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The aromatization of low molecular-weight hydrocarbons, in particular C_2H_6 and C_3H_8 , has attracted the attention of research workers at the present time both in our country and abroad. This reaction, which was described previously [1-3] in the presence of M/Al_2O_3 catalysts, was only of theoretical interest as an example of the basic possibility of converting C_2-C_3 alkanes to aromatic hydrocarbons. The aromatization of C_2H_6 and C_3H_8 on pentasils [4-8] is a new stage in the study of processes of practical significance for obtaining aromatic hydrocarbons from nontraditional feedstocks.

The aim of the present work was to study the main characteristics of the conversion of C_2H_6 and C_3H_8 to aromatic hydrocarbons in the presence of a number of modified zeolite catalysts based on pentasil HTsVM and to establish the role of the separate components of the complex bifunctional system -M/HTsVM. An essential part in this is determination of the contribution of the thermal process in high-temperature conversions of C_2 -C₃ alkanes.

EXPERIMENTAL

Investigations were carried out in a continuous-flow unit and in a pulsed microreactor [9]. Catalysts used for the aromatization of C_2H_6 and C_3H_8 were M/HTsVM zeolite systems modified with metals and/or metal oxides and prepared as in [5], HTsVM $(SiO_2/Al_2O_3 = 35, Na_2O < 0.1\%)$, and also quartz (Tables 1 and 2). Before the experiments the modified samples were activated for 3 h in a current of air at 300°C, then for a further 3 h at 520°C; HTsVM was calcined for 5 h in a current of air at 550°C; between experiments all the catalysts were regenerated for 2 h with air at 520°C. In the continuous-flow unit the catalyst batch was 1.7-1.8 g (2.5 cm³) with a supply rate of reagents of 300 ml/h, while in the pulsed microreactor 100 mg of catalyst was loaded. The volume of the pulsed sample was 0.1 ml with a carrier gas (He) rate of 1200 ml/h. The reaction products were analyzed chromatographically [9].

RESULTS AND DISCUSSION

Under the conditions studied ethane and propane undergo dehydrogenation, hydrocracking, and conversion to aromatic hydrocarbons mainly of composition C_6 - C_8 as well as higher molecular-weight products. From the results obtained (Fig. 1, Tables 1 and 2) we can note characteristic features of the aromatization reaction of C_2 - C_3 alkanes and, first of all, the fairly high efficiency of the catalysts studied. Thus, in conversion of C_2H_6 and especially C₃H₈ the relatively high catalytic (including aromatizing) activity of zeolite HTsVM not containing additions of metals or metal oxides is revealed. In conversions (X) of C_3H_8 equal to 94-99%, the yields of aromatic hydrocarbons amount to 29-37% (550-600°C). When certain modifying agents are introduced into HTsVM, the yield of aromatic hydrocarbons from C_2H_6 and $C_{3}H_{8}$ increases markedly (Tables 1 and 2). In this case, as follows from [4, 5] and the present investigation (Table 1), the most active catalysts for C_2H_6 are Pt- and Zn-containing systems, on which the yield of aromatic hydrocarbons increases by a factor of 2 in comparison with HTsVM. The effect of M/HTsVM is evidently due to the fact that the initial stages of aromatization of the alkanes studied in the presence of M/HTsVM and HTsVM are substantially different. In the first case the determining stage is dehydrogenation of the initial hydrocarbon on the surface of the metal or oxide, while in the second case the determining stage is disproportionation of hydrogen on the strongly acidic sites of the zeolite (bridging OH groups [10]) and the subsequent formation of aromatic hydrocarbons and low molecular-weight alkanes, including considerable quantities of CH4.

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| Catalyst, composition, % | T _{reac} , C | X, % | Yield, % | | | | | |
|--------------------------|-----------------------|------|-----------|-------|-----|----------|----------|--|
| | | | aromatics | | | | | |
| | | | total | G6-C8 | CH₄ | C_2H_6 | C_2H_4 | |
| HTsVM | 600 | 25 | 10 | 9 | 12 | 75 | 3 | |
| 0.5Pt/HTsVM | 500 | 30 | 10 | 7 | 17 | 70 | 3 | |
| - 1 | 550 | 40 | 12 | 10 | 18 | 60 | 10 | |
| | 600 | 37 | 20 | 14 | 15 | 63 | 2 | |
| 0.2Pt-0.05Rh/HTsV M | 600 | 24 | 17 | 10 | 3 |] 76 | 4 | |
| 0.2Pt-0.05Cu/HTsVM | 600 | 42 | 17 | 12 | 20 | 58 | 5 | |
| 0.5Pt-0.75Cr/HTsVM | 600 | 30 | 17 | 12 | 11 | 70 | 2 | |
| 0.5Zn/HTsVM | 600 | 32 | 20 | 12 | 10 | 68 | 2 | |
| 0.5Zn -0.1 Dv/HTsVM | 600 | 44 | 20 | 11 | 20 | 56 | 4 | |
| 0.5Zn-0.2Pt/HTsVM | 600 | 32 | 20 | 14 | 9 | 68 | 3 | |
| 0.5Re/HTsVM | 600 | 36 | 15 | 6 | 17 | 64 | 4 | |
| Ouartz | 600 | 11 | | - | 1 | 89 | 10 | |
| 2 mm - | 700 | 39 | - 1 | - | 7 | 61 | 32 | |

