ACTIVITY OF DIFFERENT STRUCTURAL TYPES OF ZEOLITES IN OLIGOMERIZATION OF C_3-C_4 OLEFINS

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The possibility of using X and Y zeolites and mordenite as catalysts for the oligomerization of C_2-C_4 olefins was established even in the early years of development of zeolite catalysis [1-3]. More recently, we have shown [4, 5] that the oligomerization of lower olefins proceeds vigorously on zeolites of the Pentasil type at comparatively low temperatures. The present work represents a comparative study of the activities of the Pentasil TsVK* and zeolites of other structural types in the oligomerization of propylene and isobutylene.

EXPERIMENTAL

The zeolites used as catalysts and certain characteristics of these zeolites are listed in Table 1. All of the decationized forms (with different degrees of exchange) were obtained by decomposition of the corresponding ammonium forms by heating in air at 400-450°C before use in the experiments. An exception to this procedure was made in the case of the L zeolite, the ammonium form of which was decomposed at a temperature below 400°C in order to avoid breakdown of its crystal structure.

The experiments with C_3H_6 and $i-C_4H_8$ (purity approximately 99%) were performed at temperatures up to 350°C, 0.1 MPa, and molar rates of olefin feed (U) from $1 \cdot 10^{-5}$ to $5 \cdot 10^{-4}$ moles/ sec·g. The procedures used in performing the experiments and analyzing the reaction products have been set forth in [7]. The catalyst activities in the reaction were evaluated on the basis of the liquid product yield and also on the basis of the initial oligomerization rates (r_{07}) [5], which were determined by graphical differentiation. The stability of operation of the zeolite catalysts was tested in extended runs for periods up to 4 h.

DISCUSSION OF RESULTS

In Fig. 1a we present data on the temperature dependence of the liquid product yield in the conversion of C_3H_6 and i-C₄H₈ (in the case of the i-C₄H₈, the liquid product yields at temperatures below 200°C practically coincide with the total conversion of the original olefin). It will be noted that temperatures above 200°C are required to give any conversion of C_3H_6 to liquid products on any of the four zeolites investigated (Fig. 1a). These products consist of complex mixtures of alkanes and alkenes in the C_6-C_{10} range, both straight-chain and branched. No selective formation of C_3H_6 dimer or trimer is observed. As we have reported [4], when using the Pentasil HTsVK in the 200-300°C interval, liquid products in this composition range are obtained as a result of isomerization, cracking, and other conversions of oligomers of lower olfefins [4].

In contrast to C_3H_6 , the more reactive $i-C_4H_6$ is converted to liquid products even at 40-60°C (Fig. lb). Below 200°C, with any of the zeolites that were investigated, $i-C_4H_6$ is selectively oligomerized, forming dimers and trimers, including 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2,2,4,6,6-pentamethyl-3-heptene, and 2,2,6,6-tetramethyl-4-methyl-eneheptane. With increasing temperature, the content of $i-C_4H_6$ trimers in the products increases; on all of the zeolites, the yield passes through a maximum in the 90-130°C interval (Fig. 2). Above 200°C, no $i-C_4H_6$ trimers are found in the reaction products. The highest yield of trimers is observed when the reaction is carried out on the L zeolite, in connection with the very high activity of this zeolite in $i-C_4H_6$ conversion.

And indeed, the oligomerization of $i-C_4H_8$ proceeds most intensively on the L zeolite, even at 100°C, the oligomer yield is greater than 90%, and it remains at this level all the *TsVK is a Russian acronym denoting a high-silica zeolite - Translator.

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TABLE 1. Certain Characteristics of Zeolites

Fig. 1. Temperature dependence of liquid product yield in conversions of C_3H_6 (a) and $i-C_4H_8$ (b) on zeolites HKL (l), HKE (2), HNaM (3), and HNaY (4), and HTsVK (5).

way up to 200°C. With further increases in temperature, the yield of oligomerized products drops off rapidly. From the data presented in Fig. 1b it can be seen that the activity of these zeolites in i-C₄H₈ conversions below 150°C decreases in the following series: L >> erionite \approx mordenite > Y \approx HTsVK. This order is maintained when the zeolite activities are compared on the basis of the initial oligomerization rates (Table 2). According to these data, the L zeolite has the highest value of r₀₇, more than 7 times the value obtained for zeolites of the mordenite and erionite types, and 12-15 times the value obtained for the Y zeolite and Pentasil. Further study will be required to determine the reason for such a high activity of L zeolite in the reaction of i-C₄H₈ oligomerization.

