OF PENTASILS

V. P. Sitnik, N. V. Nekrasov, T. V. Vasina,
V. I. Yakerson, and O. V. Bragin

UDC 541.127:542.97:547.213:
547.313.3:548.67

The kinetics of transformations of propane and propylene on pentasils modified with zinc, Zn/HTsVM, and the H form of zeolite were investigated. Quantitative data were obtained which revealed significant differences for HTsVM and Zn-containing catalysts in the selectivity of transformations of propane with different degrees of its conversion. The promoting effect of Zn in the Zn/HTsVM system not only on the stage of dehydrogenation of propane into propylene, but also on subsequent transformations of propylene into aromatic hydrocarbons, was demonstrated. The absence of internal diffusion inhibition of the reaction in the conditions studied was demonstrated experimentally. It was shown that aromatization of propane takes place in the kinetic region.

Aromatization of lower alkanes is a promising process which permits using nontraditional kinds of raw material as additional sources for obtaining valuable aromatic hydrocarbons (ArH): casing-head petroleum gas, liquefied gas condensate, etc. New pentasil-containing systems modified with different additives have recently been widely discussed in the literature as efficient catalysts of aromatization of lower (C_2-C_4) alkanes [1-8]. However, there are almost no data characterizing the kinetic features of the complex set of reactions which precede and accompany aromatization. The kinetics of transformations of propane and propylene in the presence of a series of zinc-modified catalysts: Zn/HTsVM and the H form of TsVM, in a wide range of conversions of the reactants were investigated in the present study. Questions related to acceleration of the individual stages of aromatization of lower alkanes on Zn-modified pentasils were discussed in consideration of the data obtained.

EXPERIMENTAL

The study was conducted in a flow setup at atmospheric pressure. From 0.06 to 1.7 g of catalyst with 0.5-1 mm grain size was placed in the reactor. Propane and propylene (purity >99%) were used in the experiments. Pentasil (TsVM type) in the H form (SiO_2/Al_2O_3 = 35; 0.06% Na_2O) and modified catalysts containing 0.5, 1, and 5% Zn, prepared from NH_4 TsVM, were used [9]. Before the experiment began, the samples were activated in a current of dry air at 520°C for 5 h. The catalysts were regenerated with air (520°C, 2 h) between experiments. The duration of an experiment was 1.5-2 h. The products of the reaction were analyzed by GLC every 30 min. The volume flow rate of the reactants varied from 120 to 1200 h^{-1} (550°C), and the degree of conversion varied from 10 to 95%. The activity of the catalysts was preserved during the experiment.

RESULTS AND DISCUSSION

The data on the change in the composition of the products of the reaction formed in transformation of propane (methane, ethane, ethylene, propylene, aromatic hydrocarbons) on the Zn-modified catalysts and H-form of TsVM are shown in Fig. 1 as a function of the contact time. For all catalysts studied, the dependence of ln (C_τ/C_0) on τ is linear, where C_τ is the current concentration of C_3H_8; C_0 is the initial concentration of C_3H_8 (Fig. 2), i.e., con-

---

*For previous communication, see [1].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 727-733, April, 1990. Original article submitted March 17, 1989.

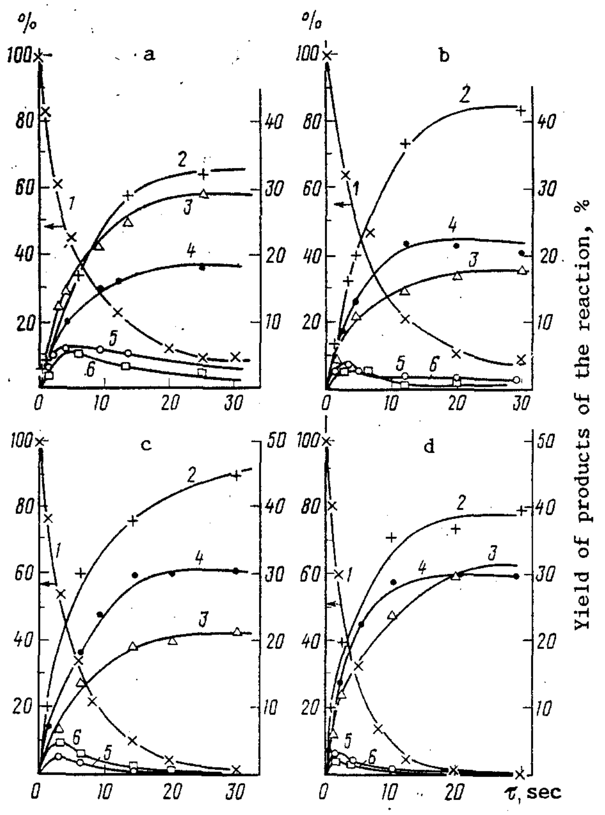
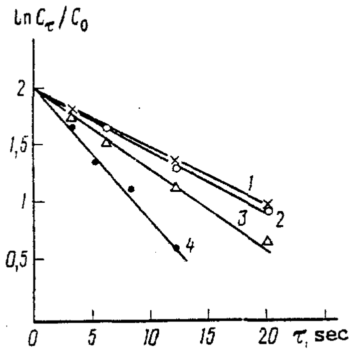


