JOURNAL OF CATALYSIS **159,** 323–331 (1996)
ARTICLE NO. 0094

Mechanisms of Heptane Isomerization on Bifunctional Pd/H-Beta Zeolites

E. Blomsma, J. A. Martens, and P. A. Jacobs

Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Leuven, Heverlee, Belgium

Received August 11, 1995; revised November 10, 1995; accepted November 15, 1995

Heptane is isomerized and cracked over Pd/H-Beta zeolite catalysts with different palladium loadings (0.1 to 1.0 wt%). On these catalysts, isoheptanes are formed according to two different reaction routes. The classic reaction mechanism is operative and involves monomolecular reaction steps. A second isomerization pathway exists in which acid catalyzed dimerization of heptene intermediates is followed by cracking into branched C_7 fragments. The contribution of each of the two mechanisms on zeolite Beta is deduced from the formation of specific isoheptanes. It depends on the Pd content and the acidity of the zeolite. The monomolecular mechanism predominates at high Pd loadings, or when the acidity of zeolite H-Beta is partially poisoned with sodium. The bimolecular mechanism is active, especially at low metal loadings of the catalyst. © 1996 Academic Press, Inc.

INTRODUCTION

Bifunctional catalytic processes such as hydrocracking, reforming, isomerization, and catalytic iso-dewaxing play a key role in the refining of oil fractions. In these hydrocarbon upgrading processes, hydrocarbon molecules are cracked and/or isomerized. In particular, boosting the octane number of a gasoline fraction by increasing the degree of branching of the alkanes is an environmentally more acceptable alternative compared to other technologies such as blending with oxygenates and aromatics.

Bifunctional catalysts consist of highly dispersed metals supported on acid zeolites (1). The balance of the hydrogenation–dehydrogenation function and the acidity is crucial as it determines activity, stability, and product selectivity (1, 2).

The conventional reaction mechanism of alkane isomerization and hydrocracking on large-pore bifunctional zeolites is monomolecular (3–8). According to this mechanism, alkanes are dehydrogenated on the metal phase, and the alkenes formed are protonated at the Brønsted acid sites yielding alkylcarbenium ions. After C–C bond rearrangement and eventually scission, isomeric or fragmented alkylcarbenium ions desorb as product alkenes that are hydrogenated at the metal phase to yield the product alkanes (7, 8). Provided the hydrogenation–dehydrogenation activity of the catalyst is sufficient to balance the acidity of the zeolite, the rearrangements of the alkylcarbenium ions become the rate limiting steps of the reaction scheme. The reaction kinetics follow a negative first order in hydrogen because dehydrogenation–hydrogenation steps are equilibrated and the equilibrium concentrations of alkene intermediates decrease with increasing hydrogen pressure.

On zeolite catalysts with strong Brønsted acidity insufficiently balanced by hydrogenation–dehydrogenation activity, bimolecular reactions of the alkene intermediates can be important.

Dimerization cracking mechanisms have been invoked in several studies to explain specific cracked product distributions from C_5–C_7 alkane conversion on bifunctional catalysts (9–15). When heptane is converted on such an unbalanced catalyst, the cracked products have carbon numbers ranging from C_3 to C_6, whereas on well-balanced catalysts, the cracked product spectrum is limited to C_3 and C_4 fragments. The C_5 and C_6 products formed in the former case have been proposed to originate from cracking of C_{14} reaction intermediates (12–15). Dimerization cracking is a well-known reaction of alkenes on acid catalysts (16–21). The contribution of dimerization cracking reactions compared to monomolecular cracking decreases with the chain length of the alkene, as illustrated by Abbot and Wojciechowski (18). On H–ZSM-5 zeolite at 400°C, the contribution of the dimerzation cracking pathway was found to be 100, 81, 13, and 0% for 1-pentene, 1-hexene, 1-heptene, and 1-octene feedstocks, respectively (18).

Platinum promoted sulfated zirconia seems to behave differently from the bifunctional zeolites. It is more active in alkane isomerization, exhibits oligomerization-cracking, and shows a positive kinetic order in hydrogen, suggesting that hydride transfer limits the reaction rate, rather than rearrangements of alkylcarbenium ions (22).

In our previous work on heptane conversion on Pd/H-Beta zeolites (23), it was found that monomolecular as well as bimolecular mechanisms contribute to the formation of C_3–C_6 products and branched heptane isomers. With increasing Pd content, the contribution of bimolecular

0021-9517/96 $18.00

reactions was found to decrease, but could not completely be eliminated.

Except for butane conversion on monofunctional acid catalysts (24–28) and on bifunctional superacid (29), isomerization of *n*-alkanes via the bimolecular mechanism received little attention in literature. In the present work, we studied in detail the bimolecular features of heptane isomerization and identified the catalyst properties favoring its occurrence.

EXPERIMENTAL

Palladium is deposited on zeolite Beta (from PQ corp.; Si/Al = 12.5; H-form) by impregnation (incipient wetness conditions) of an aqueous solution of the tetramine dichloride salt. In this way, catalysts with a palladium loading of 0.10, 0.25, and 1.00 wt% are obtained and denoted as 0.10 Pd/H-Beta, 0.25 Pd/H-Beta, and 1.00 Pd/H-Beta, respectively.

In another catalyst preparation, H-Beta is first transformed into NH_4-Beta by contacting it at room temperature with an aqueous ammonia solution at pH 8. The sample denoted as 1.00 Pd^*/H-Beta was obtained by ion exchange of 3 g of NH_4Beta with 500 ml of an aqueous solution of 5.64×10^{-4} *M* $Pd(NH_3)_4Cl_2$.

Partial poisoning of acid sites on 0.25 Pd/H-Beta was accomplished by impregnation with Na–citrate and calcination at 400°C for 1 h. The amount of Na–citrate added to the zeolite corresponded to 20% of the Al content of the zeolite. The sample is denoted 0.25 Pd/HNa-Beta.