As can be seen from Fig. 1b, on the L zeolite, an overall conversion of $i-C_4H_e$ (or liquid product yield) equal, for example, to 50%, is reached at approximately 60°C, i.e., some 50-70° lower than on the other types of zeolite. Therefore, in order to compare the 1-C₄H₈ conversions at identical temperature and identical conversion (for example, at 100°C and 30% conversion), experiments were performed at different molar rates of olefin feed. Here it could be expected that on the narrow-pore zeolites such as Pentasil and erionite, the formation of branched trimers of i-C4Hs should be hindered, and the reaction products should be enriched in dimers of the original olefin. Instead, according to the data that we obtained (Table 2), the ratio of trimer to dimer concentration in the reaction products (T/D) has the greatest value (1.1) in the case of the zeolite with the narrowest pores, the HKE, whereas in the case of the wide-pore HNaY zeolite, this ratio is only 0.5. These results, in combination with data on the adsorption of various hydrocarbons on zeolites of the Pentasil and erionite types [6, 8], suggest that the dimers and trimers that are found in the reaction products are formed primarily on the external surface of the crystallites, since if they are formed within the pores, such bulky molecules will be unable to diffuse into the gas phase. This is further evidenced by our data reported in [9] indicating complete suppression of the catalytic activity of Pentasil when its surface is selectively poisoned with 2,4,6-trimethylpyridine at temperatures up to 200°C.

For further confirmation of this hypothesis, we performed experiments at 100-200 °C with $i-C_4H_6$ on samples of erionite and Pentasil HTsVK that had been pretreated by passage of C_3H_6 at 200 °C. As previously noted, in experiments with C_3H_6 at this temperature, no liquid products are formed. However, the passage of this olefin over fresh samples of the zeolites is accompanied by a significant increase in temperature, which, according to [10], is due to processes of chemisorption and oligomerization of the alkene in the channels of the zeolite. In the current work, we found that the presence of presorbed C_3H_6 in the pores of the HTsVK or



Fig. 2. Temperature dependence of yield of $i-C_4H_8$ trimers on zeolites HKL (1), HKE (2), HNaM (3), HNaY (4), and HTsVK (5).

TABLE 2. Composition of Products from $i-C_4H_8$ Oligomerization on Zeolites of Different Structural Types (100°C, $i-C_4H_8$ conversion ~30%)

Zeolite	U, moles⁄ sec • g	Cor	nposition		- 1,5		
		2,4,4-TMP*				T/D	moles/ sec·g
		-1	-2	products trimers, C_{12}			
HKL HKE HNaM HNaY HTsVK	$\begin{array}{c c} 5\cdot 10^{-4} \\ 6\cdot 10^{-5} \\ 1\cdot 10^{-5} \\ 1\cdot 10^{-5} \\ 1\cdot 10^{-5} \\ 1\cdot 10^{-5} \end{array}$	39.1 32.7 37.9 48.9 45.8	15,8 13,8 14,4 16.0 15,1	$ \begin{array}{r} 1.7 \\ 0.9 \\ 4.0 \\ 1.3 \\ 0.4 \end{array} $	43.4 52.6 43.7 33.8 38.7	$\begin{array}{c} 0.77 \\ 4.1 \\ 0.78 \\ 0.52 \\ 0.63 \end{array}$	$ \begin{array}{c c} 16.3 \\ 2.2 \\ 2.2 \\ 1.4 \\ 1.1 \end{array} $

*2,4,4-Trimethylpentene.

HKE does not interfere with the reaction of $i-C_4H_0$ oligomerization on these zeolites; oligomers are formed with the same yields as on fresh portions of these catalysts.

In experiments with $i-C_4H_6$ at 200°C with a molar feed rate of $1 \cdot 10^{-5}$ mole/sec·g, the L zeolite, mordenite, erionite, and Pentasil manifest satisfactory stability; Over an operating period of 1.5-2 h, the product yields change very little (Fig. 3a). The most unstable of the zeolites proved to be the wide-pore HNAY zeolite with an 80% degree of exchange. This is probably a factor in the observed low activity of this zeolite in $i-C_4H_6$ oligomerization.

With increasing feed rate of the original olefin, the stability of operation of all of the zeolites drops off, and they become deactivated quite rapidly. This can be seen with particular clarity in the example of the Pentasil HTsVK, which is usually distinguished by high stability in comparison with zeolites of other structural types. As can be seen from data (Fig. 3b), at 200°C with $U = 1.0 \cdot 10^{-5}$ mole/sec*g, the yield of oligomerization products on the HTSVK remains constant at approximately 60% over the course of 4 h. An increase in U leads to rapid deactivation of the zeolite: The yield of oligomers drops to approximately half the original level in 3 h of operation. The rapid deactivation of the zeolites at 200°C with high values of U can be explained on the basis that the branched molecules of oligomers that are formed under these conditions can undergo cracking, isomerization, and other conversions only to a very slight degree. Hence they are retained in the channels of the zeolite and are sorbed on the active centers, blocking these centers. In favor of this hypothesis is the fact that narrow-pore zeolites of the Pentasil and erionite types that have been deactivated in this manner can be regenerated by heating at 250-270°C in a flow of inert gas containing no oxygen. This results in breakdown and removal of not only the products of $i-C_4H_B$ oligomerization that are adsorbed on the external surface of the crystallites, but also oligomer molecules that are formed and strongly sorbed within the channels of the zeolite. We made an analogous observation previously under conditions of conversion of C_3-C_4 alkenes at a somewhat higher temperature on a sample of Pentasil modified by vanadium [11].

