TRANSFORMATION OF CYCLIC HYDROCARBONS ON H, Ca, AND La FORMS OF ZEOLITES

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Cationic forms of zeolites are catalytically active in hydrogenation [1] and dehydrogenation [2, 3]. In contrast to 1,4-cyclohexadiene (CHD), cyclohexane (CAN) and cyclohexene (CEN) do not undergo dehydrogenation on Na forms of zeolites [2]. The dehydrogenating activity of zeolites increases upon replacing singly charged cations by multiply charged cations, and aromatic hydrocarbons begin to be formed also from CEN and CAN in addition to cracking reactions [3].

In the present work, in a study of the role of zeolite activity in the observed transformations of cyclic hydrocarbons, we investigated the reactions of CAN, CEN, and CHD on H, Ca, and La forms of various zeolites. Amorphous aluminosilicate, Al_2O_3, and SiO_2 were also studied to explain the action of zeolites.

EXPERIMENTAL

The transformations of the cyclic hydrocarbons were studied in pulse microreactors by our previously described method [2]. In some experiments, in order to improve the accuracy of the quantitative analysis of the hydrocarbon remaining on the catalyst as coke or high-molecular-weight compounds, the gas system was modified so that, after passing the injector, the compound was transferred to a reference arm of the katharometer, then to the reactor, and subsequently to the chromatography column.

The catalysts were H forms of type Y zeolites, erionite, and mordenite which were prepared through the NH_4 form [4], and Ca and La forms of erionite and mordenite prepared by ion exchange of the Na and Na,K forms with solutions of the corresponding salts. The extent of the exchange was determined relative to residual sodium by flame photometry and to the cation introduced into the zeolite by titration of the solution with Trilon B.

In the case of type Y zeolite, the catalysts were prepared with 17, 38, 55, 75, and 98 eq. % decationization. The exchange was 97 and 98.8% for erionite and mordenite, respectively. The Ca and La exchange was 86.6% for CaE, 52.9% for LaE, 69% for CaM, and 54% for LaM. In the present work, aluminosilicate was used with 9.6% Al_2O_3, 0.27% Na_2O, and 0.08% Fe_2O_3, with 340 m^2/g specific surface and 35 Å average pore radius. The silica gel used had 0.4% Al_2O_3, 0.10% Na_2O, and 0.05% Fe_2O_3, 135 m^2/g specific surface, and 19 Å average pore radius. The γ-Al_2O_3 had 220 m^2/g specific surface and 520 Å pore radius (with overall volume 0.15 cm^3/g) and <40 Å pore radius (with overall volume 0.5 cm^3/g). The impurities in γ-Al_2O_3 were 0.043% Na_2O and 0.22 Fe_2O_3.

RESULTS AND DISCUSSION

Cyclohexane undergoes mainly cracking and isomerization to methylcyclopentane (MCP) on NaY zeolite with various extents of decationization, while some of this hydrocarbon remains on the catalyst as coke or high-molecular-weight polymer deposits. However, 2.9% benzene and 7.8% toluene are also formed on the zeolite with 98% decationization, indicating dehydrogenating activity for this catalyst. Dehydrogenating activity is more evident in the conversion of CEN (Fig. 1), in which benzene and toluene are formed on all the catalysts studied in addition to the products of cracking, coke-formation, isomerization, and disproportionation. The total yield of benzene and toluene increases with increasing decationization of the zeolite. The total yield of disproportionation products (MCP and CAN) exceeds that of benzene and toluene. In earlier work [2], we found that the major products on Na forms of zeolites are MCP and CAN. Thus, the formation of benzene and toluene is not related to disproportionation and apparently is the result of the direct dehydrogenation of CEN. Toluene may be formed by the alkylation of benzene by the cracking products.

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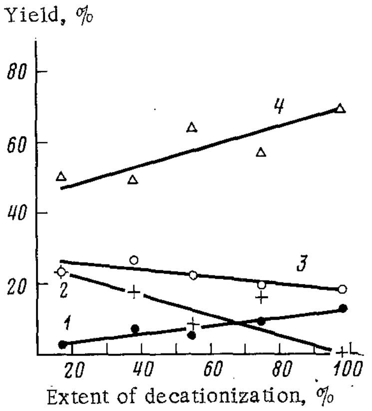


Fig. 1

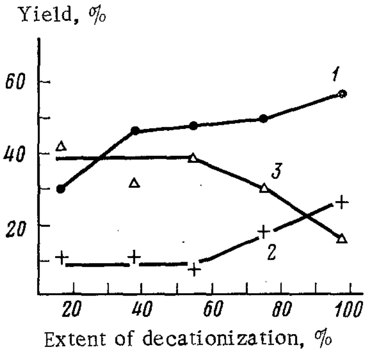
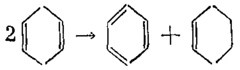


Fig. 2

Fig. 1. Yields of CEN transformation products (relative to injected hydrocarbon) on NaY zeolite with different extents of decationization at 500°C during the first pulse with 0.2-g catalyst batches: 1) total benzene + toluene; 2) sum of MCP + CAN; 3) cracking products; 4) coke.