The catalysts were activated by calcination in flowing oxygen followed by reduction in hydrogen at 400°C. Heptane was converted in a fixed bed continuous flow reactor at temperatures ranging from 190 to 250°C, a pressure of 0.3 MPa, and a molar hydrogen/feed ratio of 60. Typically, the space time W/F_0 (W = catalyst weight, F_0 = molar flow rate of heptane at reactor entrance) was adjusted to reach specific conversion levels. Reaction products were analyzed by on-line gas chromatography (HP5890 series II gas chromatograph equipped with a 50 m CPSil5 capillary column (Chrompack) and FID detector).

In all catalytic experiments, the reaction products from heptane conversion have carbon numbers in the C_3 to C_7 range. Methane, ethane, or products heavier than heptane have never been detected. The reaction products from heptane (Hp) conversion are conveniently subdivided into *monobranched isomers* (2-methylhexane (2MHx), 3-methylhexane (3MHx), and 3-ethylpentane (3EP)), *multibranched isomers* (2,2-dimethylpentane (2,2DMP), 2,3-dimethylpentane (2,3DMP), 3,3-dimethylpentane (3,3DMP), 2,4-dimethylpentane (2,4DMP), and 2,2,3-trimethylbutane-(2,2,3TMB)), and *cracked products* (having carbon numbers lower than Hp).

The reaction order in hydrogen in the heptane isomerization reaction was determined by varying the partial pressure of hydrogen (0.1–0.6 MPa) at a heptane partial pressure of 3×10^{-3} MPa.

RESULTS

For the 0.10 Pd/H-Beta, 0.25 Pd/H-Beta, 0.25 Pd/HNa-Beta, and 1.00 Pd^*/H-Beta catalysts, plots of reaction selectivities for monobranching, multibranching, and cracking against heptane conversion are shown in Fig. 1. For heptane conversions between 10 and 50%, the monobranching selectivity decreases and the multibranching and cracking selectivities increase with conversion. The selectivity pattern on the 0.25 Pd/HNa-Beta and 1.00 Pd^*/H-Beta catalysts is quite similar. With the 0.10 Pd/H-Beta and 0.25 Pd/H-Beta catalysts, the selectivity for multibranching and cracking is systematically higher at the expense of the monobranching selectivity.

For the 0.10 Pd/H-Beta, 0.25 Pd/H-Beta, 0.25 Pd/HNa-Beta, and 1.00 Pd^*/H-Beta catalysts, the distribution of the monobranched and multibranched isomerization products from heptane obtained under the reaction conditions of Fig. 1 is plotted against heptane conversion in Fig. 2. Depending on the catalyst, there are significant differences in the isoheptane product distributions. The most abundant isomer among the monobranched heptanes is 2MHx, especially with catalysts 0.10 Pd/H-Beta and 0.25 Pd/H-Beta. On the other two catalysts (0.25 Pd/HNa-Beta and 1.00 Pd^*/H-Beta) the relative importance of 3MHx and 3EP in the monobranched isomer fraction is increased. Among the multibranched heptane isomers, an increase of the Pd load-

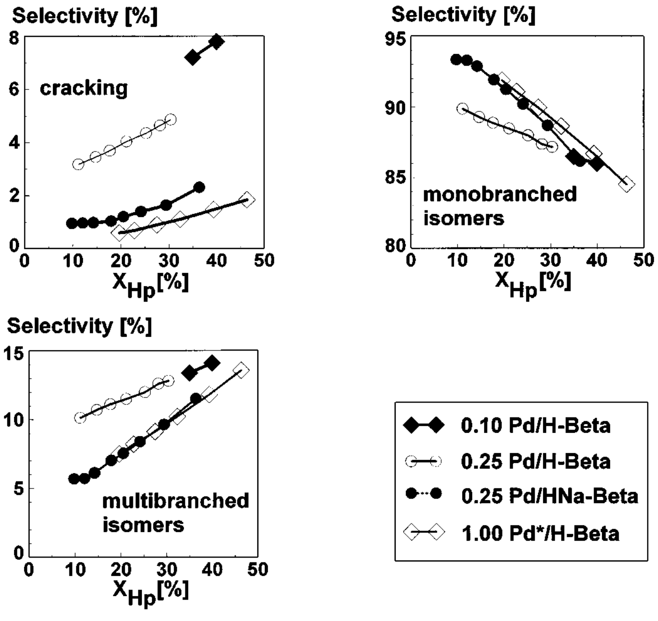

FIG. 1. Reaction selectivity at 216°C for monobranching, multibranching, and cracking against heptane conversion with different Pd/H-Beta catalysts.

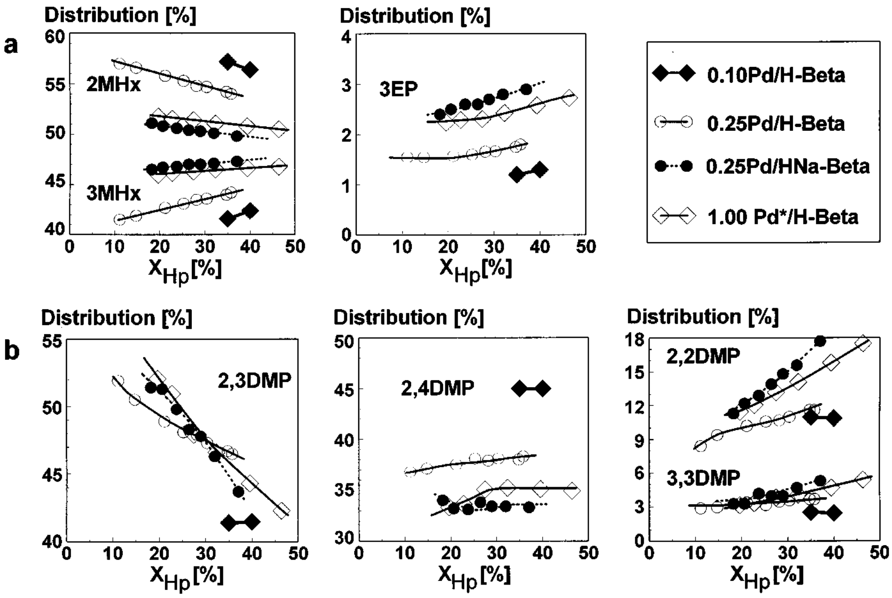

FIG. 2. Distribution of monobranched (a) and dibranched (b) isomers from heptane with different Pd/H-Beta catalysts at 216°C.

ing or poisoning of the acidity (at 0.25 Pd loading) leads to an enhanced formation of gem-dimethylbranched isomers, especially of 2,2DMP, and suppression of the formation of other isomers, especially of 2,4DMP (Fig. 2).

