JOURNAL OF CATALYSIS **174,** 177–184 (1998)
ARTICLE NO. CA971959

Hydrocracking of Isoheptadecanes on Pt/H−ZSM-22: An Example of Pore Mouth Catalysis

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Received July 21, 1997; revised October 13, 1997; accepted October 13, 1997

The isomerization hydrocracking of heptadecane on Pt/H−ZSM-22 was studied in a continuous flow type, fixed-bed, vapor-phase reactor. High yields of skeletal isomerization of heptadecane (90%) were obtained. The low tendency to cracking of isoheptadecane skeletal isomers on the ZSM-22 zeolite is explained by the limited penetration of these molecules into the micropores openings of the zeolite, preventing their cracking via the common β-scission reaction mechanisms. The reaction mechanisms of hydrocracking in pore mouths can be derived from the experimentally obtained cracking patterns. © 1998 Academic Press

INTRODUCTION

Petroleum fractions contain significant amounts of *n*-alkanes. Skeletal isomerization of *n*-alkanes is applied for improving the octane number of gasoline fractions, the low-temperature properties of jet and diesel fuels, and for the synthesis of lubricants (1). Branching isomerization of *n*-alkanes can be achieved with bifunctional heterogeneous catalysis, using noble metal containing acid zeolite catalysts working in hydrogen atmosphere (2). For instance, platinum on mordenite is used to isomerize C_5/C_6 alkane streams to boost the octane number (3).

The hydrocracking behavior of an alkane depends primarily on the degree of branching of the carbon skeleton and on the relative positions of the branchings along the main carbon chain (4, 5). The degree of branching of a carbon skeleton is obtained when considering that each tertiary and quaternary carbon atom introduces one and two branchings, respectively. In a discussion of skeletal isomerization of an *n*-alkane, it is convenient to distinguish monobranched from multibranched skeletal isomers, the latter having two or more branchings in their carbon skeleton.

In bifunctional conversions of alkanes, alkylcarbenium ions occur as reaction intermediates (4). Alkylcarbenium ions derived from multibranched isoalkanes crack according to energetically favorable β-scission pathways not available to their monobranched or linear skeletal isomers (4). It explains why it is difficult to prevent cracking in the isomerization of *n*-alkanes (2).

On traditional hydrocracking catalysts such as bifunctional faujasite zeolites, the maximum yield of multibranched isomers that can be reached from *n*-alkanes in the range from heptane (*n*-C_7) to heptadecane (*n*-C_{17}) does not exceed 30% (5). It has been demonstrated that on bifunctional faujasites, the yield of isomers from long *n*-alkanes varies in a unique way with conversion, not depending on the reaction conditions (temperature, pressure, space time) (6). The independence of the isomer yield curves on temperature implies that differences in activation energy of isomerization and cracking are small (7).

High yields of multibranched *i*-C_{17} exceeding 60% have been obtained by isomerization of *n*-C_{17} using Pt/H−ZSM-22 zeolite catalyst (8). ZSM-22 is a high-silica zeolite having the TON topology (9). It belongs to the family of so-called 10-ring zeolites (having micropores with windows circumscribed by 10 oxygen atoms) and has the narrowest channels in this group of zeolites (9). ZSM-22 contains parallel tubular pores with an almost uniform cross section of ca. 0.45×0.55 nm (9). The 10-MR pores are undulated and slightly sinusoidal. The crystallographic repeat distance in the channel direction is 0.5 nm.

Based on a detailed analysis of the *i*-C_{17} products obtained on Pt/H−ZSM-22, a mechanism of skeletal isomerization could be proposed (8, 10). The catalytic conversion of alkanes on Pt/H−ZSM-22 does not involve diffusional transportation through the micropores. Skeletal isomerization occurs on molecules adsorbed in pore mouths and on the external surfaces of the zeolite crystals. In the monobranching reaction of *n*-alkanes, only part of the molecule penetrates into a micropore opening. The skeletal

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0021-9517/98 $25.00

rearrangement takes place in the pore mouth where there is less steric hindrance (pore mouth catalysis). Further branchings in the carbon skeleton are introduced when the monobranched molecule is stretched across the external crystal surface. With the first branching pinned into one pore mouth, additional branchings are generated at positions where the carbon chain faces neighboring pore mouths (key-lock concept).