Fig. 1



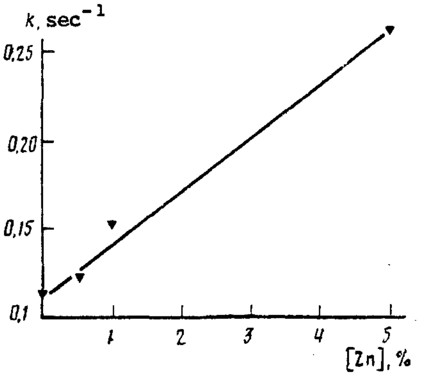


Fig. 2

Fig. 3

Fig. 1. Dependence of the change in the composition of the products of the reaction on the contact time in transformations of propane (550°C) on pentasil-containing catalysts: HTsVM (a), 0.5% Zn/HTsVM (b), 1% Zn/HTsVM (c), 5% Zn/HTsVM (d). 1) Unreacted C_3H_8; 2) ArH; 3) CH_4; 4) C_2H_6; 5) C_2H_4; 6) C_3H_6.

Fig. 2. Logarithmic dependence of the degree of conversion of propane ($\ln C_\tau/C_0$) on the contact time on: 1) HTsVM; 2) 0.5% Zn/HTsVM; 3) 1% Zn/HTsVM; 4) 5% Zn/HTsVM (550°C).

Fig. 3. Dependence of the rate constant (k, sec^{-1}) of transformation of propane on [Zn] on Zn-modified pentasils.

version of propane is described by a first-order equation, $r = kC_\tau$. The overall reaction rate increases proportionally to the [Zn] in the catalyst and increases by more than two times with an increase in the concentration of Zn from 0 to 5% (Fig. 3).

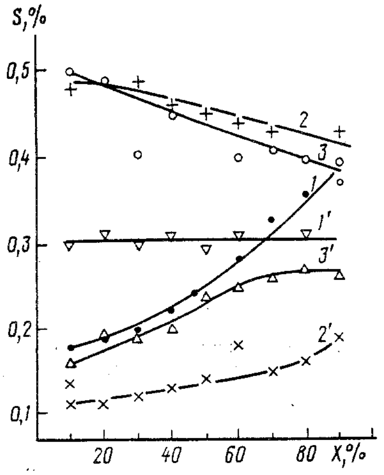


Fig. 4

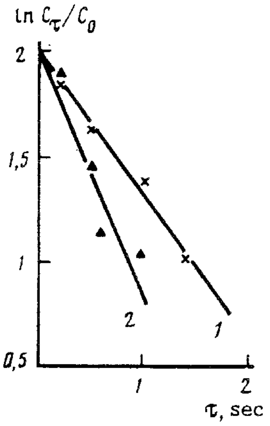


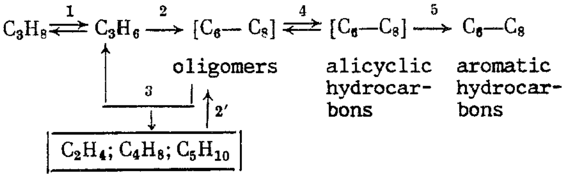
Fig. 5

Fig. 4. Dependence of the selectivity (S) of formation of aromatic hydrocarbons (1-3) and methane (1'-3') on the degree of conversion of propane on pentasil-containing catalysts of different composition: 1, 1') HTsVM; 2, 2') 1% Zn-HTsVM; 3, 3') 5% Zn/HTsVM (550°C).