The space time was varied so as to reach 84% heptane conversion at a temperature of 250°C. Under such conditions, the space-time-product-yield, A, increases in the order (Table 1)

$$0.25\ \text{Pd/HNa-Beta} < 0.10\ \text{Pd/H-Beta} < 0.25\ \text{Pd/H-Beta} < 1.00\ \text{Pd/H-Beta} < 1.00\ \text{Pd}^*\text{/H-Beta}. \quad [1]$$

The isomerization selectivity increases in the same order (Table 1).

The kinetic order in hydrogen was −0.5, −0.5 and −0.6 for samples 0.25 Pd/H-Beta, 1.00 Pd*/H-Beta, and 0.25 Pd/HNa-Beta, respectively.

Some differences in the monobranched and dibranched isomer distributions observed at low conversion levels, depending on the catalyst (Fig. 1), persist at 84% feed conversion (Table 1). Increasing the Pd content or poisoning with sodium at 0.25 wt% Pd leads to an enrichment of the monobranched isomer fraction with 3EP, at the expense of 2MHx. The same changes in the catalyst enhance the content of gem-dimethylbranched isomers in the multibranched isomer fraction (Table 1).

On the different catalysts investigated, the cracked products are mainly C_3 and C_4 (Table 1). On the 0.10 Pd/H-Beta and 0.25 Pd/H-Beta catalysts, traces of C_5 and C_6 are also formed. The ratio of isobutane/butane in the reaction products is 65 to 70 for all catalysts (Table 1).

DISCUSSION

Monomolecular Bifunctional Heptane Isomerization and Hydrocracking Mechanisms.

The conventional reaction pathways of alkanes over bifunctional zeolites can be understood based on the mechanisms of rearrangements of alkylcarbenium ions (7, 8). Only those reaction pathways in which the carbon skeleton of the alkylcarbenium ions is changed are relevant here. Since hydride shifts are much faster than C–C bond rearrangements (30), any monomolecular isomerization reaction of an acyclic alkylcarbenium ion formally belongs to one of the following two categories (31, 32):

type A isomerization, which changes the position of a side chain but does not alter the number of primary, secondary, tertiary, and quaternary C atoms in the molecule, or

type B isomerization, which changes the degree of branching and consequently the number of primary, secondary, tertiary, and quaternary C atoms in the molecule.

Type A isomerization proceeds through cyclization of the alkylcarbenium ion into an intermediate corner protonated cyclopropane structure (CPCP) followed by reopening of the cyclopropane ring (Fig. 3) (33).

Type B isomerization typically occurs when prior to the opening of the CPCP intermediate a corner-to-corner proton migration occurs (31). In order for a branching to be generated in a linear carbon chain, the proton jump should involve a displacement of the positive charge toward a corner carbon atom free of alkyl substituents. Since the corner-to-corner proton jump occurs over an important energy barrier, rearrangements of type B are always slower than rearrangements of type A (34). Type B isomerization via

TABLE 1

Detailed Product Selectivities (%) and Distribution of Mono- and Dibranched Isomer Fractions (%, within Brackets) at 84% Heptane Conversion[a]

	0.10 Pd/H-Beta	0.25 Pd/H-Beta	0.25 Pd/HNa-Beta	1.00 Pd/H-Beta	1.00 Pd*/H-Beta
A (mol/h · kg)[b]	23	48	13	53	62
2MHx	23.3 (49.5)	26.4 (48.8)	28.3 (47.7)	29.5 (48.2)	30.1 (48.1)
3MHx	22.8 (48.4)	26.2 (48.4)	28.9 (48.7)	29.5 (48.2)	30.2 (48.2)
3EP	1.0 (2.1)	1.5 (2.8)	2.1 (3.6)	2.2 (3.6)	2.3 (3.7)
2,2DMP	2.2 (16.5)	3.2 (19.4)	5.6 (24.7)	6.5 (27.0)	6.7 (26.8)
3,3DMP	0.7 (5,3)	1.1 (6.7)	2.4 (10.6)	2.8 (11.6)	3.2 (12.8)
2,4DMP	5.1 (38,3)	5.8 (35.2)	6.5 (28.6)	6.8 (28.2)	6.9 (27.6)
2,3DMP	5.3 (39,8)	6.4 (38.8)	8.2 (36.1)	8.0 (33.2)	8.2 (32.8)
2,2,3TMB	0.2	0.3	0.4	0.5	0.4
Total isom.	60.6	70.9	82.4	85.8	88.0
C_1	0.0	0.0	0.0	0.0	0.0
C_2	0.0	0.0	0.0	0.0	0.0
C_3	16.3	12.0	7.4	5.9	5.1
C_4	22.8	17.0	10.0	8.2	6.8
C_5	0.1	0.1	0.1	0.1	0.0
C_6	0.2	0.2	0.1	0.2	0.0
iC_4/nC_4	~70	~70	~65	~70	~65

[a] $T = 250°C$; $P = 0.3$ MPa; $H_2/C_7 = 60$.