In the present work, we have investigated the hydrocracking mechanisms of *i*-C_{17} molecules on the Pt/H−ZSM-22 catalyst. The cracked products have been analyzed in detail and compared with the cracked products obtained on a reference faujasite catalyst, containing much wider pores and sterically much less obstructed active sites (11).

EXPERIMENTAL

A sample of ZSM-22 (Si/Al = 30) with needle-like crystal morphology (average crystal dimensions of 0.1 × 0.1 × 1.0–4.0 μm) was synthesized according to Ref. (12). As-synthesized ZSM-22 was calcined in flowing oxygen at 823 K, ion exchanged with NH_4^+ under reflux conditions in the presence of a 200-fold molar excess of NH_4Cl with respect to the C.E.C, washed until the chloride test of the wash water with $AgNO_3$ was negative, dried at 333 K, and impregnated with aqueous solution of $Pt(NH_3)_4Cl_2$ according to the incipient wetness technique. The Pt loading was 0.5 wt%. The Y zeolite has a Si/Al ratio of 2.8 and was obtained by gentle dealumination of NH_4, NaY as explained in previous work (13). Zeolite Y was converted into its NH_4^+ form by ion exchange under reflux conditions in presence of a 30-fold molar excess of NH_4Cl with respect to the C.E.C. Zeolite Y was loaded with 0.5 wt% of platinum by ion exchange with aqueous $Pt(NH_3)_4Cl_2$ solution at room temperature. The zeolite powders were compressed into tablets, crushed, and sieved to obtain catalyst particles with diameters comprised between 0.25 and 0.50 mm. The weight of dry catalyst (W) was 200 mg.

The catalytic experiments were conducted in a tubular downflow reactor with an internal diameter of 1 cm. The catalysts were activated *in situ* in the reactor by a calcination under flowing oxygen at 673 K, followed by a reduction under flowing hydrogen at the same temperature. The *n*-C_{17} and hydrogen partial pressures at the entrance of the reactor were 900 Pa and 350 kPa, respectively. The conversion of the feed was changed by stepwise varying the reaction temperature at a constant space time, W/F_0 equal to 0.5 h kg mol^{-1}. After a change in reaction temperature, the reactor was allowed to equilibrate during at least 1 h before product sampling. The catalysts did not deactivate under the reaction conditions applied. The reaction products were analyzed on-line with a high-resolution gas chromatograph, equipped with a capillary CPSil-5 column from Chrompack (internal diameter of 0.31 mm, length of 50 m) and flame ionization detector. The elution from the column of monobranched and multibranched *i*-C_{17} isomers as separate groups was achieved by applying temperature programming between 303 and 523 K.

The yield of a cracked product fraction with carbon number i, Y_{C_i}, expressed as moles per 100 mol of feed cracked, is obtained from

$$Y_{C_i} = \frac{\frac{1}{MW_i}\sum_{j=1}^{n_i} A_{ij}}{\frac{1}{MW_f}\sum_{i=1}^{(f-1)}\sum_{j=1}^{n_i} A_{ij}} \times 100,$$

in which A_{ij} represents the peak area in the chromatogram of reaction product j, with carbon number i, n_i the number of products with carbon number i, and MW, the molecular weight. The subscript f refers to the feed.

RESULTS AND DISCUSSION

Yields of monobranched *i*-C_{17}, multibranched *i*-C_{17} and cracked products obtained at increasing reaction temperatures on the reference Pt/H−Y catalyst and on Pt/H−ZSM-22 are shown in Figs. 1A and 1B, respectively. On the two zeolites, monobranching, multibranching, and cracking are consecutive reactions.

The bifunctional conversion pathways of long *n*-alkanes can be rationalized based on a mechanism considering alkylcarbenium ions as key reaction intermediates (7, 14–16). These alkylcarbenium ions are generated by dehydrogenation of the alkane on the metal sites and addition of protons of the zeolite. The metal and acid function are said to be well balanced, when the rearrangements of the alkylcarbenium ions are rate limiting (17). Rearranged and cracked alkylcarbenium ions are deprotonated and hydrogenated on the metal function to give saturated reaction products.

The isomerization and cracking network of $C_{17}H_{35}^+$ cations relevant to the present work is explained in Fig. 2. The branching occurs via a mechanism involving substituted protonated cycloalkanes (18). It generates side chains at any carbon atom positions. The degree of branching increases with one unit at the time (6).