TABLE 1. Conversions of Ethane on Modified Pentasils

TABLE 2. Conversions of Propane on Modified Pentasils

| | Treac. % | X, % | Yield, % | | | | | |
|---------------------------------|-------------------|-----------------|---|---|--|------------------|---------------------------------------|---------------------------------------|
| Catalyst, composition, η_0 | | | aromatics | | | | | |
| | | | total | C ₆ —C ₈ | CH₄ | C_2H_6 | C_2H_4 | C ₃ H ₈ |
| HTsVM | 500 550 | 72 92 | 14 29 | 11 23 | 33 44 | 22 16 | 3 | 28 8 |
| 0,5Pt/HTsVM | 600 500 550 | 98 91 99 | 37 20 25 | 26 17 18 | $ 41 \\ 28 \\ 42 \\ 54 $ | 19 32 30 | 1 2 2 | 9+9 (C ₄) |
| 0,2Pt-0,05Rh/HTsVM | 600 500 550 | 100 85 91 | 25 27 25 25 | $ \begin{array}{c} 17 \\ 22 \\ 18 \\ 24 \end{array} $ | 54 19 35 24 | 19 36 29 | | 15 9 1 |
| 0,2Pt0,05Cu/HTsVM | 550 | 100 | 27 34 35 | 26 25 | 14 35 | $50 \\ 50 \\ 24$ | $\hat{\frac{2}{6}}$ | |
| 0,5Pt-0,75Cr/HTsVM | 500 550 600 | 95 96 98 | 29 36 34 | 25 29 24 | 22 16 34 | 43 43 27 | 1 1 3 | 5 4 2 |
| 0,5Zn/HTsVM | 500 550 600 | 54 89 97 | 30 35 46 | 27 27 33 | 15 13 14 | 8 38 35 | 1 3 2 | 46 11 3 |
| 0,5Zn-0,1Dy/HTsVM | 500 550 600 | 63 85 100 | 24 32 53 | $ \begin{array}{c} 22 \\ 26 \\ 37 \end{array} $ | 24 25 23 | 16 27 22 | 2 1 2 | 37 15 - |
| 0.5Zn -0.2 Pt/HTsVM | 550 600 | 98 98 | $ \begin{array}{c} 27 \\ 40 \end{array} $ | 22 29 | 20 30 | 50 26 | 1 2 | $\begin{vmatrix} 2\\ 2 \end{vmatrix}$ |
| 0,5Re/HTsVM | 550 | 97 | 27 | 16 22 | 13 35 | 55 30 | 23 | $\frac{3}{2}$ |
| Quartz | 600 700 | 36 88 | | - | 7 37 | 1 10 | $\begin{vmatrix} 6\\27 \end{vmatrix}$ | 64+22 12+11 |

It was of fundamental importance to establish the contribution of the effect of heating on the systems studied in the aromatization reaction of C_2H_6 and C_3H_8 . In order to do this, the catalytic action of M/HTsVM and HTsVM was studied over a wide temperature range (450-700°C) and the results obtained were compared with the data on the conversion of C_2H_6 and C_3H_8 on quartz (Fig. 1). It was shown that up to a temperature of 450-500°C thermal conversions of C_3H_8 on quartz occur at a low level (3-10%).