[b] Space-time product-yield as $= 100 \times X_{C7}/(W/F_0)$.

substituted protonated cyclobutanes (CPCB) accounts for the formation of an ethyl side chain (35, 36). The conventional reaction mechanism via CPCP and CPCB intermediates can produce all individual heptane isomers (36).

Cracking of alkylcarbenium ions proceeds via β-scission (30). This reaction involves the migration of two electrons of the C–C bond in the β position of the positively charged C atom toward to C–C bond in the α position. Thus, after the scission, this α C–C bond becomes unsaturated, while the carbon atom, originally in the γ position, ends up as the electron-deficient carbon atom of a smaller alkylcarbenium ion. Five modes of β-scission of secondary and tertiary alkylcarbenium ions are possible (37). The distinction between the mechanisms is based on the position of the side chains relative to the charged atom (Fig. 4).

Mechanism A requires three side chains positioned in α, γ, γ relative to the positively charged carbon. $C_7H_{15}^+$ and smaller carbocations are not susceptible to this type

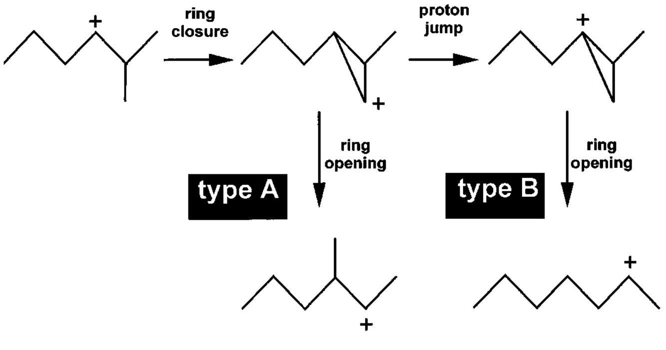

FIG. 3. Monomolecular mechanism of type A and type B isomerization, illustrated with the conversion of 2-methylhept-3-yl cation into 3-methylhept-2-yl cation and 2-heptyl cation.

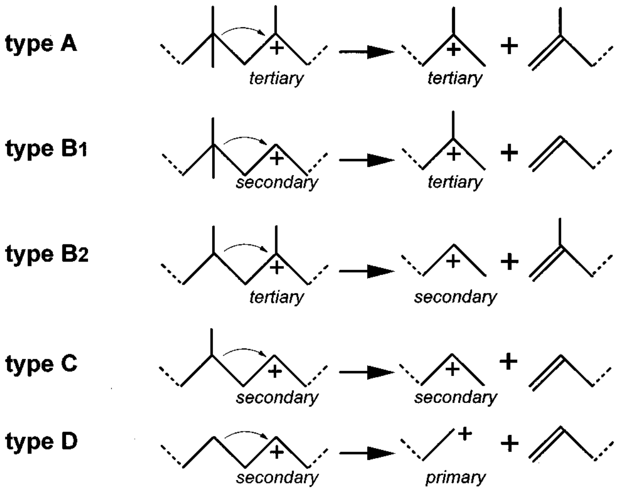

FIG. 4. β-Scission mechanisms of secondary and tertiary alkylcarbenium ions.

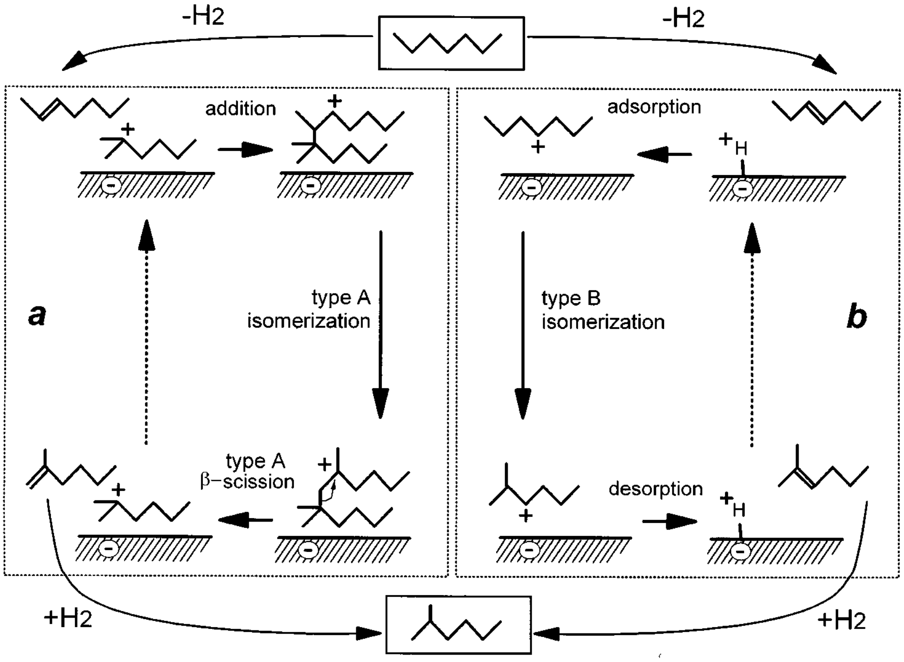

FIG. 5. Bimolecular isomerization (a) against the conventional monomolecular isomerization mechanism (b) of heptane into 2-methylhexane on a bifunctional catalyst.

of cracking. Type B_1 and B_2 scissions, which can operate on $C_7H_{15}^+$ ions, involve secondary and tertiary alkylcarbenium ions, while mechanism C involves secondary ions only. Mechanism D is *a priori* very unlikely because it involves the formation of primary ions.