Hydrocracking involves the β-scission of alkylcarbenium ions (19). In a β-scission, two electrons of a β carbon–carbon bond are transferred toward the positively charged α carbon atom to form an olefin and a smaller alkylcarbenium ion, charged at the γ carbon atom of the parent ion. The rival β-scission modes that exist, depending on the nature of the parent ion, are explained in Fig. 3. β-Scission is extremely rapid for specific tribranched ions for which both the starting and product ions are tertiary ions (type A). Other β-scission modes can operate also

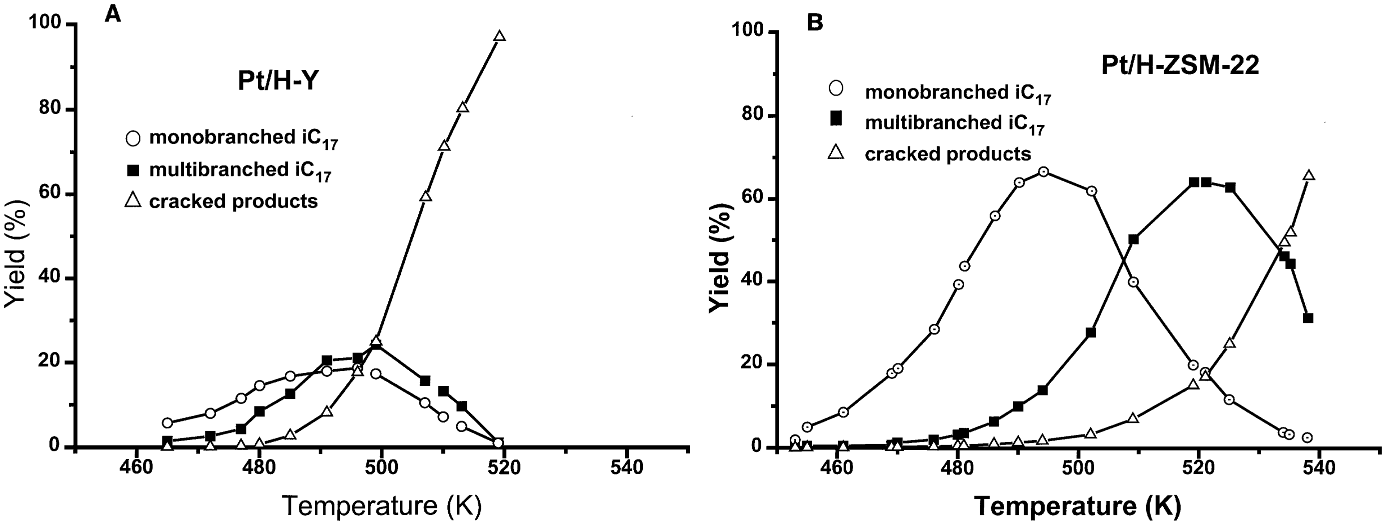


FIG. 1. Yield of mono- and multibranched i-C_{17} and cracked products from n-C_{17} against reaction temperature on (A) Pt/H–Y, and (B) Pt/H–ZSM-22.

on dibranched (B_1 and B_2) and monobranched ions (C), which involve secondary ions and are much slower. The rate of β-scission decreases in the order $A \gg B_1 = B_2 > C$ (19, 20). Type A hydrocracking generates branched fragments with four and more carbon atoms, whereas the B and C type mechanisms yield propane and larger linear and branched fragments. Carbocations with charge and side chain positions suitable for β-scission constitute only a fraction of the total number of isomers. The position of the positive charge and the side chains can be changed via hydride and alkyl shifts, respectively. Many multibranched alkylcarbenium ions can crack according to more than one mode.

On faujasite type zeolites, type A hydrocracking predominates. Its contribution to the total yield of cracked products exceeds 70% (21). Well-balanced catalysts exhibit a high selectivity for isomerization up to medium levels of conversion (22). The formation of the third branching is rapidly followed by cracking.

The yields of monobranched and multibranched i-C_{17} and cracked products obtained in the experiments of Fig. 1 have been plotted against the n-C_{17} conversion in Fig. 4. On Pt/H–Y, the maximum yield of isomers in total (amounting to 49%) is reached at 62% n-C_{17} conversion (Fig. 4A). The maximum yield of monobranched and multibranched i-C_{17} obtained is ca. 21 and 28%, respectively (Fig. 4A). Multibranching is rapidly followed by hydrocracking (Fig. 1A), which is in agreement with the bifunctional mechanism.