Fig. 2. Yields of CHD transformation products (relative to injected hydrocarbon) on NaY zeolite with different extents of decationization at 200°C during the first pulse with 0.01-g catalyst batches: 1) benzene; 2) sum of MCP, CAN, and CEN; 3) coke.

In the case of CHD (Fig. 2), in addition to coke, the transformation products are MCP, CAN, CEN, 1,3-cyclohexadiene, and benzene. The benzene yield increases from 30 to 56% with increasing decationization from 17 to 98%. The formation of CEN and the products of its subsequent transformation (CAN and MCP) apparently indicate that benzene is formed not only as the result of dehydrogenation but also of the disproportionation of CND as found on Na forms of zeolites [2]



The amount of benzene formed by direct dehydrogenation is 70, 59, and 51% at reaction temperatures of 200, 250, and 300°, respectively. These yields were found to be independent of the degree of decationization of the zeolite within experimental error.

Thus, the dehydrogenating activity of a Y zeolite increases with increasing decationization. This finding apparently indicates that this reaction occurs at acidic catalyst sites. In a study of the catalytic properties of cationic forms of Y zeolite in the transformation of cyclic hydrocarbons [3], we found that the dehydrogenating activity of the catalysts correlates with their activity in cracking, which also indicates a definite role for zeolite acidity in hydrocarbon dehydrogenation.

In the case of erionite and mordenite with a higher SiO_2/Al_2O_3 ratio, CAN and CEN mainly undergo cracking, and a significant portion of the hydrocarbon is deposited on the catalyst as coke. Also, 3.6% benzene is formed on H-mordenite. Benzene becomes one of the major products in the transformation of CND on these catalysts in addition to the product of isomerization of this hydrocarbon (Table 1).

The H forms of the different zeolites form the following series relative to activity in the dehydrogenation of CHD: HY (98%) > HE > HM, which corresponds to the series for the Na forms of these zeolites [2]. The differences in the catalytic properties of narrow-pore zeolites such as erionite and mordenite and of Y type zeolites may be related to the different effect of reagent diffusion during the reaction within the zeolite pores.

In earlier work [5], we showed that cationic forms of mordenite with multiply charged cations, in contrast to its H form, have low activity relative to the skeletal isomerization of hydrocarbons [5]. The reason for this effect apparently lies in the absence of Brönsted acidity in such catalysts [6]. The results of our experiments with the Ca and La forms of erionite and mordenite (Table 2) showed that CAN does not react on cationic forms of erionite,

TABLE 1. Transformation of Cyclohexane, Cyclohexene, and 1,4-Cyclohexadiene on H Forms of Erionite and Mordenite

Catalyst	Yield relative to injected hydrocarbon, %							
	coke	cracking products	MCP	CAN	CEN	1,3-CHD	1,4-CHD	benzene
HE	33,2*	–	–	66,8	–	–	–	–
	72,0†	15,5	9,2	3,4	–	–	–	–
	20,0‡	0,1	0,5	2,9	5,6	32,9	18,0	20,0
HM	67,9*	25,6	1,6	4,9	–	–	–	–
	73,0†	19,8	3,3	0,4	–	–	–	3,6
	20,0‡	–	–	–	3,4	29,8	33,6	13,2

*CAN transformation at 500°C; 0.2-g catalyst batch.
†CEN transformation at 500°C; 0.2-g catalyst batch.
‡CHD transformation at 300°C; 0.04-g catalyst batch.

CEN undergoes disproportionation on the La form of erionite, and the total yield of disproportionation products on the Ca form is only 8%. The cationic forms of mordenite are more active and dehydrogenation also proceeds on the La form of mordenite: 3.1 and 8.2% aromatic hydrocarbons are formed from CAN and CEN, respectively.

Comparison of these findings with the results given in Table 1 shows that judging on the basis of the amount of unreacted starting hydrocarbon, the H forms of erionite and mordenite are more reactive than the corresponding Ca forms, while the La forms of the zeolites are superior to the H forms according to some criteria. Thus, disproportionation of CEN proceeds selectively on LaE: the total yield of MCP and CAN is 72%, while it is only 12.6% on H-erionite. Dehydrogenation proceeds more rapidly on LaM than on HM.