The relative rates of alkylcarbenium ion isomerization and cracking can be expected to decrease in the order (30, 38).

$$\begin{aligned}&\text{type A } \beta\text{-scission} > \text{type A isomerization}\\ &\quad > \text{type } B_1, B_2\ \beta\text{-scission} = \text{type B isomerization}\\ &\quad\quad > \text{type C } \beta\text{-scission}. \qquad [2]\end{aligned}$$

Bimolecular Bifunctional Isomerization and Hydrocracking Mechanisms of Heptane

An example of heptane isomerization via a mechanism involving dimerization cracking is given in Fig. 5a. The reaction mechanism involves an addition of an alkene to an adsorbed tertiary alkylcarbenium ion, followed by type A isomerization and type A β-scission. After β-scission, the initial tertiary alkylcarbenium ion is regenerated and can enter a new catalytic cycle. The conventional monomolecular isomerization of heptene to 2-methylhexene occurs via type B rearrangement (Fig. 5b). The bimolecular isomerization mechanism involves faster alkylcarbenium ion reactions compared to the monomolecular one. Indeed, type A isomerization and type A β-scission are faster than type B isomerization (sequence 2). It should be taken in consideration however that the dimerization reaction in the bimolecular pathway can be rate determining.

An example of competitive bimolecular reaction pathways leading to C_3–C_6 cracked products and heptane isomers is illustrated in Fig. 6. A molecule of 2MHx and of Hp are converted into a C_{14} intermediate, that rearranges according to the faster alkylcarbenium ion transformations, viz. hydride shift and type A isomerization.

The pathway leading to heptane isomers involves a much faster β-scission than the one leading to cracked products

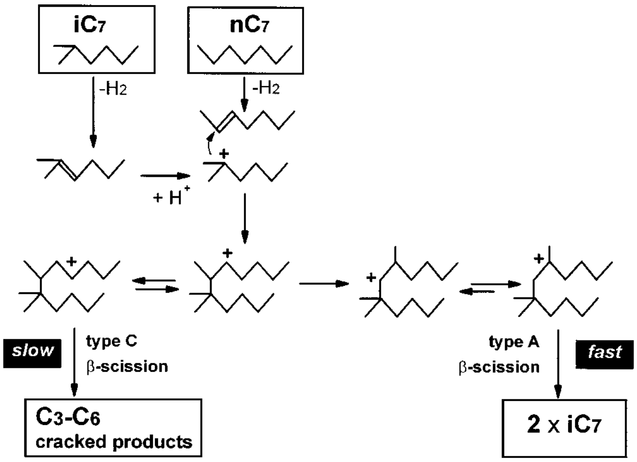

FIG. 6. A typical competition for isomerization and cracking in bimolecular pathways.

(type A versus type C β-scission). An exhaustive inspection of possible bimolecular reaction pathways with tertiary alkylcarbenium ions acting as catalytic site learns that, generally, the isomerization routes involve type A β-scission, while the cracking routes involve the slower types of β-scission. In the reaction schemes of Fig. 5 and Fig. 6, the 2-methylhex-2-yl cation reacts with the heptenes. Reaction can also occur with the 3-methylhex-3-yl cation, inducing the same rearrangement in the partner C_7 entity.

The following rules can be established for bimolecular isomerization:

(i) In order to be susceptible to bimolecular isomerization, the double bond in the alkene must be located between two secondary carbon atoms. Thus, among the heptene isomers, only hept-2-ene, hept-3-ene, 2-methylhept-4-ene, 2-methylhept-3-ene, 3-methylhept-4-ene, and 2,2-dimethylhex-3-ene are susceptible to this type of isomerization.

(ii) The position of the double bond in the alkene determines the position of the branching generated: 2-alkenes are branched at C_2, 3-alkenes at C_3, etc.

(iii) Since bimolecular isomerization proceeds via type A β-scission, isomers with an ethyl- or gem-dimethyl-branching cannot be generated (23, 39). The mono- and dibranched isomers that can be generated by the bimolecular mechanism are 2MHx, 3MHx, 2,3DMP, 2,4DMP, and 2,2,3TMB (Fig. 7).

A salient feature of the bimolecular mechanism is that it selectively generates isomers over cracked products.

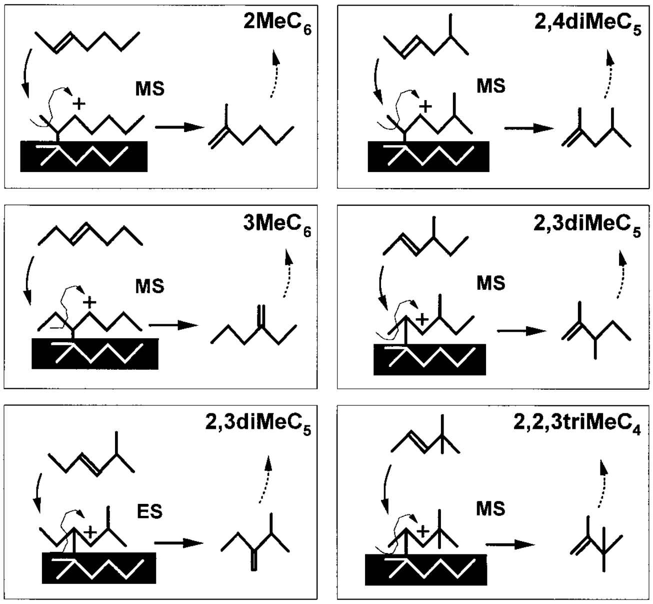

FIG. 7. Branching isomerization reactions of C_7 alkenes via dimerization cracking (MS = Methyl Shift, ES = Ethyl Shift).

