

HYDROCRACKING OF C₉ THROUGH C₁₁ NAPHTHENES ON Pd/LaY AND Pd/HZSM-5 ZEOLITES

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ABSTRACT

The pure naphthenes propylcyclohexane, butylcyclohexane, and pentylcyclohexane were comparatively converted on 0.27 Pd/LaY and 0.27 Pd/HZSM-5 zeolite under hydrogen pressure. On the Y type zeolite, the rate of hydrocracking increases sharply as the carbon number of the naphthene is raised from C₉ to C₁₁. Moreover, on this zeolite, the so-called paring reaction takes place if the naphthene contains at least ten carbon atoms. Hydrocracking is then extraordinarily selective. Mechanistically, the paring reaction requires a bulky carbocation intermediate which, expectedly, does not form in Pd/HZSM-5. As a consequence, hydrocracking is much less selective in the medium pore zeolite. This is an interesting example for a *loss of selectivity* under conditions of steric constraints. Hydrocracking of butylcyclohexane is recommended as a potential test reaction for estimating the effective pore width of zeolites with unknown structures.

INTRODUCTION

In the past, valuable insight was gained into the mechanisms of hydrocarbon conversion by model compound studies over bifunctional catalysts. Most of these investigations were conducted with various alkanes. It has been emphasized [1] that such model alkanes should contain at least eight carbon atoms if non-typical side reactions are to be avoided. Recently, the conversion of n-decane in acidic zeolites loaded with a noble metal has been proposed as a test reaction for estimating effective pore widths of zeolites with unknown structures [2].

Much less work has been done with alkyl substituted naphthenes, in spite of the fact that such hydrocarbons represent another major class of petroleum constituents. In this context, the research done at

Chevron more than two decades ago [3] deserves particular attention. These early investigations were performed with non-zeolitic catalysts, e.g., sulfided Ni/SiO₂-Al₂O₃ and a variety of cyclic hydrocarbons. In a recent study, the reactions of C₆ through C₈ naphthenes in bifunctional Y and pentasil type zeolites were compared [4]. These prior investigations are now extended to C₉ through C₁₁ naphthenes. An interesting example for a reaction will be presented which proceeds much *less selective* in a zeolite of medium pore width than in large pore catalysts.

EXPERIMENTAL

The pure naphthenes propylcyclohexane (P-CHx, purity >99.9 wt.-%), butylcyclohexane (B-CHx, purity 99.1 wt.-%), and pentylcyclohexane (Pe-CHx, purity 99.4 wt.-%) were comparatively converted on 0.27 Pd/LaY-72 and 0.27 Pd/HZSM-5 zeolite under hydrogen pressure. The flow type apparatus with a fixed bed reactor has been described elsewhere [5].

The Pd content, the molar ratio Si/Al, and the degree of lanthanum exchange of the Pd/LaY zeolite amounted to 0.27 wt.-%, 2.46, and 72 equiv.-%, respectively [4]. HZSM-5 zeolite was prepared according to ref. [6] by first stirring a gel with the molar composition 41.5 SiO₂ : 1 Al(NO₃)₃ : 10 NaOH : 70 TtPAOH : 11 NH₄OH : 3200 H₂O : 525 glycerol for five days at 200 °C in a stainless steel autoclave. The resulting material was calcined in air at 400 °C for two days, ion exchanged with a 2n solution of NaCl, and then again calcined at 540 °C. It was then ion exchanged with a 2n solution of NH₄Cl at 80 °C and calcined in flowing oxygen, the temperature being 540 °C. In all calcination steps, the heating rate was 20 °C/h. X-Ray diffraction showed that the sample was crystallographically pure. Morphologically, it consisted of rectangular crystallites with a size of about 5 μm. IR spectroscopy indicated OH stretching bands at ca. 3610 and 3745 cm⁻¹. The latter band has been assigned to extra lattice or amorphous material [7]. Chemical analysis gave molar ratios Si/Al and Al/Na of 40 and 38, respectively. To obtain the bifunctional form, HZSM-5 was exchanged with the theoretical amount of [Pd(NH₃)₄]Cl₂ in water, such as to achieve a Pd content of 0.27 wt.-%. Both zeolite catalysts were pressed binder-free and used in a particle size between 0.2 and 0.3 mm. They were pretreated successively in a purge of O₂ at 300 °C, a purge of N₂ at 350 °C and a purge of H₂ at 300 °C.