Up to 95% of n-C_{17} conversion, Pt/H–ZSM-22 forms large amounts of monobranched i-C_{17} (Fig. 4B). Multibranched isomers become the main product fraction at conversion levels from 95 to 99% (Fig. 4B). Their yield reaches a maximum of 64 at 99% conversion (Fig. 4B). On Pt/H–ZSM-22, cracking starts occurring at an n-C_{17} conversion of 90%. Even at 99% feed conversion, the cracking yield is limited and amounting to 18% only. In comparison to the Pt/H–Y zeolite, on Pt/H–ZSM-22 much higher reaction severities are necessary to crack the i-C_{17} molecules (Fig. 1).

The yields of cracked product fractions distributed according to the carbon numbers at a cracking yield of 25% are depicted in Fig. 5. On Pt/H–Y, the most abundant cracked products have carbon numbers within the range from C_4 to C_{13}, as expected for a cracking through β-scission of alkylcarbenium ions with tribranched carbon skeletons (4, 5). On Pt/H–ZSM-22 the yield distribution is somewhat skewed toward the lighter components.

The content of branched fragments in the individual cracked product fractions obtained at different cracking yields on Pt/H–Y and Pt/H–ZSM-22 has been plotted in Fig. 6. On Pt/H–Y, branched molecules predominate in each carbon number fraction, confirming a large contribution of type A hydrocracking of multibranched isomers. On Pt/H–ZSM-22, linear fragments predominate in the light cracked product fractions (Fig. 6), suggesting that cracking occurs according to B_1, B_2, and C type mechanisms. The content of branched isomers in the cracked product fractions increases with increasing carbon number of the fraction.

The key feature of the ZSM-22 zeolite is the limited penetration of branched molecules into this zeolite (8, 10). The penetration of an isoalkane molecule into a pore of ZSM- 22 gets stuck when the first branching in the carbon chain hits the window. Likewise, the alkylcarbenium ions with branched carbon skeletons occurring as reaction intermediates should be located partly inside and partly outside

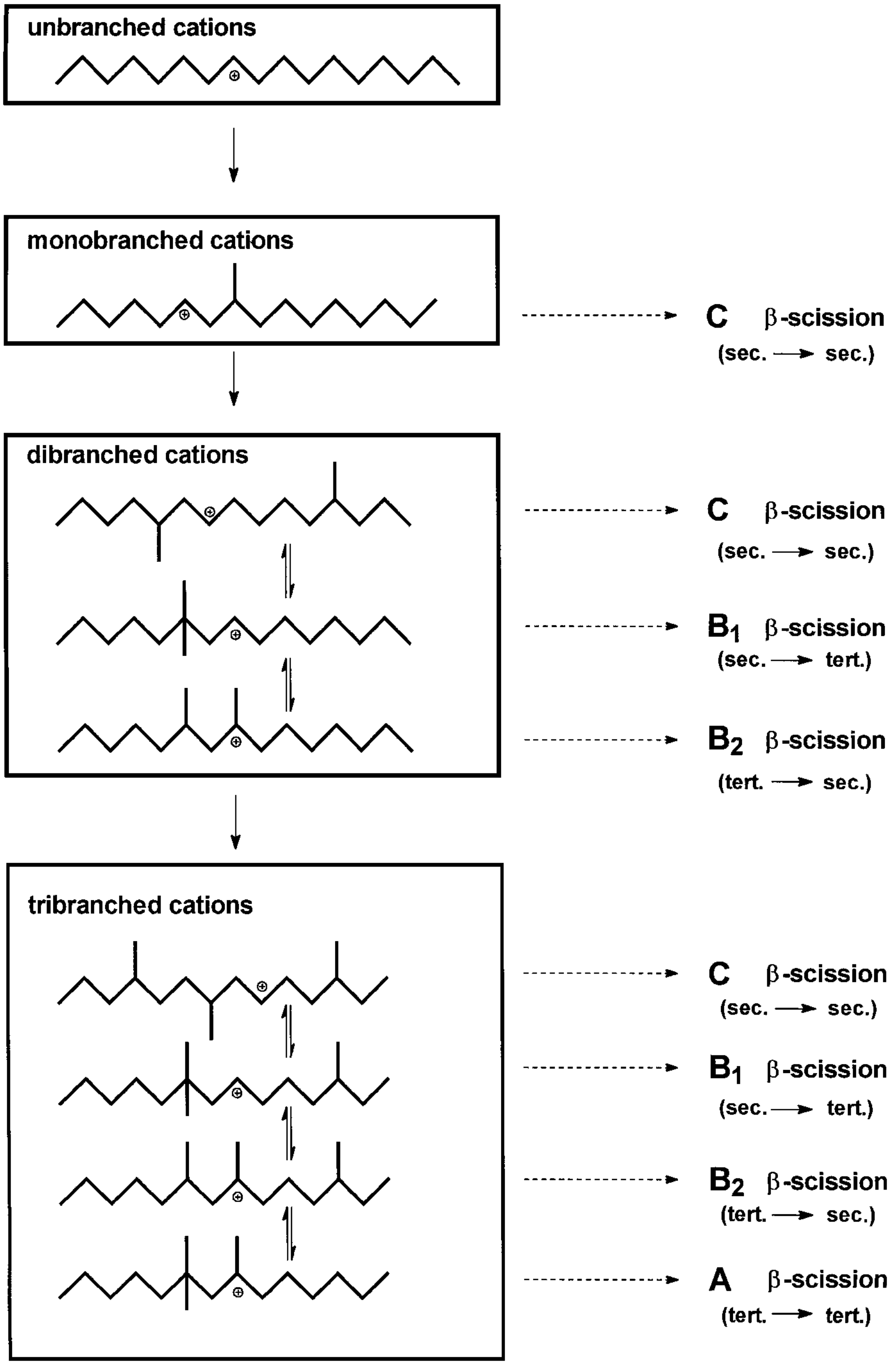
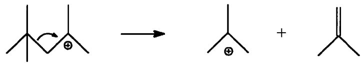
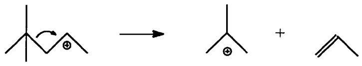
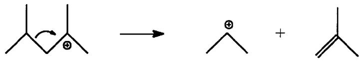
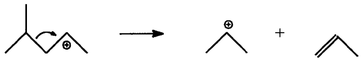