Impact of Molecular Shape Selectivity on Bimolecular Reactions

The impact of molecular shape selectivity on the oligomerization of alkenes has received attention for H–ZSM-5 zeolite as catalyst (15, 16). In the conversion of C_2–C_5 alkenes on H–ZSM-5 zeolite, it has been argued that for steric reasons, no reactions can occur in the tubular channel segments, and consequently the formation of a new carbon–carbon bond should occur at the channel intersections (16). Since the two molecules are located in two different channel segments meeting at an intersection, dimerization requires that the reactive centers (a C=C double bond in one molecule and a positively charged carbon atom in the other one) are located near the end of the carbon chains (15). Zeolite Beta has also a tubular intersecting pore structure, the pore diameters being 0.05 to 0.1 nm wider than in ZSM-5. It can be assumed that in zeolite Beta, C–C bond formation during dimerization also takes place preferentially in the channel intersections, and the dimerization reactions involving reactive centers at the end of the carbon chains are favored. This is particularly relevant for the conversion of Hp into 2MHx and 3MHx. The bimolecular mechanism of Hp isomerization into 2MHx involves the formation of a C–C bond with the C_2 carbon position of heptene, while in the pathway leading to 3MHx, the C_3 carbon position is involved (Fig. 7). The C_{14} intermediate involved in 2MHx formation has three methyl side chains. The C_{14} intermediate leading to 3MHx formation is more bulky and contains two methyl and one ethyl side chain. Another significant difference is that the reaction pathway leading to 2MHx involves a methyl shift, whereas the pathway leading to 3MHx involves an ethyl shift in the C_{14} intermediate (Fig. 7). From experiments on the isomerization of C_{10} alkanes in Beta zeolites (39), it is known that the formation of ethylbranchings as well as positional shifts of ethyl side chains are sterically hindered. The more bulky nature of the C_{14} intermediate involved in the formation of 3MHx compared to 2MHx can be appreciated from the molecular models of Fig. 8.

Contribution of Bimolecular and Monomolecular Reaction Mechanisms

Discrimination among the monomolecular and bimolecular mechanism is possible, based on the formation of specific isoheptanes. Thus on catalysts exhibiting the bimolecular isomerization, the formation of 3EP, 2,2DMP, and 3,3DMP is expected to be suppressed. For the series of Beta zeolites studied, the formation of these isomers increases in the order (Fig. 2, Table 1)

$$0.10\ \text{Pd/H-Beta} < 0.25\ \text{Pd/H-Beta} < 0.25\ \text{Pd/HNa-Beta} < 1.00\ \text{Pd/H-Beta} < 1.00\ \text{Pd}^*\text{/H-Beta}. \quad [3]$$

This sequence shows that the bimolecular mechanism can be suppressed by increasing the hydrogenation–

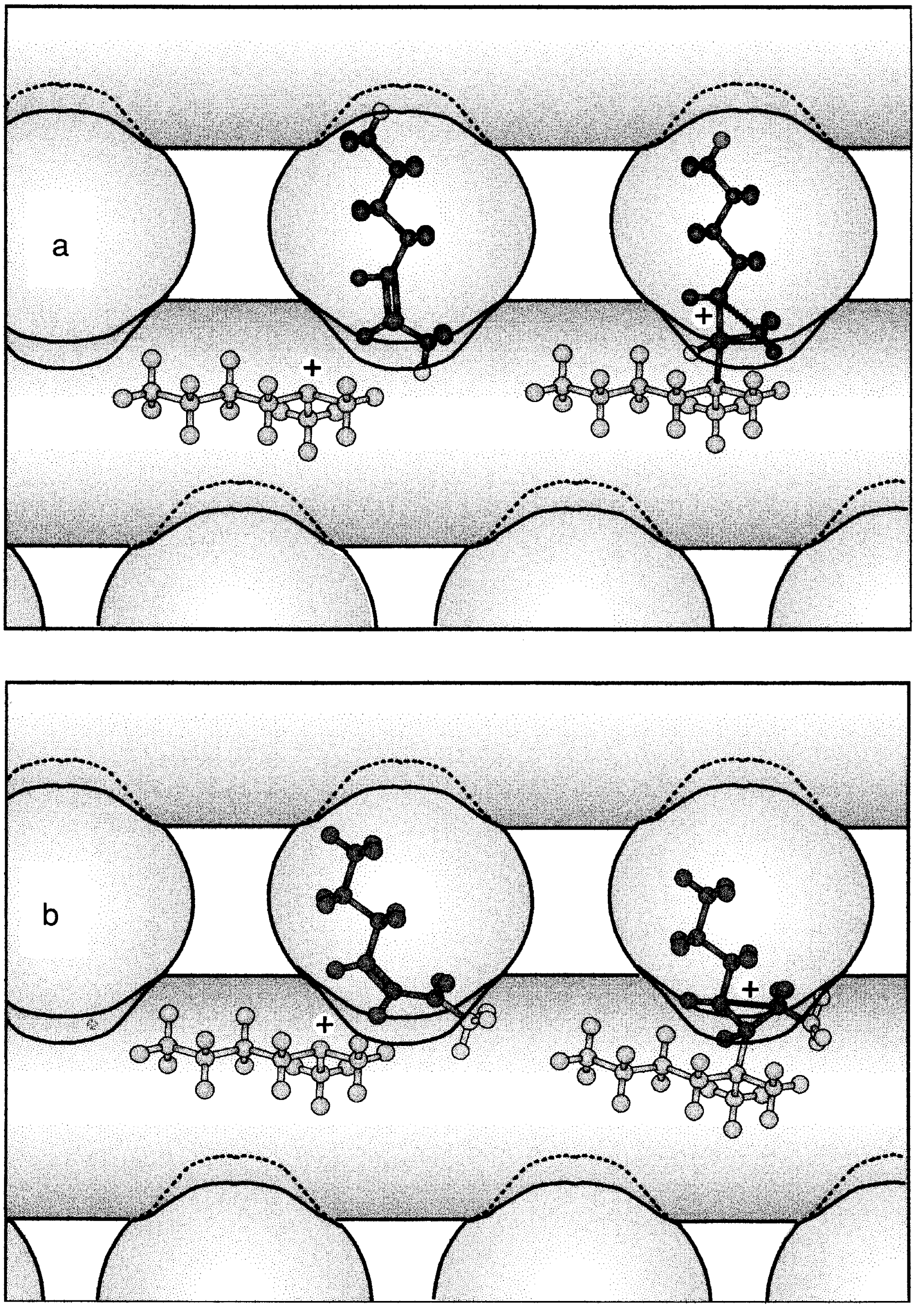

FIG. 8. Addition of hept-2-ene (a) and hept-3-ene (b) to 2-methyl-2-hexyl cation in the pore intersections of zeolite Beta, illustrating schematically enhanced crowding in (b).

dehydrogenation capacity, or alternatively by decreasing the acidity of the catalyst.

