Journal of Catalysis **198,** 29–40 (2001)
doi:10.1006/jcat.2000.3102, available online at http://www.idealibrary.com on IDEAL®

Reaction Pathways of 1-Cyclohexyloctane in Admixture with Dodecane on Pt/H–ZSM-22 Zeolite in Three-Phase Hydroconversion

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Received May 17, 2000; revised August 23, 2000; accepted October 13, 2000; published online February 8, 2001

Isomerization and hydrocracking of a mixture of 1-cyclohexyloctane and dodecane were performed on Pt/H-ZSM-22 in a three-phase Robinson Mahoney reactor with complete internal mixing ($T = 523$–543 K, $P = 7$–8 MPa, H_2/HC $= 5$). The reaction products from 1-cyclohexyloctane were analyzed in detail and compared with those obtained in the absence of dodecane in a fixed-bed vapor-phase reactor ($T = 460$ K, $P = 0.45$ MPa, H_2/HC $= 450$). In the presence of dodecane, the main reaction pathway involved contraction of the six-membered ring to a five-membered ring with concomitant elongation of the octyl chain by one carbon. Subsequently, the nonyl chain underwent methyl branching at carbon positions far from the ring. Methyl branching rearrangements of the cyclohexane ring of 1-cyclohexyloctane were suppressed in the presence of dodecane. In the reaction product fraction of heptylmethylcyclohexanes, all cis–trans and positional isomers were formed except the 1,1′-heptylmethylcyclohexane isomer. The isomer distributions were explained with pore mouth and key–lock catalysis. Pt/H-ZSM-22 did not favor the paring reaction. The distribution of cracked products, and especially the abundant formation of alkylcyclopentanes, was in agreement with cracking through β-scission in the chain rather than by ring dealkylation typical of the paring reaction. Ring opening in 1-cyclohexyloctane and its isomers is a less important side reaction. © 2001 Academic Press

Key Words: **hydrocracking; hydroisomerization; pore mouth catalysis; key–lock catalysis; ZSM-22; 1-cyclohexyloctane; paring reaction.**

INTRODUCTION

Bifunctional catalysts composed of dispersed noble metal and acidic oxide are used in several industrial processes related to petroleum refining and production of petrochemicals such as hydrocracking, reforming, hydroisomerization, and isodewaxing (1, 2). The converted hydrocarbon streams are complex mixtures with paraffins and naphthenes as the main compounds.

The bifunctional reaction mechanisms were studied by several research teams using model compounds and laboratory-scale reactors (3–10). The reaction pathways of paraffin and naphthene hydroisomerization and hydrocracking on bifunctional Y-type zeolite catalysts were explained in terms of alkylcarbenium ion chemistry in an unconstrained molecular environment (3–7, 9). The carbenium ions are formed by protonation of unsaturated hydrocarbons on the acid sites; the latter are formed by dehydrogenation of saturated compounds formed on the metal function. Both saturated and unsaturated components can be physisorbed prior to reaction. The reaction mechanism of skeletal isomerisation involves the formation of protonated cyclopropanes and larger cyclic alkylcarbonium ions (3, 5, 9, 11). That mechanism is responsible for stepwise changes in the degree of branching and is significantly slower than ring contractions and expansions and positional shifts of alkyl groups along carbon rings and chains (9, 11). Hydrocracking proceeds through β-scission of carbon bonds in alkylcarbenium ions (12).

Souverijns *et al.* (9) studied the conversion pathways of 1-cyclohexyloctane representing a typical naphthene molecule contained in hydrotreated gasoil. They studied this conversion using a Pt/H–Y zeolite catalyst in a vapor-phase, continuous-flow, fixed-bed reactor (9). The primary reaction step was methyl branching of the ring. Subsequently, the methyl group was shifted over the ring to the 1′ position and transferred to the octyl chain. After methyl group transfer from the ring to the first or second carbon atom of the long alkyl chain, the molecule became susceptible to dealkylation by β-scission; this paring of methyl groups from a ring is known as the paring reaction (7, 10).

Compared to those on Pt/H-Y, on Pt/H-ZSM-22 zeolite catalyst the hydroisomerization reaction pathways of 1-cyclohexyloctane under similar reaction conditions were significantly different (9, 11). Among the heptylmethylcyclohexanes which are important reaction products on Pt/H-ZSM-22 as well as Pt/H-Y, the formation of 1,3-cis, 1,2-trans, and 1,2-cis forms was kinetically suppressed in favor

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0021-9517/01 $35.00

of the 1,4-trans, 1,3-trans, and 1,4-cis substituted isomers. Another family of hydroisomerization products formed especially on Pt/H-ZSM-22 had a methyloctyl substituent on a five-membered ring. The methyl group was preferentially positioned at carbon positions of the octyl chain far from the ring. On Pt/H-ZSM-22 direct branching of the long *n*-alkyl side chain was a more important reaction pathway than that on Pt/H-Y. Hydrocracking in general and dealkylation in particular was suppressed on Pt/H-ZSM-22 since the formation of isomers with tertiary carbon atoms at the first or second position in the chain counting from the ring and which are particularly susceptible to cracking through β-scission did not occur.

ZSM-22 has narrow parallel pores with windows that cannot be crossed by cyclopentane nor cyclohexane rings (11). The selectivity of Pt/H-ZSM-22 catalyst was explained by pore mouth and key–lock catalysis (Fig. 1). In the pore mouth mode, the long alkyl chain penetrates into the pore, while the ring remains at the pore mouth as it cannot cross the first window of the pore. This was confirmed experimentally by Denayer (13) who studied chromatographically the physisorption of naphthenes on ZSM-22. It was found that the Henry coefficient at 473 K of *n*-hexane is 14 times larger than that of cyclohexane. For larger molecules such as *n*-octane and cyclooctane an even larger difference was found whereas for a non-shape-selective zeolite such as NaY the Henry coefficients of naphthenes are comparable to those of paraffins. Moreover, on ZSM-22, the physisorption enthalpy of cycloalkanes is 20–30 kJ/mol lower than the corresponding *n*-alkane, pointing at a physisorption at the surface or the pore mouth. As the value of cyclooctane is only marginally higher than that for cyclohexane (55.9 versus 54.2 kJ/mol), and considering the higher number of carbon atoms, this would point at a stronger interaction at the pore mouth of cyclohexane than for cyclooctane. This seems reasonable, considering the size of these molecules.

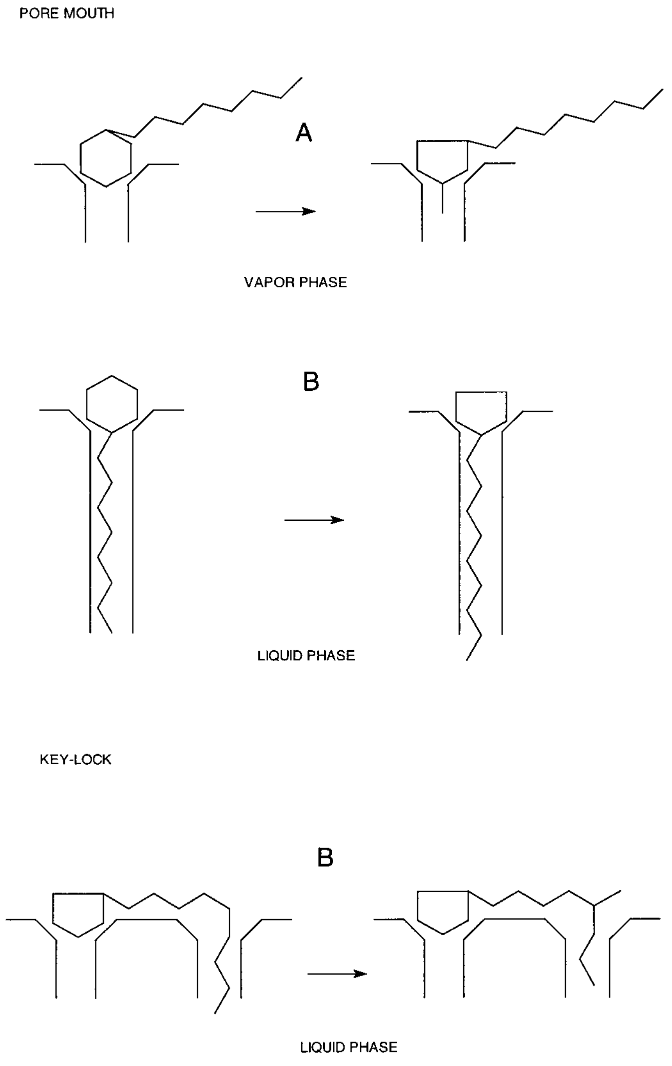

FIG. 1. Schematic representation of pore mouth and key lock physisorption and reaction of 1-cyclohexyloctane.