FIG. 2. Isomerization and β-scission reaction network of $C_{17}H_{35}^{+}$ alkylcarbenium ions.

the micropore. Alkylcarbenium ions in zeolites are to be regarded as short-lived, highly energetic, positively charged species that are stabilized by interaction with basic oxygens in the zeolite lattice (23, 24). It can be expected that alkylcarbenium ions in ZSM-22 are most stable when the positively charged carbon atom is located inside the micropore, where electric fields and electric field gradients are largest. Assuming that the stabilization of alkylcarbenium ions with positively charged carbons interacting with the external surface of the zeolite crystals is less effective, the suppressed cracking of i-C_{17} isomers on Pt/H–ZSM-22 can be explained as follows.

Specific types of β-scission reactions are unfavorable (Fig. 7). Mechanisms A and B_2 are hampered on ZSM-22,

Mode	**β-scission reaction**	**ions involved**[a]	**requirements for parent ion**			**yield of branched products (%)**
			minimum size	minimum branching	branching positions	
A		tert. → tert.	$C_8H^+_{17}$	tribranched	α,γ,γ	**100**
B₁		sec. → tert.	$C_7H^+_{15}$	dibranched	γ,γ	**50**
B₂		tert. → sec.	$C_7H^+_{15}$	dibranched	α,γ	**50**
C		sec. → sec.	$C_6H^+_{13}$	monobranched	γ	**0**

a, tert. = tertiary, sec. = secondary

FIG. 3. Notations and characteristic features of the β-scission modes of acyclic alkylcarbenium ions (from Refs. (19) and (20)).