Methylbranching of heptane according to the classic bifunctional mechanism, involving CPCP and CPCB intermediates, leads to the formation of an excess of 3MHx with respect to 2MHx, and a small amount of 3EP (Table 2). Literature data on the composition of the isomerization products at low heptane conversion levels on bifunctional faujasite-type zeolites (Pt/HY and Pt/CaY) are in agreement with this conventional mechanism (Table 2). For the Pd/H-Beta catalysts, there are significant deviations, since 2MHx is now the most abundant isomer (Table 2). The deviation is more pronounced with 0.25 Pd/H-Beta than with 1.00 Pd*/H-Beta. The preferential formation of 2MHx in Beta zeolites is therefore ascribed to the occurrence of bimolecular reactions in a shape selective environment (Fig. 8).

The formation of multibranched isomers on the different zeolite Beta catalyst is in agreement with the occur-

TABLE 2

Distribution of Monobranched Isomers Obtained from Heptane over Bifunctional Faujasites (1.0 wt% Pt/USY and 0.5 wt% Pt/CaY) and Bifunctional Beta Zeolites (0.25 Pd/H-Beta and 1.00 Pd*/H-Beta) below 5% Conversion and Prediction According to the Monomolecular Branching Mechanism via CPCP and CPCB Intermediates

	Predicted (36)	Pt/USY (36)	Pt/CaY (4)	0.25 Pd/H-Beta	1.00 Pd*/H-Beta
2MHx	40.0	42.2	44.6	57.0	53.2
3MHx	56.6	53.5	52.3	41.6	45.0
3EP	3.4	3.4	3.1	1.4	1.9

rence of monomolecular and bimolecular mechanisms, depending on the Pd loading and acidity poisoning. Among the dibranched isomers, only 2,3DMP and 2,4DMP can be formed via the dimerization cracking pathway (Fig. 7). The 2-methylhex-4-ene molecule (leading to 2,4DMP) has a more favorable double bond position to allow dimerization in the pore structure of zeolite Beta, compared to the 3-methylhex-2-ene molecule (leading to 2,3DMP) since it leads to a less crowded C_{14} intermediate (Fig. 7). It is expected that a high dimerization cracking activity of the catalyst will lead to an enrichment of 2,4DMP compared to 2,3DMP in the fraction of the multibranched isomers, which is confirmed by the experimental data (Table 1, Fig. 2).

The formation of 2,2,3TMB via the bimolecular isomerization pathway is unlikely since the C_{14} intermediate required is very bulky (five methyl branchings on four adjacent C atoms). Furthermore, its formation starts from 2,2-dimethylhex-3-ene, an isomer with gem-dimethylbranching that can only be obtained via the conventional monomolecular reaction mechanism.

The zeolite 1.00 Pd*/H-Beta has the lowest contribution of bimolecular reactions as judged from the composition of isoheptanes (Table 1). The significant difference in the distribution of monobranched isomers on this catalyst and the bifunctional faujasites (Table 2) suggests that bimolecular reactions remain important. On 1.00 Pd*/H-Beta, all cracked products are formed through the monomolecular mechanisms, as C_5 and C_6 products are not formed. It confirms that bimolecular reactions leading to cracked products are much slower compared to bimolecular reactions leading to isomers, as suggested by the mechanistic considerations (Fig. 6).

The reaction order in hydrogen of -0.5 on the 1.00 Pd*/H-Beta catalyst is another indication that the conventional monomolecular mechanism is not followed. The bifunctional Beta zeolites show catalytic behavior that is intermediate between that of bifunctional faujasites (hydrogen kinetic order of -1) and that of platinum promoted sulfated zirconia (hydrogen kinetic order of $+1$), on which there is evidence for the occurrence of bimolecular reactions (22).

Partial poisoning of the acidity of the 0.25 Pd/H-Beta catalyst with sodium leads to a more negative reaction order in hydrogen (-0.6 instead of -0.5). The suppression of the bimolecular mechanism by poisoning of the acidity is also apparent from the product distribution (Table 1, Fig. 2).

The relative contribution of a bimolecular mechanism is expected to be dependent on reaction conditions as temperature, pressure, and conversion level, as well as on the carbon number of the alkane feed. Research is in progress to rationalize the impact of those reaction parameters.

CONCLUSION

Heptane conversion on zeolite Beta catalysts promoted with palladium occurs through a combination of monomolecular and bimolecular mechanisms. An important feature of the bimolecular reaction mechanism is that it generates in a selective manner isomers. The bimolecular mechanism of isomerization can be an energetically advantageous pathway favoring 2-methylbranching and involves fast alkylcarbenium ion rearrangements. The bimolecular mechanism abundantly produces 2MHx, 3MHx, 2,3DMP, and 2,4DMP, while the conventional monomolecular mechanism can produce all individual heptane isomers, including gem-dimethylbranched and ethylbranched isomers. In the bimolecular reaction mechanism, an enhanced selectivity toward 2MHx can be explained by transition state shape selectivity on the formation of C_{14} intermediates in the micropore intersections of zeolite Beta. Partial poisoning of the acidity of zeolite Beta by introducing sodium leads to smaller contribution of the bimolecular reaction route. The kinetic order in hydrogen for heptane isomerization on Pd/H-Beta catalysts is -0.5, which is located between that expected for the conventional bifunctional mechanism of bifunctional faujasite zeolites (-1) and that on platinum promoted sulfated zirconia ($+1$). This intermediate behavior probably reflects the intermediate acidity of zeolite Beta between faujasite zeolites and sulfated zirconia.