This physisorption behavior of cycloalkanes is not unexpected when examining the measurements for linear and branched alkanes (14). Here it was shown that only linear alkanes can penetrate the pores of ZSM-22. Branched alkanes adsorb only on the external surface and in the pore mouths, and can only penetrate with their linear part into the pore. This was evidenced most clearly from the physisorption enthalpies which correlate well with the length of this linear part.

A further confirmation of this is found in the physisorption entropies which are 2 orders of magnitude higher for branched alkanes than for *n*-alkanes. This cannot be due to there being more physisorption sites available for branched molecules, and one cannot imagine there being more freedom of branched molecules in the pores. Hence, branched alkanes and, by extension, naphthenes adsorb on the external surface and at the pore mouths of ZSM-22. They only have the linear chain part in the pore. These findings were recently confirmed by very elaborate measurements by IR and calorimetry (15).

Moreover, on the basis of all these findings from physisorption studies and using this surface physisorption model, the gas-phase conversion of *n*-alkanes on Pt/H-ZSM-22 could be very well rationalized (16).

Adsorbed in the pore mouth mode the only possible reaction is a contraction of the ring and an elongation of the alkyl chain by one carbon atom. In terms of alkylcarbenium ion chemistry, this is a fast reaction, as it does not alter the degree of branching. In the alternative pore mouth physisorption mode, the ring is located in the pore mouth, with the chain outside the pore. This physisorption mode leads to ring branching. In the key–lock mode two pore mouths are involved (Fig. 1): the ring is located in one pore mouth, with the alkyl chain stretched across the external crystal surface reaching a neighboring pore mouth with the tail of the *n*-alkyl chain. The branching occurs in that part of the chain that is located in a pore mouth.

In a previous study dealing with skeletal isomerization of *n*-paraffins on Pt/H-ZSM-22, it was observed that the key–lock mode was favored over the pore mouth mode when the catalyst was operated in the liquid phase under conditions where the pores are filled with adsorbed *n*-paraffin molecules (17).

In the present work we investigated the impact of pore filling on the conversion of 1-cyclohexyloctane by admixing dodecane and performing the reaction in the liquid phase.

EXPERIMENTAL

The ZSM-22 zeolite was synthesized according to a recipe described elsewhere (18), calcined, exchanged with ammonium cations, and impregnated with an aqueous solution of $Pt(NH_3)_4Cl_2$ to obtain a Pt loading of 0.5 wt% (19). The Pt dispersion of such a sample is 30%. This low value indicates that most of the platinum metal is present as large particles on the external surface of the zeolite crystallites (20). Catalyst pellets were prepared by compressing the dry zeolite powder into flakes, which were crushed and sieved. Catalyst pellets with diameters between 0.8 and 1.0 mm were used in the reactor. These catalyst pellets were calcined in oxygen and subsequently reduced in hydrogen at 400°C without intermittent cooling. The absence of mass transfer limitations in the intercrystalline pores was verified.

1-Phenyloctane (Janssen, 99%) was hydrogenated in a batch reactor on Pd/carbon black catalyst. The 1-cyclohexyloctane thus obtained was previously used as a pure feed to a fixed-bed continuous-flow vapor-phase microreactor (9, 11), denoted in short as a vapor-phase reactor. In these previous experiments the reaction pathways of 1-cyclohexyloctane on both Pt/ZSM-22 and Pt/US-Y zeolite were investigated. In the present work, a mixture of 1-cyclohexyloctane with *n*-dodecane in a molar ratio of 5:95 was converted in a Robinson Mahoney type three-phase reactor (17), denoted for convenience as the liquid-phase reactor. The reaction conditions in the vapor- and liquid-phase reactors are specified in Table 1.

TABLE 1

Range of Reaction Conditions for the Hydroconversion Experiments of 1-Cyclohexyloctane in the Vapor-Phase and Liquid-Phase Reactors

		Vapor-phase reactor	Liquid-phase reactor
		Fixed bed; plug-flow	Mixed flow
Pressure	(Mpa)	0.45	7–8
Temperature	(K)	460	523–543
H_2/HC ratio	(mol/mol)	450	5
W/F_0	(kg · s/mol)	1,800	616

The identification and quantification of the individual components in the reaction products was performed using a GC–MS system equipped with an HP-PONA column and using a Chrompack CP 9000 gas chromatograph with a TCD and FID detector, and previously established chromatographic elution sequences (9, 11).

The conversion of a component i, X_i, was defined by

$$X_i = \frac{F_i^0 - F_i}{F_i^0} \qquad \text{(mol/mol)}, \qquad [1]$$

with F_i^0 representing the inlet liquid molar flow rate and F_i the outlet liquid molar flow rate.

The mean conversion between 1-cyclohexyloctane and *n*-dodecane was defined by

$$\bar{X} = \frac{\sum_i^{\mathrm{NFEED}} \left(F_i^0 - F_i\right)}{\sum_{i=1}^{\mathrm{NFEED}} F_i^0} \qquad \text{(mol/mol)}, \qquad [2]$$

in which i represents the feedstock components, i.e., *n*-dodecane and 1-cyclohexyloctane. The yield of naphthene branched isomers, naphthene cracked products, and ring-opening products from 1-cyclohexyloctane was defined by

$$Y_i = \frac{F_i \mathrm{MW}_i}{\sum_{j=1}^{\mathrm{NFEED}} F_j^0 \mathrm{MW}_i} \qquad \text{(kg/kg)}. \qquad [3]$$

MW_i represents the molecular weight of the particular feed or product component i, and F_i^0 represents the inlet liquid molar flow rate and F_i the outlet liquid molar flow rate. It was not possible to identify all the cracked products from 1-cyclohexyloctane. The production of C_9–C_{11} naphthenes was minimal and the formation of these compounds will not be discussed. Moreover the identification of the C_6, C_7, and C_8 naphthenes was enough to explain the shape selective on Pt/H-ZSM-22 catalyst. Paraffin cracked products were produced from *n*-dodecane and 1-cyclohexyloctane, respectively; therefore, the quantification of these compounds produced by only 1-cyclohexyloctane was performed as follows: the moles of C_6, C_7, and C_8 naphthene cracked products were accompanied by C_8, C_7, and C_6 paraffin cracked products, respectively. By this assessment the molar amount of paraffin formed by cracking of 1-cyclohexyloctane can be calculated. The molar amount of other paraffin cracked products formed by secondary cracking of the ring-opening products is calculated via the total mass balance of the 1-cyclohexyloctane conversion.