Fig. 5. Logarithmic dependence of the degree of conversion of propylene ($\ln C_\tau/C_0$) on the contact time on the catalysts: 1) HTsVM; 2) 1% Zn/HTsVM (550°C).

Incorporation of relatively small amounts of Zn (0.5-1%) in the zeolite results in significant redistribution of the products of the reaction in comparison to the H form of TsVM: the yield of ArH increases sharply and the yield of methane decreases. The relative proportion of ethane increases and the proportion of methane decreases with an increase in the contact time. The yields of ethylene and propylene pass through a maximum (Fig. 1), which indicates the participation of these hydrocarbons in secondary transformations. Important differences are observed in the change in the composition of the products of the reaction as a function of the degree of conversion of propane on HTsVM and the modified pentasils (Fig. 4). On the Zn-modified catalysts, the selectivity of formation of ArH initially increases sharply in comparison to HTsVM, and decreases slightly with an increase in the conversion; the selectivity of methane formation increases. The selectivity with respect to methane is constant on HTsVM, while the selectivity of formation of ArH increases with an increase in the degree of conversion of C_3H_8.

Analogous differences in the selectivity of transformations of propane were observed in [3] on HZSM-5 and ZnZSm-5; this finding was attributed to a change in the rate of dehydrogenation of propane on Zn-modified catalysts and correspondingly to a change in the mechanism of the reaction of aromatization of propane. The scheme of transformation of propane into ArH on H and modified (Zn,Ga) ZSM catalysts reported below is discussed in [3, 8]:



This point of view is also confirmed in [6, 10]. We note, however, that the stage of formation of alicyclic hydrocarbons (4) is not very probable. The data obtained in [11] indicate that aromatization of alkanes, olefins, cyclanes, and a number of oxygen-containing compounds on the H form of pentasil in rigorous conditions (450°C and higher) takes place through preliminary fragmentation of the initial substances with the formation of low-molecular-weight unsaturated particles. The particles located in the channels of the pentasil form unsaturated oligomers of C_6-C_{10} composition, which apparently simultaneously undergo cracking, aromatization, and coke formation. The sequences of stages 1, 2, 4, and 5 in the

TABLE 1. Selectivity (S, %) of Formation of Reaction Products from Propane on the H Form and Zn-Modified Pentasils (550°C)

Catalyst	HTsVM	0.5% Zn/HTsVM	1% Zn/HTsVM	5% Zn/HTsVM
		$X=20\%$		
Methane	31,6	21,5	10,1	20
Ethylene	20	12	8	5
Ethane	20	22,5	24,5	23
Propylene	9,5	11	8	4
Benzene	5,4	11,6	15	14,7
Toluene	9,5	13,6	19,9	19,6
Xylenes	2,7	5,8	10	4,9
C_9+ArH	1,3	1,9	4,8	9,8
S with respect to ΣArH	18,9	33	49,7	49
		$X=40\%$		
Methane	31,1	21,5	12,8	20
Ethylene	13,5	85	5,6	5,5
Ethane	19,0	23	26,1	25
Propylene	14,5	7,5	10,3	4,5
Benzene	7,6	11,1	17,6	11,3
Toluene	9,8	17,4	19,8	11,3
Xylenes	3,3	6,3	2,7	2,8
C_9+ ArH	1,1	4,7	5,0	19,6
S with respect to ΣArH	21,8	39,5	45,1	45
		$X=90\%$		
Methane	32	21	20	26
Ethylene	5	3	2	3
Ethane	20	26	30	28
Propane	3	2	1	2
Benzene	14	19	17	10
Toluene	18	20	20	12
Xylenes	4	5	6	9
C_9+ ArH	3	4	4	10
S with respect to ΣArH	38	47	46	40

scheme results in the formation of ArH, and stage 3 results in cracking of oligomers with the formation of light hydrocarbons. In the presence of zinc, the rate of stage 1 increases [3, 8] due to the occurrence of the following reactions:

$$C_3H_8 + Zn^{2+} = CH_3 - \overset{+}{C}H - CH_{3(ads)} + [H - Zn]^+$$

$$CH_3 - \overset{+}{C}H - CH_{3(ads)} + [ZnH]^+ = C_3H_6 + H_2 + Zn^{2+}$$

Incorporation of zinc apparently has little effect on stages 2-4, since the rates of these stages is much higher than the rate of stage 1: Conversion of propylene takes place much more rapidly than conversion of propane on Zn/ZSM and the H form of ZSM [3]. In addition, quasiequilibrium between propane and propylene is established in the system due to acceleration of stage 1 and the presence of free hydrogen formed in dehydrogenation of propane on the Zn-containing catalyst, i.e., a constant propane/propylene ratio is preserved. For this reason, an equal proportion of propane is converted into ArH, and the selectivity with respect to aromatization is thus constant.