ACKNOWLEDGMENTS

This work is part of the Ph.D. of E.B., sponsored by Shell Research BV. J.A.M. acknowledges the flemish NFWO for a position as Senior Research Associate. A research grant from the Belgian Government within the frame of the IUAP is highly appreciated.

REFERENCES

1. Ward, J. W., *Stud. Surf. Sci. Catal.* **16**, 587 (1983).
2. Maxwell, I. E., and Stork, W. H. J., *Stud. Surf. Sci. Catal.* **58**, 571 (1991).
3. Weitkamp, J., *in* "Hydrocracking and Hydrotreating," (J. W. Waid and G. A. Quader, Eds.), ACS Symp. Ser. Vol. 20, p. l. Am. Chem. Soc., Washington, DC, 1975.
4. Weitkamp, J., *Ind. Eng. Chem. Prod. Res. Dev.* **21**, 550 (1982).
5. Vansina, H., Baltanas, M. A., and Froment, G., *Ind. Eng. Chem. Prod. Res. Dev.* **22**, 526 (1983).
6. Steijns, M., Froment, G., Jacobs, P., Uytterhoeven, J., and Weitkamp, J., *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 654 (1981).
7. Weisz, P. B., *Adv. Catal.* **13**, 137 (1962).
8. Coonradt, M. L., and Garwood, W. E., *Ind. Eng. Chem. Prod. Res. Dev.* **3**, 38 (1964).
9. Burnett, R. L., and Hughes, T. R., *J. Catal.* **31**, 55 (1973).
10. Abbot, J., and Wojciechowski, B. W., *Can. J. Chem. Eng.* **66**, 825 (1988).
11. Corma, A., and Wojciechowski, B. W., *in* "Symposium on Advances in Catalytic Cracking" Div. Petr. Chem., Washington, D. C. Meeting, p. 861. Am. Chem. Soc., New York, 1983.
12. Lopéz Agudo, A., Asensio, A., and Corma, A., *J. Catal.* **69**, 274 (1981).
13. Giannetto, G., Perot, G., and Guisnet, M., *Stud. Surf. Sci. Catal.* **20**, 265 (1984).
14. Leglise, J., Chambellan, A., and Cornet, D., *Appl. Catal.* **69**, 15 (1991).
15. Smirniotis, P. G., and Ruckenstein, E., *J. Catal.* **140**, 526 (1993).
16. Dejaifve, P., Véndrine, J. C., Bolis, V., and Derouane, E. G., *J. Catal.* **63**, 331 (1980).
17. Abbot, J., Corma, A., and Wojciechowski, W., *J. Catal.* **92**, 398 (1985).
18. Abbot, J., and Wojciechowski, B. W., *Can. J. Chem. Eng.* **63**, 278, 451, 462 (1985).
19. Quann, R. J., Green, L. A., Tabak, S. A., and Krambeck, F. J., *Ind. Eng. Chem. Res.* **27**, 565 (1988).
20. Kissin, Y. V., *J. Catal.* **146**, 358 (1994).
21. Knifton, J. F., Sanderson, J. R., and Dai, P. E., *Catal. Lett.* **28**, 223 (1994).
22. Iglesia, E., Soled, S. L., and Kramer, G. M., *J. Catal.* **144**, 238 (1993).
23. Blomsma, E., Martens, J. A. and Jacobs, P. A., *J. Catal.* **155**, 141 (1995).
24. Bearez, C., Chevalier, F., and Guisnet, M., *React. Kinet. Catal. Lett.* **22**, 405 (1983).
25. Corma, A., Juan-Rajadell, M. I., López-Nieto, J. M., Martinez, A., and Martínez, C., *Appl. Catal. A* **111**, 175 (1994).
26. Adeeva, V., Lei, G. D., and Sachtler, W. M. H., *Appl. Catal. A* **118**, L11 (1994).
27. Yaluris, G., Rekokske, J. E., Aparicio, L. M., Madon, R. J., and Dumesic, J. A., *J. Catal.* **153**, 54 (1995).
28. Flora, T. T., and Horvát, N., *Appl. Catal. A* **123**, L197 (1995).
29. Garin, F., Seyfried, L., Girard, P., Maire, G., Abdulsamad, A., and Sommer, J., *J. Catal.* **151**, 26 (1995).
30. Brouwer, D. M., *in* "Nato Adv. Stud. Inst. Ser. E" (R. Prins and G. C. A. Schuit, Eds.), Vol. 39, p. 137. 1980.
31. Weitkamp, J., and Farag, H., *Acta Phys. Chem., Szeged* **2**, 327 (1978).
32. Brouwer, D. M., and Oelderik, J. M., *Recl. Trav. Chim. Pays-Bas* **87**, 721 (1968).
33. Chevalier, F., Guisnet, M., and Maurel, R., *in* "Proceedings 6th International Congress on Catalysis, London 1976" (G. C. Bond, P. B. Wells, and F. C. Tomkins, Eds.), p. 478. The Chemical Society, London, 1977.
34. Saunders, M., and Budiansky, S. P., *Tetrahedron* **35**, 929 (1979).
35. Martens, J. A., and Jacobs, P. A., *J. Catal.* **124**, 357 (1990).
36. Martens, J. A., and Jacobs, P. A., *in* "Theoretical Aspects of Heterogeneous Catalysis" (J. B. Moffat, Ed.), p. 52. Van Nostrand–Reindhold, New York, 1990.
37. Weitkamp, J., Jacobs, P. A., and Martens, J. A., *Appl. Catal.* **8**, 123 (1983).
38. Martens, J. A., Jacobs, P. A., and Weitkamp, J., *Appl. Catal.* **20**, 283 (1986).
39. Martens, J. A., Jacobs, P. A., and Weitkamp, J., *Appl. Catal.* **20**, 239 (1986).