RESULTS AND DISCUSSION

The evolution of the individual conversions of 1-cyclohexyloctane and dodecane with the mean conversion is shown in Fig. 2. The C_{12} paraffin was more reactive than the C_{14} naphthene. The skeletal isomerization products

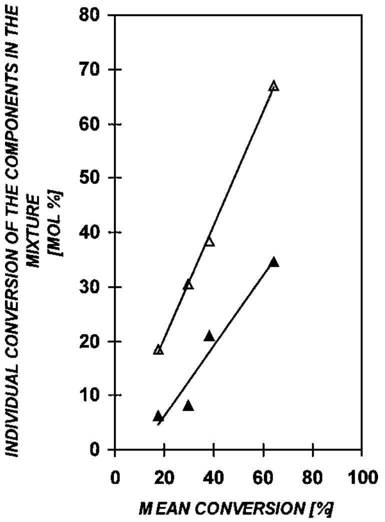

FIG. 2. Individual conversion of 1-cyclohexyloctane and dodecane against mean conversion (▲, 1-cyclohexyloctane; △, dodecane).

from dodecane exhibited the typical features previously reported in detail (17, 23). The conversion of dodecane will not be discussed further in this paper.

On the bifunctional Pt/USY zeolite catalyst there exists a unique relationship between the selectivity and the total conversion (21, 22). On a shape selective catalyst the selectivity may include a certain dependence on the reaction conditions; however, these effects are expected to be limited (19) so that the main differences in product distributions observed in this work are attributed to the difference in aggregation state, i.e., the vapor or the liquid phase, and to the presence or absence of an *n*-alkane solvent. In addition to the arguments presented in the Introduction to explain why *n*-alkyl naphthenes only physisorb in the pore mouth with the linear substituent, it has been measured that linear paraffins such as dodecane physisorb much more strongly than iso-paraffins and naphthenes (13, 14). Hence, the dodecane in the admixture effectively will block the intracrystalline pores and as no platinum is available there, no reaction will occur in the pores. All reaction will occur at the surface of the crystals. It can therefore be stated that intracrystalline transport will not affect the reactions considered.

The reaction products from 1-cyclohexyloctane were grouped in four product families, viz. (i) isomers which are naphthenes with 14 carbon atoms, (ii) ring-opening products which are C_{14} normal and branched paraffins, (iii) cracked products arising from C_{14} naphthenes, and (iv) cracked products arising from C_{14} paraffins. The yields of these product families in the liquid-phase reactor are reported in Fig. 3a. Data previously obtained in a vapor-phase reactor (11) are presented in Fig. 3b. In the vapor phase, the isomer yields were high (Fig. 3b). Naphthene cracking became important only at conversions exceeding 80%. There was very little ring opening. In the liquid-phase reactor, isomerization was also the main conversion, but hydrocracking of C_{14} naphthenes was much more abundant than that in the vapor-phase reactor. Ring-opening products and cracked products from ring-opening products were formed in larger yields than in the vapor phase. This ring-opening was probably catalyzed by the platinum metal and favored in the presence of a low hydrogen concentration in the liquid phase. Methane and ethane which are typical

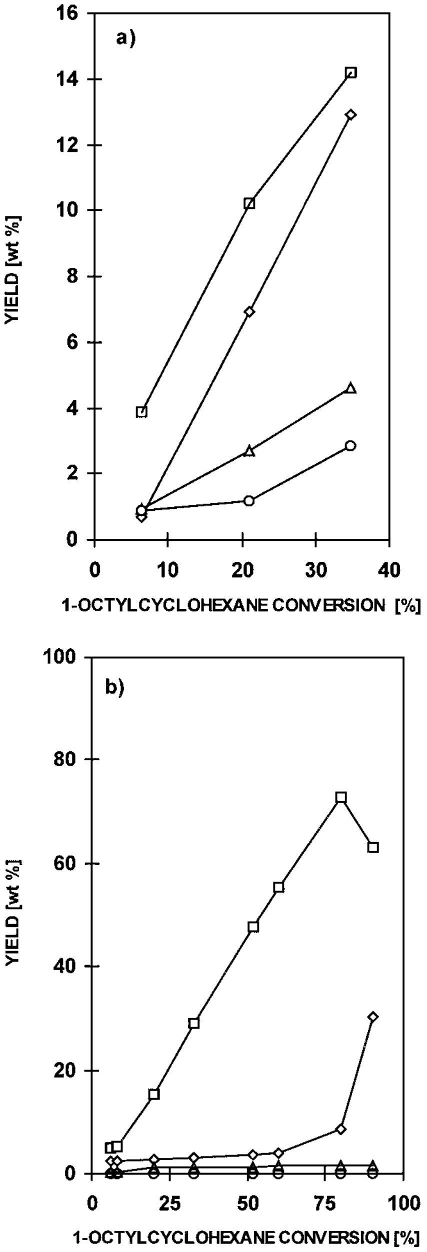

FIG. 3. Yield of reaction product lumps from hydrocracking and isomerization of 1-cyclohexyloctane on Pt/H-ZSM-22 against 1-cyclohexyloctane conversion in liquid-phase reactor (a) and vapor-phase reactor (b): □, isomers; ◇, cracked products from C_{14} naphthenes; △, ring-opening products; ○, cracked ring-opening products.

hydrogenolysis products were indeed observed. The lower yield of primary products (isomers) and the higher yield of secondary products (cracked products) in the liquid phase compared to the case in the vapor phase can be explained by a difference in physisorption mechanism (Fig. 1). On the basis of a simplified consecutive reaction scheme the influence of the reactor type on the selectivity pattern was calculated (24) and it was found to be negligible at the conversion level investigated.

Hydroisomerization Pathways

The isomerization of 1-cyclohexyloctane led to products with a five-membered ring or a six-membered ring. The distribution of isomers according to ring type obtained in the liquid and vapor phases is shown in Figs. 4a and 4b, respectively. Despite the presence of a significant fraction of unidentified isomers, it was possible to conclude that the formation of substituted cyclopentanes was favored in the liquid phase; the formation of substituted cyclohexanes was favored in the vapor phase. On the Pt/Y in the vapor phase an even lower amount of cyclopentanes was formed (9). The only possible isomer the formation of which does not involve a branching rearrangement of carbon skeleton is 1-cyclopentylnonane. Unfortunately, this isomer had the same chromatographic retention time as 1-cyclohexyloctane. Its presence in the GC peak of 1-cyclohexyloctane was evidenced with MS, but due to the overlapping with the larger peak stemming from the unconverted feed, its formation could not be quantified. The 1-cyclopentylnonane was accounted for with the unconverted feed. All other identified isomers contained two tertiary carbon atoms next to secondary and primary carbon atoms and consequently had a branching degree of two, compared to a branching degree of one for the feed molecule. Isomers with a quaternary atom were not formed in measurable quantities. The distribution of isomers according to the presence of either two *n*-alkyl substituents, or one isoalkyl substituent on the ring in liquid- and vapor-phase reactors, is presented in Figs. 5a and 5b, respectively. Rings with one isoalkyl substitutent were most abundantly formed in the liquid-phase reactor; rings with two *n*-alkyl substituents were most abundant in the vapor-phase reactor.

The distribution of di-*n*-alkyl substituted cycloalkanes at two conversion levels in the liquid- and vapor-phase reactors is reported in Table 2. Specific cyclopentanes and cyclohexanes with two *n*-alkyl substituents were formed, namely cyclohexanes with methyl and heptyl, or ethyl and hexyl substituents and cyclopentanes with ethyl and heptyl, propyl and hexyl, and butyl and pentyl substituents. For all these isomers the positional and the cis–trans isomers were formed.