From the data presented in Table 3, it can be seen that the breakdown of oligomers of C_2 -C₄ olefins sorbed on the surface of narrow-pore zeolites of the Pentasil and erionite types gives an identical set of alkanes and C_2 -C₅ alkenes. It is interesting to note that upon regeneration of HTsVK zeolite that has been deactivated by products of oligomerization of various olefins, definite differences are observed in the distribution of the products from breakdown of the oligomers. However, these differences are far greater for breakdown of oligomers



Fig. 3. Timewise variation of liquid product yield in $i-C_4H_8$ conversion. a) On zeolites HKL (1), HNaM (2), HKE (3), HTsVK (4), and HNaY (5) at 200°C with U = $1 \cdot 10^{-5}$ moles/sec•g. b) On HTsVK zeolite at 200°C with U = $1 \cdot 10^{-5}$ (1), 2.4 $\cdot 10^{-5}$ (2), and 6.2 $\cdot 10^{-5}$ moles/sec•g (3).

TABLE 3. Composition of Products from Breakdown of Oligomers of Various Olefins, Chemisorbed on Narrow-Pore Zeolites

Zeolite	Original olefin	Composition of breakdown products, wt. %								
		ΣC_2	C_3H_8	C_3H_6	<i>i</i> ~C ₄ H ₁₀	n-C4H10	C4H8	Σ C ₅		
HTSVK	$\begin{bmatrix} C_{2}H_{4} \\ C_{3}H_{6} \\ n-C_{4}H_{8} \\ i-C_{4}H_{3} \end{bmatrix}$	17,2 11,8 6.9 11,0	$6.0 \\ 7.5 \\ 3.9 \\ 4.3$	$22.6 \\ 15.8 \\ 13.0 \\ 21.6$	10,5 18,5 10,8 8,4	2,5 3,5 7,4 3,1	19.5 23,1 30,2 31,2	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		
HKE	C ₃ H ₆	-	0,8	14,0	9.3	9,6	48.6	17.7		

of one and the same alkene sorbed on zeolites differing in structural type. For example, the structure of the oligomer molecules is determined primarily by the parameters of the zeolite pore structure, and to a smaller degree by the nature of the original olefin,

The temperature at which we initially observe rapid breakdown of oligomers filling the zeolite channels $(250-270^{\circ}C)$ coincides satisfactorily with the start of the temperature interval in which there is a rapid increase in C₈H₆ conversion and in the yield of liquid products from conversion of this olefin (Fig. 1a). In this specific temperature interval, apparently, C₈H₆ molecules obtain access to active centers in the pores of the zeolite that were previously blocked, active centers on which both the oligomerization reaction and other conversions of the original olefins and its oligomers can take place. Consideration should also be given to a possible increase in the rates of desorption of branched products. As can be seen from data obtained by selective poisoning of the external surface of the Pentasil by 2,4,6-trimethylpyridine, the main contribution to the catalytic conversions of i-C₄H₈ at temperatures above 250°C is likewise made by active centers localized in the channels of the zeolite [9]. The results we have obtained are consistent with data reported by other investigators [10].

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CONCLUSIONS

1. On zeolites of the L, mordenite, erionite, Y, and Pentasil types at 50-200°C, isobutylene undergoes selective dimerization and trimerization, whereas oligomerization of prop-ylene on these zeolites is observed only above 200°C and is accompanied by isomerization, cracking, and other conversions of the oligomers that are formed.

2. The highest activity in isobutylene oligomerization is manifested by L zeolite, the lowest activity by the Pentasil type zeolite, which also loses its stability of operation (characteristic for Pentasils) when the molar rate of olefin feed is increased.

3. On narrow-pore zeolites (Pentasil and erionite) below 200°C, isobutylene is selectively dimerized and trimerized mainly on active centers localized on the outer surface of the crystallites, since the zeolite channels are blocked by strongly chemisorbed oligomers.

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CATALYTIC CONVERSIONS OF C3 CYCLIC OLEFINS IN THE PRESENCE OF Ni(0) COMPLEXES.

COMMUNICATION 1. (n²-METHYLENECYCLOPROPANE)BIS(TRIPHENYLPHOSPHINE)NICKEL:

CATALYTIC ACTIVITY AND ROLE IN DIMERIZATION AND TRIMERIZATION OF

METHYLENECYCLOPROPANE

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In the catalytic cycle of dimerization and trimerization of methylenecyclopropane (MCP) on Ni(0) complexes, including complexes modified with phosphines [1-3], n^2 -methylenecyclopropane complexes of Ni(0) have been suggested as the primary intermediates [4, 5]. However, no direct data have been available for confirmation of this hypothesis.

Here we are reporting on a study of conversions of MCP in the presence of $(\eta^2$ -methylenecyclopropane)bis(triphenylphosphine)nickel (Kt-1), the synthesis of which was described in [6], and also an investigation of the behavior of the Kt-1 itself under conditions of catalysis, with the aim of elucidating its role in MCP conversion reactions.

DISCUSSION OF RESULTS

In the presence of Ni(COD)₂ - $PK_n^{-1}R_{3-n}^2$ (COD = 1,5-cyclooctadiene; n = 1-3; series of compounds includes PPh₃), MCP is subjected to dimerization, trimerization, and oligomerization, trimers or oligomers being formed preferentially [3].

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