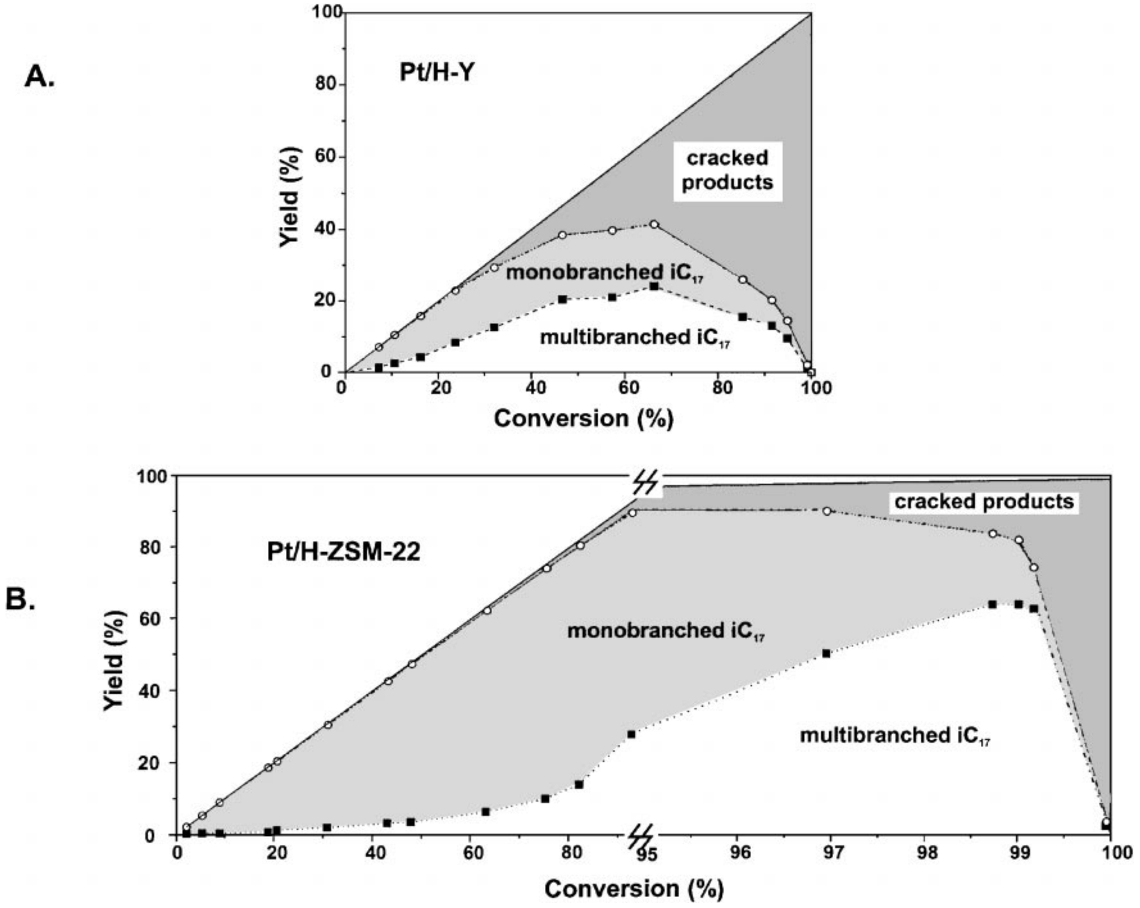


FIG. 4. Composition of the reaction products (wt%) lumped as monobranched and multibranched i-C_{17}, cracked products, and unconverted feed against n-C_{17} conversion on (A) Pt/H−Y and (B) Pt/H−ZSM-22 (experiment of Fig. 3).

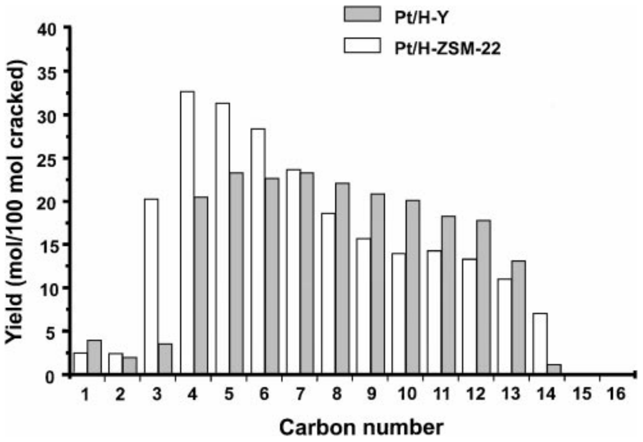


FIG. 5. Yield of cracked product fractions per carbon number at 25% cracking yield of $n\text{-C}_{17}$ on Pt/H−Y and Pt/H−ZSM-22.