In order to clarify specific features of the action of zeolites in the transformation of cyclic hydrocarbons, we also studied several nonzeolite oxide catalysts: amorphous aluminosilicate, γ-Al_2O_3, and SiO_2. Table 3 shows that the composition of the products of the transformation of CEN on aluminosilicate is close to that on zeolite NaY with 17% decationization (see Fig. 1). In the case of γ-Al_2O_3 and SiO_2, the major reaction is disproportionation with the formation of MCP and CAN. These catalysts are close to LaE and CaM in activity (see Table 2). The finding of disproportionation on SiO_2 indicates that this reaction may take place not only on acid catalysts but also on inert supports with only slight acidity.

Table 3 shows that CHD undergoes dehydrogenation on the oxide catalysts studied, and aluminosilicate is on the level of NE and NM relative to the benzene yield (see Table 1) but much lower than NY (see Fig. 1). The samples of γ-Al_2O_3 and SiO_2 were less reactive relative to dehydrogenation (1.7-2.0% benzene yield) and similar to the Na forms of zeolites [2].

Thus, CAN undergoes cracking and isomerization to MCP on the catalysts studied, and a significant portion of the starting compound is retained on the catalyst as coke or high-molecular-weight compounds. Dehydrogenation was found only on zeolite HY with 98% decationization and on LaM (see Table 2). In the case of CEN, disproportionation is found in addition to the above-mentioned processes, while dehydrogenation proceeds to a greater extent than in the transformation of CAN. The catalysts studied fall into two groups relative to the ratio of the disproportionation products MCP/CAN. This ratio is 2-19 on acid zeolites such as Be, Mg, Ca, La, and H forms of zeolite Y (Table 4). The MCP/CAN ratio is usually 0.3-0.7 on catalysts without acid sites such as Na forms of zeolites and SiO_2. This discrepancy is apparently a result of the different nature of the intermediate complexes, and the MCP/CAN ratio for CEN transformation products may indicate the presence or absence of catalyst acidity. CaE, LaE, and CaM zeolites behave as nonacidic catalysts analogous to SiO_2; the MCP/CAN ratio for these catalysts is 0.4-0.5 (see Table 4). This finding accounts for the lower acidity of CaM relative to HM in the isomerization of CAN [5]. In contrast to CaM, the La form of this zeolite is a typical acidic catalyst since the MCP/CAN ratio is 5.8 (see Table 4).

A correlation is noted between the MCP/CAN ratio in the CEN transformation products and the benzene yield in the dehydrogenation of CHD: the catalyst activity in CHD dehydrogenation increases with increasing MCP/CAN ratio. Thus, for example, the benzene yield on SiO_2 in the dehydrogenation of CHD is 1.7% (see Table 3) with MCP/CAN = 0.42 (see Table 4), while the benzene yields on H forms of zeolite Y range from 30.1 to 56.1% (see Fig. 1) as the MCP/CAN ratio increases from 10 to 14 (see Table 4). This indicates that the dehydrogenation of the hydrocarbons studied occurs on acid zeolite sites.

TABLE 2. Transformation of Cyclohexane and Cyclohexene on Ca and La Forms of Erionite and Mordenite at 500°C (0.2-g batches, 0.25-0.50 mm fraction, first pulse)

Zeolite	Cation	Yield relative to injected hydrocarbon, %						
		coke	cracking products	MCP	CAN	CEN	benzene	toluene
Erionite	Ca*	–	–	–	100	–	–	–
	Ca†	–	–	2,5	5,5	92,0	–	–
	La*	–	–	–	100	–	–	–
	La†	14,0	1,7	21,0	51,0	12,3	–	–
Mordenite	Ca*	23,2	–	–	76,8	–	–	–
	Ca†	–	4,5	28,8	57,7	9,0	–	–
	La*	46,2	28,2	4,7	17,8	–	1,0	2,1
	La†	72,5	18,0	1,3	–	–	2,1	6,1

*Transformstion of CAN

†Transformation of CEN.

TABLE 3. Transformation of Cyclohexene and 1,4-Cyclohexadiene on Various Catalysts, First Pulse

Catalyst	Yield relative to injected hydrocarbon, %							
	coke	cracking products	MCP	CAN	CEN	1,3-CHD	1,4-CHD	benzene
Aluminosilicate	52,5*	20,2	18,9	5,9	–	–	–	2,5
	44,3†	–	–	–	7,9	3,8	25,7	18,3
γ-Al_2O_3	19,0*	2,8	15,1	50,6	10,1	–	–	2,4
	19,3†	–	–	–	–	1,5	77,2	2,0
SiO_2	13,0*	–	18,7	44,8	23,5	–	–	–
	13,8†	–	–	–	–	2,2	82,3	1,7

*Transformation of CEN (0.2-g catalyst batch, 500°C).