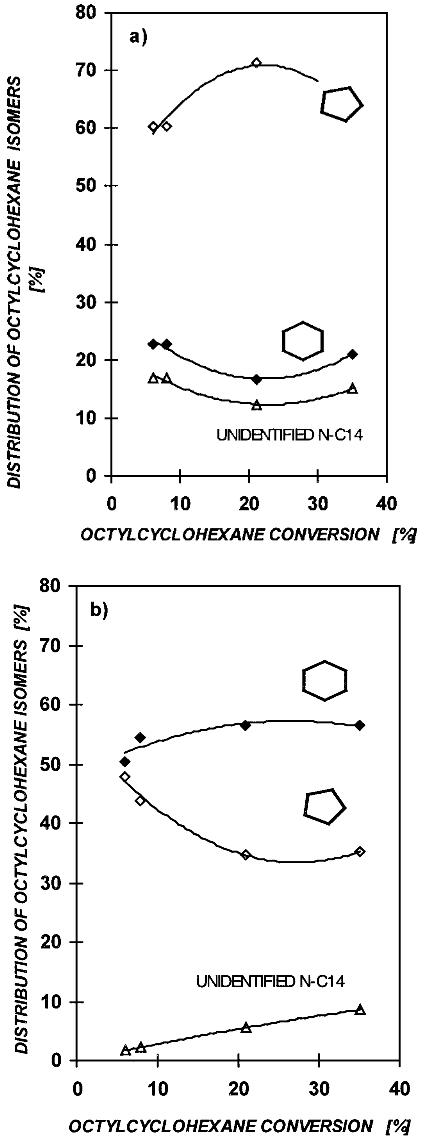

FIG. 4. Distribution of 1-cyclohexyloctane isomers according to the type of ring against 1-cyclohexyloctane conversion in liquid-phase reactor (a) and vapor-phase reactor (b).

At conversion levels of ca. 8% and 34% in vapor- and liquid-phase reactors, the formation of di-*n*-alkylcycloalkanes decreased as follows (Table 2):

heptylmethylcyclohexanes > heptylethylcyclopentanes
> hexylethylcyclohexanes > hexylpropylcyclopentanes

This sequence reflects consecutive ring contractions and expansions and a shortening long *n*-alkyl substituent with concomitant elongation of the short one. The formation of pentylbutylcyclopentanes, requiring still more isomerization steps, was observed in the vapor-phase reactor (11), but not in the liquid-phase reactor.

The distribution of positional and cis–trans heptylmethylcyclohexane isomers obtained at three conversion levels in the two reactors is reported in Table 3. The

TABLE 2

Distribution of Di-*n*-alkyl-Substituted Cycloalkane Feed Isomers (mol%) at Different 1-Cyclohexyloctane Conversion Levels on Pt/H-ZSM-22 and on Pt/H-Y

	Pt/H-ZM-22,		Pt/H-Y,	Pt/H-ZM-22,		Pt/H-Y,
	Vapor phase[a]	Liquid phase	Vapor phase[c]	Vapor phase[a]	Liquid phase	Vapor phase[c]
Conversion (%)	9	8	10	34	35	35
Heptylmethyl-cyclohexanes[b]	53.0	52.6	68.5	51.2	49.6	65.4
Heptylethyl-cyclohexanes	27.0	30.2	—	17.6	23.3	—
Hexylethyl-cyclohexanes	9.5	16.5	1.9	12.3	20.1	3.7
Hexylpropyl-cyclopentanes	3.5	5.3	—	3.5	6.9	—
Pentylbutyl-cyclopentanes	7.0	—	2.7	15.4	—	2.5
Others	—	—	26.8	—	—	26.7

[a] Data obtained from (11).
[b] Overlapped with methyloctylcyclopentane.
[c] Data obtained from (9).

1,1′-heptylmethylcyclohexane isomer was not formed in any of the experiments with Pt/H-ZSM-22. On Pt/H-Y zeolite, this isomer represents 10% of this product fraction, independent of the total conversion, since on Pt/H-Y catalyst the thermodynamic equilibrium is achieved for the heptylmethylcyclohexane isomers (Table 3). The formation of 1,3 and 1,4 substituted cyclohexanes was favored on Pt/H-ZSM-22 in the liquid phase as well as in the vapor phase (Table 3), confirming the pore mouth catalysis. Cis isomers were more abundant in the reaction products obtained in the liquid-phase compared to those in the vapor phase.

The isomers having a monoisoalkyl-substituted ring were mostly cyclopentanes. This product fraction was also analyzed in detail and compared with the results from previous experiments in the vapor-phase reactor (Table 4). The

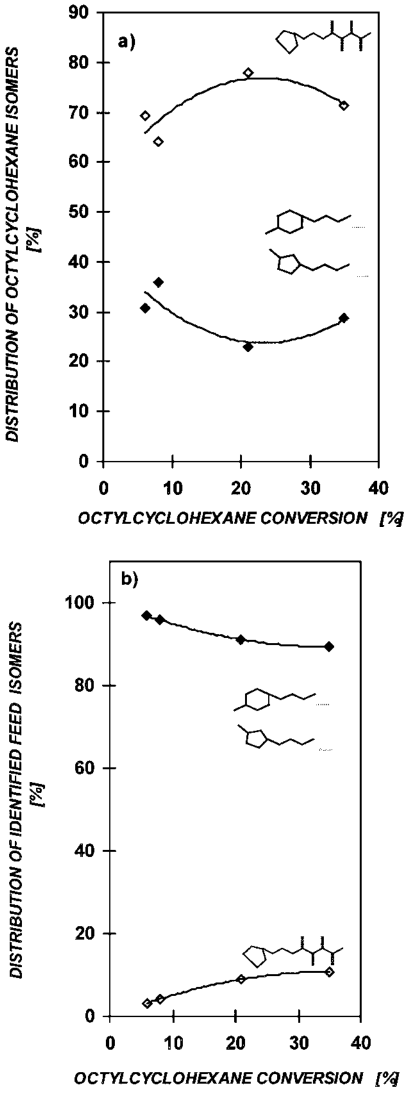

FIG. 5. Distribution of 1-cyclohexyloctane isomers according to the number of alkyl substituents on the ring against 1-cyclohexyloctane conversion in liquid-phase reactor (a) and vapor-phase reactor (b).

TABLE 3

Distribution of Positional and Cis–trans Heptylmethylcyclohexane Vapor and Liquid Reaction Products as a Function of the Conversion on Pt/H-ZSM-22 and the Equilibrium on Pt/H-Y

	Pt/H-ZSM-22		Pt/H-ZSM-22		Pt/H-ZSM-22		Pt/H-Y
	Vapor phase[a]	Liquid phase	Vapor phase[a]	Liquid phase	Vapor phase[a]	Liquid phase	Vapor phase[b]
Conversion (%)	7	8	20	21	34	35	Equil.
1,1′-Heptylmethylcyclohexane	—	—	—	—	—	—	9.5
1,2-*c*-Heptylmethylcyclohexane	—	—	0.5	—	1.0	—	1.0
1,3-*c*-Heptylmethylcyclohexane	21.8	26.3	24.5	18.2	29.0	49.7	41.5
1,4-*c*-Heptylmethylcyclohexane	12.5	25.7	11.8	37.4	10.0	16.8	5.0
1,4-*t* + 1,3-*t* + 1,2-*t*-Heptylmethylcyclohexane	65.7	48.0	63.2	44.6	60.0	33.5	43.0

[a] Data obtained from literature (11).
[b] Data obtained from literature at equilibrium (9, 11).