as the positively charged carbon in the cation fragment that is obtained after the scission is unavoidably at a position outside the micropore. Mechanisms B_1 and C appear to be the most likely mechanisms for β-scission on Pt/H−ZSM-22, as parent and product alkylcarbenium ions can interact favorably with the micropore walls (Fig. 7). The skeletal multibranching mechanism of long alkanes on ZSM-22 favors the formation of dibranched $i\text{-C}_{17}$ molecules in which two tertiary carbons are separated by several methylene carbons along the main chain and disfavors the formation of isomers with vicinal and geminal branching positions (8). Consequently, the favored isomers are susceptible to type C hydrocracking only, and mechanism C is expected to be the main cracking pathway. In addition to this, the proposed pore mouth catalysis model limits considerably the number of possible type C β-scissions (Fig. 7). For instance, the model precludes the occurrence of β-scissions of alkylcarbenium ions in which the positively charged carbon atom is located in the main chain between two tertiary carbon atoms, since there exists no sorption mode (pore mouth or key-lock) according to which this part of the molecule is accommodated inside a micropore. A further requirement for a cation to be susceptible to β-scission via the C mode is the presence of an n-alkyl substituent on a tertiary carbon atom counting at least three carbon atoms (Fig. 2). This constitutes a further limitation of the number of cracking modes of the favored dibranched $i\text{-C}_{17}$ isomers, in which one of the tertiary carbons has two methyl and one $i\text{-C}_{14}$ substituents. Thus, this model of selective β-scissions in pore mouths provides a rationale for the slow cracking of multibranched $i\text{-C}_{17}$ molecules on ZSM-22 and for the high skeletal isomerization yields.

The content of branched isomers in the different carbon number fractions of cracked products provides additional evidence for the proposed model (Fig. 6). Type C cracking does not yield $i\text{-C}_4$ (4). The C_4 fraction obtained on Pt/H−ZSM-22 is particularly rich in $n\text{-C}_4$ (Fig. 5). The small amount of isobutane in the cracked products must originate from the less favorable B_2 or A types of cracking and most likely from B_1 type of scissions of 2,2-dimethylpentadec-4-yl cations (Fig. 8a). In the fragmentations yielding C_5 and C_{12} fractions, there is only one dibranched cation (2,3-dimethylheptadec-5-yl cation) that yield $i\text{-C}_5$ and $n\text{-C}_{12}$ fragments according to type C cracking, while many isomers yield $n\text{-C}_5$ and $i\text{-C}_{12}$ (Figs. 8b and 8c). With type C cracking, the probability of having a branching in the short fragment is always lower than in the large fragment, explaining the evolution of the branched isomer content with carbon number of the cracked products (Fig. 6).

According to the pore mouth catalysis model, the zeolite mass fraction that is effectively contributing to the conversions is very limited. In the present example of heptadecane isomers in Pt/H−ZSM-22, it is estimated that the active layer of the crystal represents 0.5 wt%. Nevertheless, the activity of the Pt/H−ZSM-22 catalyst is similar to that of a Pt/H−Y zeolite for which it is generally assumed that the entire crystal is active.

CONCLUSIONS

On Pt/H−ZSM-22, $n\text{-C}_{17}$ can be extensively isomerized with very limited cracking. On Pt/H−ZSM-22, the yield of multibranched $i\text{-C}_{17}$ reaches 64 at 99% conversion, compared to 28 at 60% conversion on a typical bifunctional faujasite catalyst. A pore mouth mechanism of hydrocracking is proposed to explain this behavior. The micropores of ZSM-22 zeolite are so narrow that only linear alkyl groups of hydrocarbon molecules can enter. In the pore mouths, the formation of $i\text{-C}_{17}$ molecules with branching configurations that are favorable to fast cracking reactions is inhibited. In addition, the cracking of these molecules is suppressed because the alkylcarbenium ions involved

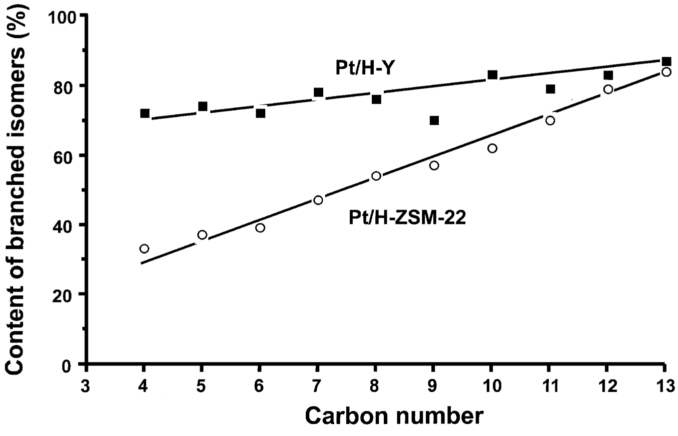


FIG. 6. Content of branched products in the cracked product fractions at 10% cracking yield of $n\text{-C}_{17}$ on Pt/H−ZSM-22 and Pt/H−Y.