†Transformation of CHD (0.01-g catalyst batch, 200°C).

TABLE 4. MCP/CAN Ratios in the CEN Transformation Products on Various Catalysts during Pulse Operation of a Microreactor

Catalyst	T., °C	Total CEN conversion, %	Yield of MCP + CAN, %	MCP/CAN
NaA;, NaY; NaE; NaM	500	3–46	6–46	0,3–0,7 [2]
Be-, Mg-, Ca-, La-forms Y	500	100	8–17	6–19 [3]
0,66 CaX; 0,34 CaY; 0,86 HY	320–357	53–98	18–27	2,3–5 [7, 8]
HY – extent of decationization 17–98%	500	100	8–15	10–14
0,97 HE	500	100	13	2,7
0,99 HM	500	100	3,7	8,2
0,86 CaE	500	8	8	0,4
0,53 LaE	500	88	72	0,4
0,69 CaM	500	91	84	0,5
0,54 LaM	500	100	8,1	5,8
Amorphous $Al_2O_3 \cdot SiO_2$	500	100	24,8	3,2
γ-Al_2O_3	500	90	65,7	0,3
SiO_2	500	77	63,5	0,4

CONCLUSIONS

1. The transformation of cyclohexane, cyclohexene, and 1,4-cyclohexadiene was studidd on H, Ca, and La forms of type Y zeolites, erionite, and mordenite as well as on amorphous aluminosilicate, γ-aluminum oxide, and silicon dioxide in a pulse microreactor. These hydrocarbons undergo cracking, isomerization, disproportionation, and dehydrogenation at 200-500°C.

2. The catalysts studied fall into two groups relative to the methylcyclopentane/cyclohexane ratio in the cyclohexene transformation products: the catalysts without acid sites (Na forms of zeolites and SiO_2) have ratios less than unity, while the catalysts with acid sites (multiply charged cationic and H forms of zeolites and amorphous aluminosilicate) have ratios above unity.

3. The dehydrogenating activity of the catalysts studied increases in going from non-acidic to acidic catalysts.

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SOME ASPECTS OF THE MECHANISM OF THE CATALYTIC DEHYDROCYCLOOLIGOMERIZATION OF ETHYLENE AND ETHANE TO AROMATIC HYDROCARBONS

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In the presence of a series of supported metal oxide catalysts as well as γ-Al_2O_3, ethylene undergoes dehydrocyclotrimerization to yield benzene and other aromatic hydrocarbons (AH) [1-3].

In the present work, we examined the pathways for the cyclooligomerization of ethylene. In particular, we studied the possibility of aromatizing ethylene through the intermediate formation of C_4-C_6 aliphatic hydrocarbons. For this purpose, ethylene cyclotrimerization (ECT) was studied under comparable conditions on different catalysts as well as the cyclooligomerization of butylene and various butylene–ethylene mixtures. In addition, other possible pathways for the formation of AH were studied such as through higher molecular weight compounds which, under ECT conditions, undergo decomposition and aromatization.

EXPERIMENTAL

Four catalyst (Ct) samples were used: 0.6% Pt/$Al_2O_3 \cdot F$ (I), 0.6% Rh/$Al_2O_3 \cdot F$ (II), γ-$Al_2O_3 \cdot F$ (III) ($F = 3.4\%$, $S_H = 180\ m^2/g$), and an industrial reforming catalyst AP-56 (IV). In order to prepare Ct (I) and (II), samples of (III) were impregnated with the corresponding aqueous solutions of H_2PtCl_6 and $RhCl_3$. The catalysts were treated with H_2 for 1 h at 530° immediately before the experiments.

Ethylene, mixtures of butylene isomers, 1-hexene, 1-dodecene, 1-methylcyclopentene, cyclohexadiene, benzene, toluene, and p-xylene with 98.5-99.9% purity were used as the starting hydrocarbons. The lower olefin mixtures used were 87.5% C_2H_4 and 12.5% C_4H_8, 75% C_2H_4 and 25% C_4H_8, and 50% C_2H_4 and 50% C_4H_8. Gas–liquid chromatography was used for monitoring.

The cyclooligomerization of the binary ethylene–butylene mixtures given above and of pure C_2H_4 and C_4H_8 was studied by the pulse method [1]. The studies were carried out on Ct (I), (III), and (IV) at 500-550°C and on Ct (II) at 420-500°C.* The catalyst batches were

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*Since ECT on rhenium catalysts proceeds at 80-100°C below the temperature of the platinum catalysts and Al_2O_3 [4], the runs with the rhenium catalysts were carried out at correspondingly lower temperatures.

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