TABLE 4

Distribution of 1-Cyclopentyl-*m*-methyloctanes (mol %) as a Function of the Conversion of 1-Cyclohexyloctane on Pt/H-ZSM-22 and on Pt/H-Y

	Pt/H-ZSM-22		Pt/H-Y	Pt/H-ZSM-22		Pt/H-Y
	Vapor phase[a]	Liquid phase	Vapor phase[b]	Vapor phase[a]	Liquid phase	Vapor phase[b]
Conversion (%)	14.0	8.0	13.4	34.0	35.0	35.0
1-Cyclopentyl-7-methyloctane	32.3	32.1	0	23.2	32.3	0
1-Cyclopentyl-6-methyloctane	N.D.[c]	18.4	N. D.	N. D.	5.8	N.D.
1-Cyclopentyl-5-methyloctane	16.9	27.8	10.9	15.4	20.6	18.0
1-Cyclopentyl-4-methyloctane	22.1	8.3	11.1	21.1	20.7	16.0
1-Cyclopentyl-3-methyloctane	14.8	3.1	10.9	14.5	11.2	23.5
1-Cyclopentyl-2-methyloctane	13.8	5.1	40.8	13.6	3.4	29.5
2-Cyclopentylnonane	0	3.5	26.4	12.2	5.9	13.0

[a] Data obtained from literature (11).
[b] Data obtained from literature (9).
[c] N.D., not detected.

fraction comprises 1-cyclopentyl-*m*-methyloctanes, with *m* in the range from 2 to 7, together with 2-cyclopentylnonane. The following observations were made: the preferred isomer had the methyl group at the C_7 position, i.e., the position most remote from the ring. The formation of isomers with the methyl group close to the five-membered ring, and especially 2-cyclopentylnonane, was suppressed. At the same conversion level, this suppression was more pronounced in the vapor-phase than in the liquid-phase experiments. The behavior of Pt/H-ZSM-22 was totally different from that of Pt/H-Y, on which the formations of 1-cyclopentyl-2-methyloctane and 2-cyclopentylnonane are kinetically favored, viz. Table 4. On the Pt/H-Y zeolite with wide pores, the methyl groups are generated by contraction of the ring and subsequently transferred to the long alkyl side chain (9).

In conclusion, inspection of all these detailed product features on Pt/H-ZSM-22 showed that in the liquid phase in the presence of dodecane, some reaction pathways are favored and others suppressed (see Fig. 6). The main isomers were cyclopentanes with one isoalkyl substituent. Their formation from 1-cyclohexyloctane requires a ring contraction and concomitant side chain elongation followed by branching of the nonyl chain. This reaction pathway was more important than the generation of a second side chain on the ring, which was the dominant reaction pathway in the vapor-phase experiments (11). On a Pt/H-Y zeolite, the six-membered ring of 1-cyclohexyloctane was much more reactive toward branching than the side chain (9). On the Pt/H-ZSM-22 zeolite under vapor-phase reaction conditions, the side chain was already relatively more reactive toward branching (11). Under the present liquid-phase

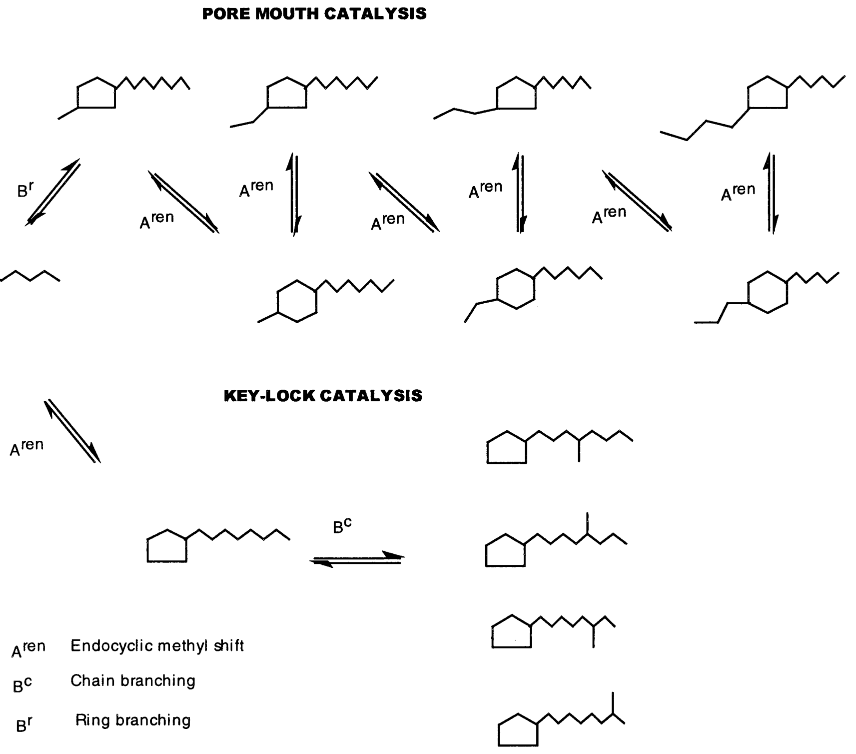

FIG. 6. 1-Cyclohexyloctane isomerization pathways occurring on Pt/H-ZSM-22 zeolite.

reaction conditions, the alkyl group was more reactive than the six-membered ring toward branching.

The suppressed reactivity of the ring toward branching in the liquid-phase experiments can be quantitatively explained with physisorption according to the pore mouth and key–lock model (Fig. 1) and competition with dodecane. For steric reasons, the five-membered ring or six-membered ring of the naphthene molecules cannot cross the 10 oxygen atom window of the ZSM-22 zeolite (11). The acid catalytic centers responsible for ring branching are located inside the micropore. To enable reaction, the naphthene molecule must be adsorbed with its ring in the pore mouth. This physisorption mode with only a limited number of carbon atoms of the molecule in contact with the zeolite micropore is expected to be energetically disfavored in the presence of large concentrations of linear alkane molecules such as dodecane that can much better interact with the micropore. In the alternative reaction modes of naphthene molecules, i.e., the key–lock mode and pore mouth mode with the chain inside (Fig. 1), interaction of alkyl chains of the naphthene molecule with a micropore is established. In these modes the physisorption of naphthene molecules is expected to be less suppressed by competitive physisorption and reaction of dodecane. Reactions of the alkyl chain according to the pore mouth and key–lock mode lead to the formation of 1-cyclopentylnonane and isomers with methyl branching in the chain. According to this model, the significant differences observed between the vapor- and liquid-phase experiments are caused by the presence of dodecane.

Hydrocracking Pathways

The Pt/H-ZSM-22 catalyst shows low hydrocracking activity toward long *n*-alkanes, a property that is at the basis of its excellent isodewaxing properties (25). The low tendency to cracking of the skeletal isomerization products from long *n*-alkanes can be explained by the position of the methyl branchings in the isomers, and the pore mouth and key–lock catalysis concept (26, 27). Hydrocracking proceeds through β-scission of alkylcarbenium ions. The fastest β-scissions involve tertiary or secondary alkylcarbenium ions with a tertiary or quaternary carbon atom in the γ position. The Pt/H-ZSM-22 catalyst does not favor the formation of skeletal isomers with tertiary or quaternary carbon atoms separated by one methylene carbon atom, susceptible to such cracking via fast β-scissions (19). In such isomers, the distance between the branchings is too short for a favorable interaction with the zeolite according to the key–lock mode. On Pt/H-ZSM-22, hydrocracking of paraffins proceeds via β-scissions of secondary or tertiary alkylcarbenium ions into smaller secondary alkylcarbenium ions (19).

Hydrocracked products from 1-cyclohexyloctane and its isomers comprise paraffins and naphthenes. The presence of dodecane and its aliphatic cracked products in the liquid-phase experiments rendered the analysis of the aliphatic cracked products from 1-cyclohexyloctane and its isomers impossible. The discussion on the cracking of the C_{14} naphthenes in the liquid phase will be based on the formation of alicyclic cracked products. The C_5, C_6, C_7, and C_8 naphthene reaction products were analyzed in detail. The distribution of the C_6, C_7, and C_8 naphthene reaction products obtained in the liquid phase is given in Table 5. The molar yield of C_6, C_7, and C_8 naphthenes per 100 moles of feed molecules cracked is plotted against the 1-cyclohexyloctane conversion in Fig. 7.