However, under more severe conditions (600°C and above) purely thermal processes (Fig. 1a) begin to play a very important part in the conversion of C_3H_8 . In this case, as was to be expected from [11], C_2H_6 is much more stable than C_3H_8 both thermally and in the presence of catalysts. Under the conditions studied the main products of the thermal conversions of C_2H_6 and C_3H_8 on quartz are gaseous hydrocarbons. At 600°C ethane is mainly converted (X = 10-11%) to C_2H_4 (10%). When the temperature of the reaction is raised to 700°C, a significant increase in the decomposition of C_2H_6 occurs (Table 1). In conversions of C_3H_8 the thermal contribution is even more important, especially at high temperatures (Fig. 1a). At 600°C the following are formed from C_3H_8 : methane (7%), ethane (1%), ethylene (6%), propylene (22%). At higher temperatures (700°C) a small quantity of aromatic hydrocarbons ($\sim 3\%$) is also obtained (Table 2). Taking into account what has been stated above, it can be concluded that



Fig. 1. Dependence of degree of conversion (a) of C_2H_6 (1', 3', 4') and C_3H_8 (1-4) and the yield of aromatic hydrocarbons (b) on temperature on different catalysts: 1, 1') Pt/HTsVM; 2) Zn-Dy/HTsVM; 3) HTsVM; 4, 4') quartz.



Fig. 2. Dependence of yield of C_6-C_8 hydrocarbons on pulse number (n) of alkane in the presence of Pt/HTsVM (550°C): 1) C_2H_6 ; 2) C_3H_8 ; 3) C_4H_{10} ; 4) C_3H_8 on Zn-Dy/HTsVM.

activation of the lower alkanes takes place by the combned action of the zeolite base and its modifying component. The important role of the metal, especially Pt in the system Pt/HTsVM, is clearly seen from the data of Fig. 2. Thus, in the conversions of C_2 - C_4 alkanes a clearly marked development of the aromatizing activity of the Pt-zeolite system occurs during the reaction. It has been established previously [5] that a similar development occurs for Ptand Pd-containing VK zeolites in aromatization of C_2H_4 and C_2H_6 and the activity of Pt/HTsVM correlates with the electronic state of Pt [12] within given limits. At the same time, on catalysts not containing metals the development of catalytic activity is not observed. Consequently, the development process is due directly to the presence of a metal in the composition of the catalytic system studied.

For some time there have been discussions in the literature about the merits of promoting VK zeolites with certain metal oxides together with Group VIII metals, the former being in a number of cases effective components in catalytic systems for the aromatization of lower alkanes. Modified zeolite systems with Ga, Zr, Zn, and Cu/ZSM are of particular interest [13-16].

In the present work a number of zeolite-containing catalysts modified by metals or metal oxides (Tables 1 and 2) have been prepared and tested in the aromatization of C_2H_6 and C_3H_8 . It can be seen from the results obtained that the conversions of C_2H_6 and C_3H_8 are successfully catalyzed by Pt- and Zn-containing pentasils. On the majority of the samples investigated the yield of aromatic hydrocarbons from C_2H_6 is approximately doubled in comparison with

the initial H form of the zeolite, and it reaches 17-20%. In the case of $C_{3}H_{8}$ high activity was displayed by Zn-containing systems additionally modified with added amounts of platinum or dysprosium. The yield of aromatic hydrocarbons from $C_{3}H_{8}$ on the most active samples amounted to 46-53% with X = $\sim 100\%$ (Table 2). Replacement of Pt by other metals (or oxides) or introduction of modifying components into the Pt-zeolite system slightly changes the selectivity of the catalyst action in the conversion of $C_{3}H_{8}$. In this case cracking of the initial hydrocarbon decreases, as is indicated by the reduction in yield of decomposition products of $C_{3}H_{8}$ (CH₄, $C_{2}H_{6}$), and furthermore the disproportionation of hydrogen increases, resulting in an increased yield of aromatic hydrocarbons (Table 2).

It is important to note that for zeolite-containing catalysts modified by zinc compounds (Zn, Zn-Dy) a somewhat different type of development of activity in the given catalytic systems occurs during the aromatization of C_3H_8 in contrast to metal-zeolite catalysts containing Group VIII metals (Fig. 2).

It can be concluded from the results obtained that the activation of C_2-C_3 alkanes is successfully achieved in the presence of bifunctional zeolite catalysts of type metal(and/or oxide)-pentasil, and the effect of the modifying component on the aromatization of C_2H_6 and C_3H_8 varies considerably.

CONCLUSIONS

1. Platinum- and zinc-containing catalysts based on pentasil HTsVM have been studied in the aromatization of C_2 - C_3 alkanes. It is shown that modification of the H form of the zeolite by zinc oxide (0.5% Zn) doubles the yield of aromatic hydrocarbons from ethane. For propane, the yield of aromatic hydrocarbons on the most active samples reaches 53%.

2. It is shown that HTsVM successfully aromatizes propane with a yield of up to 37% based on alkane admitted.

3. The contribution of thermal process to the conversion of C_2-C_3 alkanes in the range 500-700°C has been determined. It amounted to about 10% for propane (500°C) and ethane (600°C).

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