The stages in which cleavage of hydrogen atoms occurs apparently take place on the H form of zeolite according to a mechanism of hydride transfer, i.e., the presence of hydrogen acceptors plays the decisive role for the occurrence of the reaction. The proportion of hydrogen acceptors (intermediate products of the reaction) increases with an increase in the degree of conversion of propane, and the overall rate and selectivity of the reaction change as a consequence; actually, the selectivity of formation of ArH decreases with an increase in the volume flow rate. According to [3, 12], aromatization on HZSM is a later stage in the sequence of oligomerization, cracking, and other reactions, and takes place according to the mechanism of hydride transfer. The results obtained in incorporation of hydrogen in the reaction medium indicate the different character of the mechanism of cleavage of hydrogen on the H and Zn forms of ZSM. In the case of HZSM, addition of hydrogen or nitrogen to propane has a similar effect: the conversion decreases slightly (by 14%) with no marked change in the selectivity. Addition of hydrogen to propane on Zn/ZSM results in a 37% decrease in the conversion and a sharp decrease in the selectivity for ArH [3].

TABLE 2. Selectivity (S, %) of Formation of Reaction Products from Propylene on HTsVM and Zn/HTsVM (550°C)

Catalyst	HTsVM	1% Zn/HTsVM
	$X=40\%$	
Methane	5	2
Ethylene	37	28
Ethane	8	5
Propane	8	12
C_4+C_5-aliphatic hydrocarbons	12	10
Benzene	5	8
Toluene	13	18
Xylenes	10	15
C_9+ArH	2	2
S with respect to ΣArH	30	43
Rate constant of conversion of propylene, sec^{-1}	1,44	2,56

The study of transformations of propane on the catalysts investigated here showed that the propylene/propane ratio changes little after attaining a maximum in the presence of Zn/HTsVM, while it increases with an increase in the conversion on HTsVM (550°C):

Degree of conversion	20	30	40	50	60	70	80	90
HTsVM 1%	2.2	5.7	9.3	12	14	16	18	26
Zn/HTsVM	2.0	3.7	6.7	10	11.3	11.0	11.0	10

It follows from the data obtained in conversion of propane and propylene on HTSVM and Zn-containing pentasils (Tables 1 and 2) that almost identical products are formed from these hydrocarbons.

Conversion of propylene on modified catalysts and on the H form of TsVM takes place significantly more rapidly than conversion of propane: the corresponding rate constants in the case of propylene are one order of magnitude higher than for propane (1.44 and 0.113 sec^{-1} on HTsVM; 2.56 and 0.154 sec^{-1} on 1% Zn/HTsVM, respectively). In turn, the rate of conversion of propylene and the selectivity with respect to ArH (Table 2) is slightly higher on Z-modified pentasils than on HTsVM (Fig. 5). As a consequence, not only the rate of the stage of dehydrogenation of propane into propylene, but also the rate of subsequent transformation of propylene increase in the presence of Zn.

It was shown in a special series of experiments that the degree of conversion remained almost constant when the linear flow rate was changed from 0.3 to 3 liters/h and the volume flow rate of the initial hydrocarbon was kept constant, which indicates the absence of external diffusion inhibition of the reaction.

It is more difficult to judge the presence or absence of internal diffusion inhibition, since traditional experimental methods of determining the effect of internal diffusion, comparison of the reaction rates when the size of the granules of catalysts is changed, is impossible in the case of pentasils. The calculation methods based on a comparison of the rates of diffusion and chemical transformation are also unsuitable due to the absence of reliable values of the diffusion coefficients of the different components in a complex mixture. Nevertheless, it is possible to propose some estimations of the region of occurrence of the reaction. Considering the data reported above on the different rates of conversion of propylene and propane on the same catalysts, and assuming the occurrence of the reaction with propylene in the internal diffusion region (the observed reaction rate is equal to the rate of diffusion of the most difficultly transported components), it is possible to state that the rate of conversion of propane is one order of magnitude lower than the rate of diffusion of these components. As a consequence, it is possible to conclude that internal diffusion inhibition is absent in conversion of propane.