In the liquid-phase experiments, cyclopentane was not formed. In principle, it could be formed by dealkylation of 1-cyclopentylnonane, which is an intermediate in the transformation of 1-cyclohexyloctane into 1-cyclopentyl-*m*-

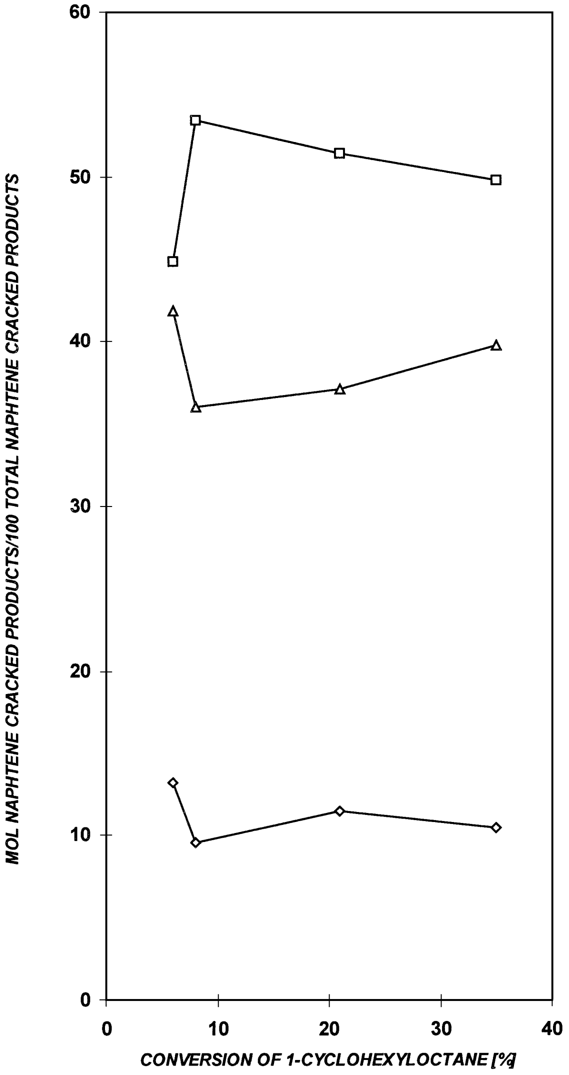

FIG. 7. Molar yield of C_6, C_7, and C_8 naphthenes per 100 total moles of naphthene cracked products as a function of 1-cyclohexyloctane conversion: ◇, C_6; □, C_7; △, C_8.

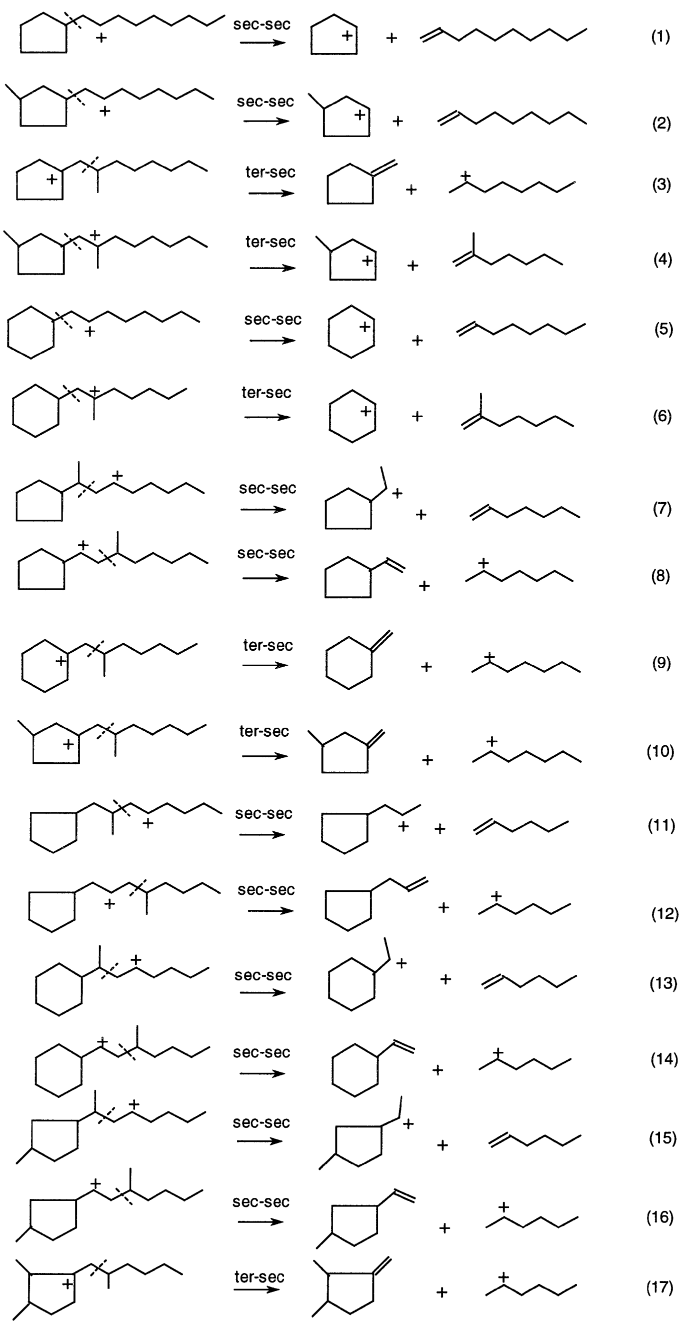

FIG. 8. Mechanism of naphthene cracking reactions performed on Pt/H-ZSM-22 zeolite.

methyloctanes. Hence, dealkylation of the five-membered ring, involving a β-scission on a secondary alkylcarbenium ion into a secondary cyclic alkylcarbenium ion (Fig. 8, Eq. 1) was a very slow reaction.

C_6 naphthenes are formed, but less abundantly than C_7 and C_8 naphthenes (Fig. 7). Cyclohexane formation corresponds to a dealkylation of the ring (Fig. 8, Eqs. 5 and 6), and is a very slow process in comparison to cyclopentane formation. Methylcyclopentane is the main C_6 naphthene formed (Table 5). This molecule can be formed through a β-scission that does not correspond to a dealkylation, but a scission of a carbon–carbon bond in the chain (Fig. 8, Eq. 3).

C_7 naphthenes are abundant cracked products (Fig. 7). The cyclic C_7 fraction of the cracked products comprises ethylcyclopentane, methylcyclohexane, and dimethylcyclopentanes (Table 5). Ethylcyclopentane is the main product of this fraction (Table 5). Its content in the C_7 naphthene fraction decreases with conversion, while that of methylcyclohexane and dimethylcyclopentanes increases, indicating that ethylcyclopentane is a primary cracked product. Methylcyclohexane and dimethylcyclopentanes are at least partially formed by secondary isomerization of this primary cracked product. Ethylcyclopentane can be formed through β-scissions in the chain of alkylcarbenium ions derived from 1-cyclopentylmethyloctanes (Fig. 8, Eqs. 7

TABLE 5

Distribution of Cracked Products in Liquid Phase as a Function of 1-Cyclohexyloctane Conversion on Pt/H-ZSM-22