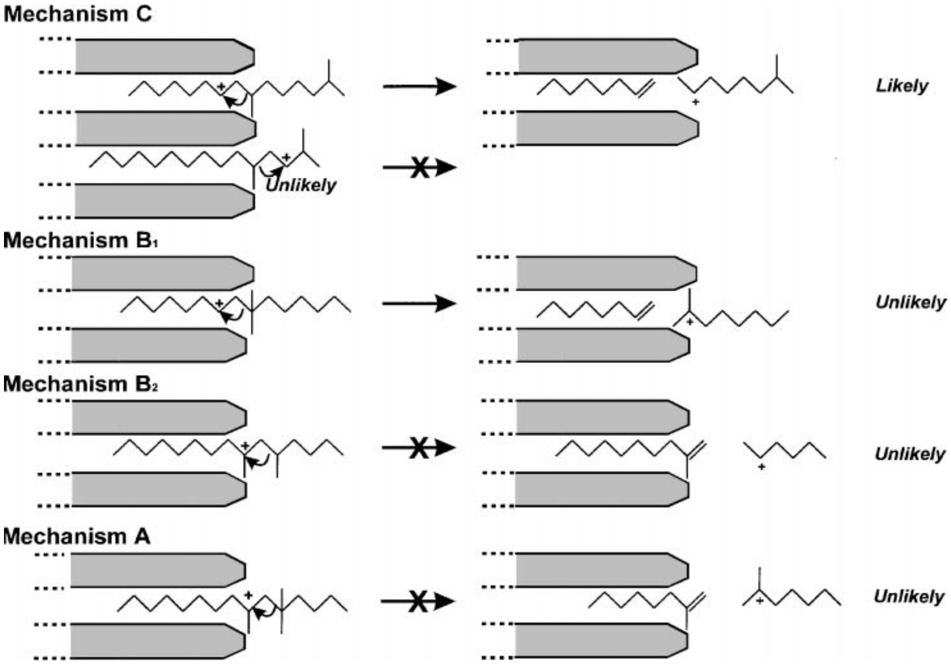


FIG. 7. Examples of likely and unlikely β-scission reaction of $C_{17}H_{35}^{+}$ alkylcarbenium ions in the pore mouths of ZSM-22 crystals.

in the mechanisms cannot be stabilized, since these isomers cannot be favorably physisorbed and cracked. The main hydrocracking pathway involves the slow β-scission mechanism C, converting a secondary alkylcarbenium ion into a shorter secondary alkylcarbenium ion and a short alkene.

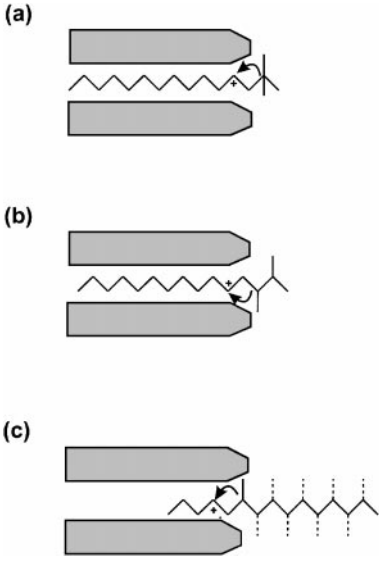


FIG. 8. (a) Type B_1 β-scission of 2,2-dimethylpentadec-4-yl cation leading to i-C_4 and n-C_{13} fragments. (b and c) Type C β-scissions of dibranched i-C_{17}s leading to (b) i-$C_5 + n$-C_{12} and (c) n-$C_5 + i$-C_{12} fragments. In (c), several positions for the methylbranching are possible, indicated with dashed line segments.

ACKNOWLEDGMENTS

J.A.M. acknowledges the Flemish FWO for a research position as Research Director; W.S. acknowledges the Flemish IWT for a fellowship. This research has been sponsored by the Belgian government within the frame of an IUAP Center of Excellence program.

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