The products formed from the model naphthenes were analyzed by high resolution capillary GLC in the on-line mode. Polypropylene gly-

col was routinely employed as stationary phase. Supplementary off-line analyses were carried out on a different stationary phase, viz. SE 54, using liquid product samples which were condensed at ca. $-190\text{ }^{\circ}\text{C}$ from the product stream.

In all catalytic runs, the partial pressures of the feed hydrocarbon and hydrogen at the reactor inlet were 19.4 kPa and 2.0 MPa, respectively. The reaction temperature was varied between 200 and 300 $^{\circ}\text{C}$. Unless otherwise stated, W/F_{HC} amounted to 140 g·h/mol.

RESULTS AND DISCUSSION

Conversions and yields. During hydroconversion of naphthenes, the following reactions must be distinguished: Skeletal isomerization, aromatization, ring opening to alkanes with the carbon number of the feed, and hydrocracking into products with a lower carbon number. No aromatics were detected under the conditions applied in this study. Typical product yields are shown in Fig. 1. The naphthenes formed by isomerization and the alkanes formed by ring opening were lumped because, at these elevated carbon numbers, they could not be resolved satisfactorily. Conversions can be derived from the data in Fig. 1 by summing up $Y_{\text{Iso.}} + Y_{\text{Ro.}} + Y_{\text{Cr.}}$. It will be noted that both zeolites do not differ too much in their activities. However, marked differences are encountered in the selectivities: On Pd/HZSM-5 there is only little iso-

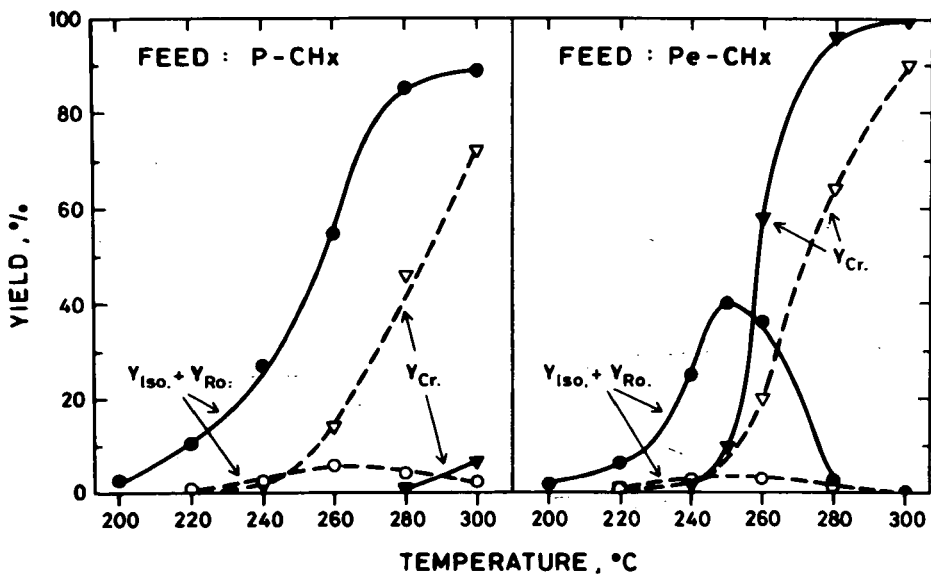


Fig. 1. Yields of products from propylcyclohexane and pentylcyclohexane on Pd/LaY (full curves) and Pd/HZSM-5 (dashed curves).

merization and ring opening, irrespective of the carbon number of the feed and the conversion. On Pd/LaY, by contrast, there is no hydrocracking at all, as long as the conversion is limited to a certain value. It is an important result that, on the large pore zeolite, propylcyclohexane is hydrocracked much more sluggishly than its homologue with two additional carbon atoms.

Fig. 2 clearly demonstrates that, in the homologous series of naphthenes, the rate of hydrocracking in *large pore* zeolite catalysts increases drastically from C₉ to C₁₁. It will be shown below that this is a direct consequence of the mechanism of ionic β -scission. Earlier experiments with a comparable catalyst revealed [8] that *alkanes* exhibit an analogous jump in the rate of hydrocracking between C₇ and C₉ (see dashed curve in Fig. 2).