	Conversion (%)			
	6	8	21	35
C_6 Fraction				
MeCyC5	86.6	90.1	96.1	92.6
CyC6	13.4	9.9	3.9	7.4
C_7 Fraction				
1,1′-Dimethylcyclopentane	N.D.[c]	N.D.	N.D.	N.D.
1-*t*-3-Dimethylcyclopentane	14.1	15.9	17.6	17.0
1-*c*-3-Dimethylcyclopentane	10.0	13.1	14.6	18.0
1-*t*-2-Dimethylcyclopentane	0	1.1	1.2	1.7
Methylcyclohexane[a]	14.4	16.9	17.2	19.5
Ethylcyclopentane	61.4	52.9	49.4	43.6
C_8 Fraction[b]				
1,1,3-Trimethylcyclopentane	—	N.D.	N.D.	N.D.
1-*t*-2-*c*-4-Trimethylcyclopentane	—	0	0.7	0
1-*c*-2-*t*-4-Trimethylcyclopentane	—	N.D.	N.D.	N.D.
1,1,2-Trimethylcyclopentane	—	0	0	0.8
1-*c*-2-*c*-4-Trimethylcyclopentane	—	N.D.	N.D.	N.D.
1-*c*-2-*t*-3-Trimethylcyclopentane	—	1.9	7.4	4.1
1,1-Dimethycyclohexane	—	N.D.	N.D.	N.D.
1-*c*-3-Dimethylcyclohexane	—	0	1.4	10.3
1,3-Dimethylcyclohexane	—	0.6	4.7	4.1
1-*t*-4-Dimethylcyclohexane	—	4.6	8.2	2.1
1-*t*-2-Dimethylcyclohexane	—	N.D.	N.D.	N.D.
1-Ethyl-3-methylcyclopentane	—	7.8	11.2	15.0
1-Ethyl-3-methyl-*c*-cyclopentane	—	10.6	15.2	15.9
1-Ethyl-2-methylcyclopentane	—	N.D.	N.D.	N.D.
1-Ethyl-1-methylcyclopentane	—	N.D.	N.D.	N.D.
iso-Propylcyclopentane	—	N.D.	N.D.	N.D.
n-Propylcyclopentane	—	42.6	43.2	38.5
Ethylcyclohexane	—	1.2	7.4	9.1

[a] Overlapped with 1-*c*-2-dimethylcyclopentane.

[b] At conversion of 6%, too few C_8 cracked products were analyzed to form a representative distribution.

[c] N.D., not detected.

and 8). The reaction of Eq. 7 is similar to the preferred cracking pathway of isoparaffins: the positive charge is on a secondary carbon atom of a linear alkyl group, which can be positioned inside the pore and stabilized by the atoms of the pore wall. In Eq. 8, the charged carbon is located between the ring and the branching in the chain. There is no way to locate the charged carbon atom inside the zeolite micropore. The formation of methylcyclohexane via cracking in a chain has to proceed via the reaction of Eq. 9, Fig 8. The parent molecule, viz. a 1-cyclohexyl-*m*-methylheptane, is much less abundantly formed than 1-cyclopentyl-*m*-methyloctane (Fig. 4a), explaining the low formation of methylcyclohexane compared to ethylcyclopentane. Dimethylcyclopentanes represent a significant fraction of the C_7 naphthenes (Table 5). The formation of 1,3-dimethylcyclopentanes is favored. Their formation can be explained by cracking in the chain of the group of 1-methylcyclopentyl-*m*-methylheptanes (Fig. 8, Eq. 10) in which the formation of the 1,1 and 1,2 forms is disfavored, as was observed in the composition of the group of methylheptylcyclohexanes isomers.

The C_8 naphthene reaction products are composed of propylcyclopentane, ethylcyclohexane, dimethylcyclohexanes, ethylmethylcyclopentanes, and trimethylcyclopentanes (Table 5). The abundant formation of propylcyclopentane in this fraction can be explained by considering the different possibilities for cracking through β-scission in a chain (Fig. 8, Eqs. 11–17). Propylcyclopentane, ethylcyclohexane, methylethylcyclopentane, and trimethylcyclopentanes can all be formed through two types of β-scissions in the chain, converting a secondary alkylcarbenium ion into a smaller secondary carbenium ion and a smaller olefin, or a tertiary alkylcarbenium ion into a smaller secondary carbenium ion and an olefin.

The formation of a particular C_8 naphthene is dependent on the formation of the specific parent feed isomer. Propylcyclopentane is the main C_8 naphthene product obtained from the abundantly formed 1-cyclopentyl-*m*-

TABLE 6

Distribution of Cracked Products in the Vapor Phase as a Function of 1-Cyclohexyloctane Conversion on Pt/H-ZSM-22

	Conversion (%)							
	33	46	62	76	80	88	90	93
			C_6 Fraction					
MeCyC5	100	100	83.8	79.4	75.1	65.6	52.8	48.7
CyC6	0	0	16.2	20.6	24.9	34.4	47.2	51.3
			C_7 Fraction					
1,1′-Dimethylcyclopentane	N.D.[d]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1-*t*-3-Dimethylcyclopentane	20.4	19.7	19.6	16.4	14.6	11.6	10.6	10.2
1-*c*-3-Dimethylcyclopentane	15.4	15.7	15.3	13.4	11.8	9.6	8.8	8.6
1-*t*-2-Dimethylcyclopentane	0	0	0	2.9	3.3	3.9	4.3	5.6
Methylcyclohexane[a]	40.1	39.7	42.3	48.8	54.2	62.2	64.4	63.9
Ethylcyclopentane	24.1	24.8	22.8	18.3	15.7	12.6	11.9	11.6
			C_8 Fraction					
1,1,3-Trimethylcyclopentane	0	0	0	0	0	0.9	1.1	1.2
1-*t*-2-*c*-4-Trimethylcyclopentane	0	0	0	0	0	1.3	1.6	2.1
1-*c*-2-*t*-4-Trimethylcyclopentane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,1,2-Trimethylcyclopentane	0	0	0	0	0	1.2	1.3	1.9
1-*c*-2-*c*-4-Trimethylcyclopentane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1-*c*-2-*t*-3-Trimethylcyclopentane	0	0	0	0	0	2.3	2.3	2.6
1,1-Dimethycyclohexane	0	0	0	0	0	0	0	0.9
1-*c*-3-Dimethylcyclohexane	—	—	—	—	—	—	—	—
1,3-Dimethylcyclohexane	—	—	—	—	—	—	—	—
1-*t*-4-Dimethylcyclohexane[b]	26.0	16.8	18.6	13.4	17.2	13.7	12.4	10.6
1-*t*-2-Dimethylcyclohexane	0	0	0	0	8.4	9.8	9.2	8.4
1-Ethyl-3-methylcyclopentane	20.6	23.7	22.9	21.8	16.3	11.9	10.2	8.6
1-Ethyl-3-methyl-*c*-cyclopentane	16.5	20.1	10.2	17.1	12.6	10.6	9.1	7.8
1-Ethyl-2-methylcyclopentane	0	0	0	0	0	1.7	2.1	2.9
1-Ethyl-1-methylcyclopentane	0	0	0	0	2.6	2.7	2.6	3.6
iso-Propylcyclopentane	0	0	0	0	0	0	0.9	1.0
n-Propylcyclopentane	—	—	—	—	—	—	—	—
Ethylcyclohexane[c]	36.9	39.4	40.3	47.6	42.9	43.8	47.0	47.9

[a] Overlapped with 1-*c*-2-dimethylcyclopentane.

[b] Overlapped with 1,3-*c*-dimethylcyclohexane and 1,3-dimethylcyclohexane.

[c] Overlapped with *n*-propylcyclopentane.

[d] N.D., not detected.

methyloctane isomers through Eqs. 11 and 12, Fig. 8. This cracking mode fits the pore mouth model. Ethylcyclohexane can be formed through a similar β-scission (Eqs. 13 and 14, Fig. 8), but the 2-cyclohexyloctane isomer involved is formed in trace amounts only. The formation of ethylmethylcyclopentanes starts from tribranched substituted cyclopentanes, necessitates an additional branching step, and is less important (Fig. 8, Eqs. 15 and 16). Four branchings in the parent naphthene are required to obtain trimethylcyclopentane as cracked product (Fig. 8, Eq. 17). Trimethylcyclopentanes are most likely obtained through secondary isomerization of less branched C_8 naphthenes.

It is concluded that on the Pt/H-ZSM-22 catalyst, cracking in a branched C_8 or C_9 alkyl substituent is favored over ring dealkylation. In the liquid phase, chain branching is more important than ring branching, explaining why the isomerization is rapidly followed by cracking (Fig. 3a). The opposite situation was encountered in the vapor phase. In the vapor phase, ring branching was more important than chain branching, explaining why cracking was much more suppressed than in the liquid phase (Fig. 3b).