It also follows from a comparison of the data obtained in transformations of propane and propylene on Zn-promoted catalysts that significantly fewer products of cracking (methane,

ethane) are formed in the case of propylene than for propane (Tables 1 and 2). Cracking of the initial alkane should thus be considered the source of light hydrocarbons in the case of propane. Incorporation of zinc in the zeolite changes the rate of cracking of propane very little. At the same time, the aromatizing activity increases markedly due to acceleration of the first stage of dehydrogenation of propane and also due to acceleration of the following stages.

On the whole, quantitative data which characterize the promoting effect of Zn in the Zn/HTsVM system both on conversion of propane into propylene and on subsequent conversions of propylene into ArH were obtained in the study. Experimental data which support the occurrence of the reaction of aromatization of propane in the kinetic region were obtained.

LITERATURE CITED

1. T. V. Vasina, V. P. Sitnik, A. V. Preobrazhenskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 528 (1989).
2. T. G. Khaimova, D. A. Mkhitarova, and N. M. Trenina, Neftepererab. Neftekhim., No. 7, 18 (1986).
3. T. Mole, J. R. Anderson, and G. Greer, Appl. Catal., 17, 141 (1985).
4. M. S. Scurrell, Appl. Catal., 32, 1 (1987).
5. T. Inui, Y. Manino, F. Okazumi, et al., Ind. Ing. Chem. Res., 26, No. 4, 647 (1987).
6. H. Kitagawa, Y. Sendoda, and Y. Ono, J. Catal., 101, 12 (1986).
7. Kh. M. Minachev, V. B. Kazanskii, A. A. Dergachev, et al., Dokl. Akad. Nauk SSSR, 303, No. 2, 412 (1988).
8. N. S. Gnep, J. Y. Doyemet, A. M. Seco, et al., Appl. Catal., 43, 155 (1988).
9. O. V. Bragin, T. V. Vasina, S. A. Isaev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 32 (1988).
10. M. S. Scurrell, Appl. Catal., 41, 89 (1988).
11. O. V. Bragin, B. K. Nefedov, T. V. Vasina, et al., Dokl. Akad. Nauk SSSR, 225, No. 1, 103 (1980).
12. J. R. Anderson, K. Foger, T. Mole, et al., J. Catal., 58, 114 (1979).

KINETICS OF THE REACTION OF SUPEROXIDE ANION-RADICAL WITH OLEFINS

M. Ya. Meskina, L. M. Baider,
and I. P. Skibida

UDC 541.127:541.138.3:541.515:
546.21-128.2:547.538

Kinetic investigation of the reaction of electrochemically generated $O_2^{\cdot-}$ with perfluorooctene, styrene, and cyclohexene in acetonitrile, in the presence of tetraethylammonium perchlorate used as a background electrolyte, revealed that $O_2^{\cdot-}$ reacts with styrene and perfluorooctene at the double bond, and the reactivity of the olefins with respect to $O_2^{\cdot-}$ decreases with decrease in the electrophilicity of the substituents at the double bond: perfluorooctene > styrene > cyclohexene. The main transformation products of styrene are phthalic and benzoic acid esters.

The superoxide anion-radical $O_2^{\cdot-}$ plays an important role in biochemical processes. Three basic types of reaction of $O_2^{\cdot-}$ with substrates in aprotic media were established: a one-electron transfer [1, 2], a nucleophilic substitution [3, 4], and deprotonation [5, 6], in which $O_2^{\cdot-}$ acts as a medium-strength reducing agent, a nucleophile, and a weak base, repsectively. The mechanism of the reaction of $O_2^{\cdot-}$ with alkenes has not been clarified up to this day.

Nonactivated alkenes are generally fairly inert to $O_2^{\cdot-}$ and can be oxidized only in the presence of activating additives such as a sulfo-ion, acyl chloride, or sulfonyl chlorides.

N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 733-737, April, 1990. Original article submitted March 3, 1990.