Selectivities of hydrocracking in Pd/LaY. Pertinent selectivities of hydrocracking the C₉ through C₁₁ naphthenes on the large pore zeolite are depicted in Fig. 3. All curves are nearly symmetrical indicating an essentially pure primary cracking [8]. P-CHx gives mainly C₄ + C₅ beside smaller amounts of C₃ and C₆. This carbon number distribution resembles the one which is obtained from n-nonane on, e.g., Pt/CaY zeolite [8]. The occurrence of some C₈ and C₇ as well as the

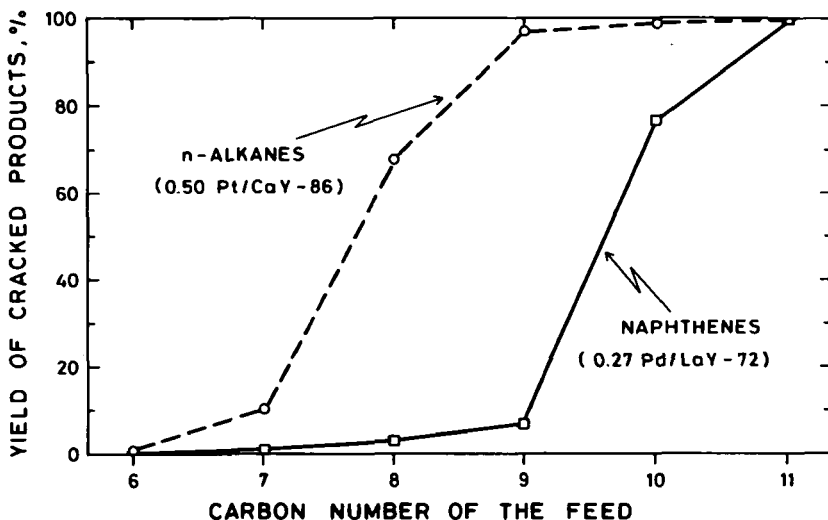


Fig. 2. Hydrocracking reactivities of n-alkanes and naphthenes on comparable Y type zeolite catalysts (n-alkanes: T = 310 °C, P_{HC} = 220 kPa, P_{H₂} = 3.7 MPa, W/F_{HC} = 85 g·h/mol, cf. ref. [8]; naphthenes: T = 300 °C, P_{HC} = 19.4 kPa, P_{H₂} = 2.0 MPa, W/F_{HC} = 140 g·h/mol, M-CPn and M-CHx, unpublished results from this laboratory, E-CHx cf. ref. [4], P-CHx, B-CHx, and Pe-CHx, this study).

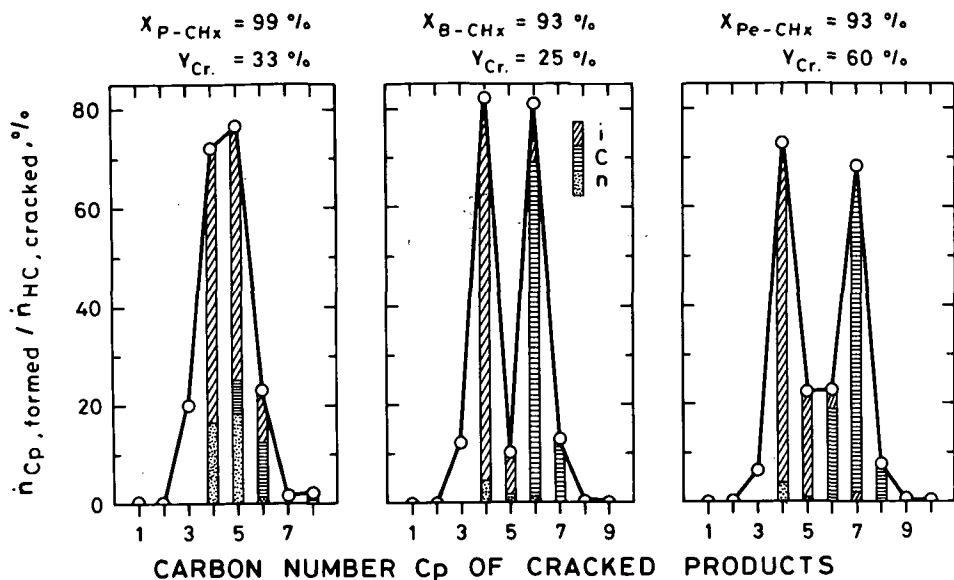


Fig. 3. Selectivities of hydrocracking on Pd/LaY zeolite (P-CHx: T = 300 °C, W/F_{P-CHx} = 570 g·h/mol; B-CHx: T = 280 °C, W/F_{B-CHx} = 140 g·h/mol; Pe-CHx: T = 260 °C, W/F_{Pe-CHx} = 140 g·h/mol).