In the vapor phase, the naphthene cracked product distributions (Table 6) were significantly different from those in the liquid phase. Especially the formation of alkyl-substituted cyclohexanes was more important. It reflects the more abundant formation of isomers with six-membered rings in the vapor phase (Fig. 4b). Unfortunately, in the vapor-phase experiments, it was not possible to determine in sufficient detail the composition of the feed isomers at the very high conversion levels where cracking sets in. Such information would have made it possible to detect whether these cyclohexanes are formed through cracking in an isoalkyl ring substituent, or by ring dealkylation.

The molar yield of C_5–C_9 aliphatic and alicyclic hydrocarbons per 100 moles of feed cracked in the vapor-phase experiment is shown at 30% cracking yield in Table 7. Under these conditions, there is little ring-opening (Fig. 3b). If there were pure primary cracking, the molar yield of C_5 paraffins and C_9 naphthenes should be equal. The same holds for C_6 paraffins and C_8 naphthenes, C_7 paraffins and C_7 naphthenes, C_8 paraffins and C_6 naphthenes, and C_9 paraffins and C_5 naphthene. This symmetry is absent, indicating that there was some secondary cracking of the heaviest cracked products.

TABLE 7

Carbon Number Distribution of Cracked Products at Cracking Yield of 30% in the Vapor-Phase Reactor

Cracked products	Moles/100 moles cracked
C_5 paraffins	28.8
C_9 naphthenes	22.2
C_6 paraffins	23.1
C_8 naphthenes	19.5
C_7 paraffins	19.1
C_7 naphthenes	22.2
C_8 paraffins	6.8
C_6 naphtenes	11.0
C_9 paraffins	2.2
C_5 naphthenes	0.0

TABLE 8

Distribution of Cracked Products in Vapor Phase as a Function of 1-Cyclohexyloctane Conversion on Pt/H-Y

	Conversion (%)			
	32.6	61.6	81.8	91.7
C_6 Fraction				
MeCyC5	72.0	80.0	81.0	81.5
CyC6	28.0	20.0	19.0	18.5
C_7 Fraction				
1,1′-Dimethylcyclopentane	N.D.[b]	N.D.	N.D.	N.D.
1-1-3-Dimethylcyclopentane	5.8	9.7	12.3	13.9
1-*c*-3-Dimethylcyclopentane	9.2	14.3	16.6	15.4
1-*t*-2-Dimethylcyclopentane	5.2	8.6	10.7	12.6
Methylcyclohexane[a]	79.8	62.7	53.6	48.7
Ethylcyclopentane	0.0	4.7	6.8	9.4
C_8 Fraction				
1,1,3-Trimethylcyclopentane	0.0	3.8	3.5	3.1
1-*t*-2-*c*-4-Trimethylcyclopentane	4.6	5.4	5.4	5.1
1-*c*-2-*t*-4-Trimethylcyclopentane	0.0	0.0	0.0	0.2
1,1,2-Trimethylcyclopentane	0.0	0.0	0.2	0.0
1-*c*-2-*c*-4-Trimethylcyclopentane	0.0	1.5	1.5	1.1
1-*c*-2-*c*-3-Trimethylcyclopentane	0.0	0.3	3.5	3.5
1,1-Dimethycyclohexane	0.0	1.2	1.6	3.0
1-*c*-3-Dimethylcyclohexane	4.5	8.4	8.9	10.9
1-*t*-3-Dimethylcyclohexane	5.5	5.4	5.1	3.7
1-*t*-4-Dimethylcyclohexane	23.9	24.1	22.8	24.8
1-*t*-2-Dimethylcyclohexane	7.6	7.1	6.3	3.9
1-*c*-2-Dimethylcyclohexane	17.2	15.2	13.6	11.2
1-Ethyl-2-methylcyclopentane	4.2	3.9	4.1	5.8
iso-Propylcyclopentane	0.0	0.0	0.2	0.1
n-Propylcyclopentane	3.0	2.4	1.4	1.8
Ethylcyclohexane	27.1	18.2	16.3	15.7
Other C_8 naphthenes	0.0	2.9	5.6	6.2

[a] Overlapped with 1-*c*-2-Dimethylcyclopentane.

[b] N.D. not detected.

On the Pt/H-Y catalyst, in contrast to the Pt/ZSM-22, all the β-scission cracking mechanisms are possible, especially the (t,t) β-scission which requires branchings in the α,γ,γ positions with respect to the charged carbon atom. Table 8 shows the distribution of C_6, C_7, and C_8 naphthene cracked products obtained in the vapor phase on the Pt/H-Y catalyst.

Methylcyclopentane is also the main C_6 naphthene formed as it occurred on Pt/H-ZSM-22; however, in Table 8 a higher formation of cyclohexane with respect to that on Pt/H-ZSM-22 at the same conversion level can be observed. Dealkylation reactions starting from secondary or tertiary alkyl carbenium ions lead to this molecule (Fig. 8, Eqs. 5 and 6).

For the C_7 fraction the very high formation of methylcyclohexane is attributed to the more abundant formation of six-membered-ring isomers of 1-cyclohexyloctane and especially the heptylmethyl-cyclohexanes compared to the five-membered-ring isomers (Table 2). By secondary isomerization of methylcyclohexane the formation of ethyl- and dimethylcyclopentanes increases with the conversion. The non-shape-selective character of the Pt/H-Y is evidenced by the higher amount of 1,2-dimethylcyclopentane formed than on Pt/H-ZSM-22 (Tables 5 and 6) where in particular at low conversion this component is not formed. 1,1′-Dimethylcyclopentane which is normally formed on Pt/US-Y, but not on Pt/ZSM-22, was not detected in any of the experiments.

Similar to the behavior observed for the C_7 fraction, cyclohexanes are more abundant than cyclopentanes in the C_8 fraction. Ethylcyclohexane, the monobranched six-membered-ring component in this fraction, is the most important component formed; however, its relative importance decreases with the conversion, which is attributed to secondary isomerization to dimethylcyclohexanes. On the Pt/H-Y catalyst the 1,1′-dimethyl-cyclohexane can be formed (Table 8) which was not produced on Pt/H-ZSM-22.

CONCLUSIONS

The isomerization and hydrocracking reaction pathways of 1-cyclohexyloctane are strongly dependent on the presence of a long paraffin such as dodecane. Cyclopentane and cyclohexane are too large for penetration into the ZSM-22 micropores. In the presence of dodecane fitting much better in the pore, the reactions of the ring are suppressed and the conversions occur preferentially in the long alkyl chain of the naphthene molecule. In the presence of dodecane, 1-cyclohexyloctane undergoes first a ring contraction with side chain elongation, favored by physisorption of the long *n*-alkyl chain in the pore mouth. The nonyl chain undergoes methyl branching with a peculiar selectivity pattern that is imposed by key–lock physisorption. The 1-cyclopentyl-*m*-methyloctanes are sensitive to cracking through β-scission in the chain. In the absence of dodecane, the six-membered ring of 1-cyclohexyloctane can be adsorbed in a pore mouth and undergo methyl branching. Subsequent ring contractions and expansions result in elongation of the short alkyl substituent and shortening of the long one. These isomers lacking methyl branching on the alkyl substituents are much less sensitive to cracking, explaining why in the absence of dodecane, significantly higher isomerization yields were obtained.

ACKNOWLEDGMENTS

J.A.M. acknowledges a Ph.D. fellowship to the Mexican Petroleum Institute. This research has been done as a part of the program Interuniversitaire attractiepolen, funded by the Belgian government, Diensten van de Eerste Minister—Federale diensten voor wetenschappelijke, technische en culturele aangelegenheden.

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