slight surplus of C₆ and C₅ over C₃ and C₄, respectively, can be attributed to a disproportionation type of side reaction [9]. B-CHx and Pe-CHx give distribution curves which differ extremely from those encountered with paraffinic model hydrocarbons, e.g., n-decane and n-undecane [8]. In particular, very little C₅ or C₅+C₆, respectively, are formed from these naphthenes. Note also that the i-alkanes strongly prevail in the C₄ and C₅ fractions, whereas the C₆ and C₇ moieties consist of naphthenes to a very large extent. All these features of hydrocracking C₁₀ and C₁₁ naphthenes on large pore catalysts have been reported earlier by Chevron researchers who used a non-zeolitic NiS/SiO₂-Al₂O₃ catalyst and a variety of isomeric C₁₀ and C₁₁ naphthenes [3,10]. Even tetramethylcyclohexanes gave essentially identical product distributions. In a formal sense, then, the methyl substituents were pared from the naphthenic ring and released as i-butane. Hence, the Chevron group coined the term *paring reaction*.

The mechanism of the paring reaction is easily understood on the basis of bifunctional catalysis and conventional carbocation chemistry. Following a recent nomenclature proposal [11], the naphthenic system tends to undergo *exocyclic type A* β-scission which requires a minimum of 10 carbon atoms [9]. Precursors of these type A β-scissions are

α, α, γ -tribranched carbenium ions which are formed by rapid ionic rearrangements from a carbenium ion with the skeleton of the feed. Two exocyclic type A β -scissions are possible for C_{10} naphthenes. They are shown in Fig. 4 (top). It is evident that, after the usual stabilization steps involved in bifunctional catalysis, they both lead to *i*-butane and methylcyclopentane as the exclusive products. These are, indeed, strongly favored on Pd/LaY (Fig. 3). In the lower part of Fig 4, some type B [11] β -scissions are sketched which explain the occurrence of several side products (propane, *n*-butane, cyclohexane, and C_7 naphthenes).

It is evident from Fig. 4 that type A β -scissions start from a relatively bulky precursor which carries at least one quaternary carbon atom. It is questionable whether such precursors can be accommodated or formed in a medium pore zeolite such as Pd/HZSM-5 [12] at the temperatures employed in this study. If not, then one would expect that hydrocracking in Pd/HZSM-5 necessarily proceeds via type B (or even type C [11]) β -scissions. It can be shown that such a route would render hydrocracking of C_{10} or C_{11} naphthenes much *less selective* in Pd/HZSM-5 than in a large pore zeolite.

Selectivities of hydrocracking in Pd/HZSM-5. Selectivities of hydrocracking in Pd/HZSM-5 are shown in Fig. 5. The deviations from symmetry are now much stronger indicating a considerable extent of secondary cracking reactions. It is, moreover, seen that on Pd/HZSM-5,

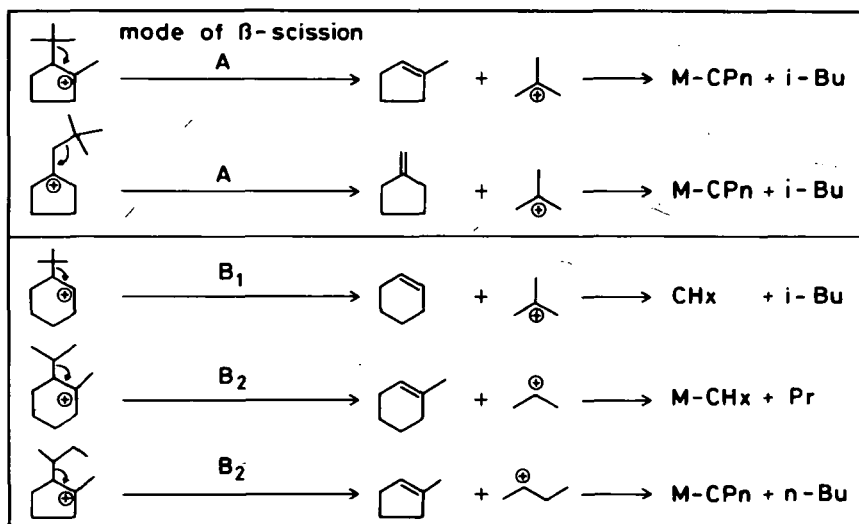


Fig. 4. Exocyclic type A and type B β -scissions (for nomenclature see ref. [9] or [11]) of cycloalkylcarbenium ions with 10 carbon atoms (probable mechanisms of cleavage in Pd/LaY).

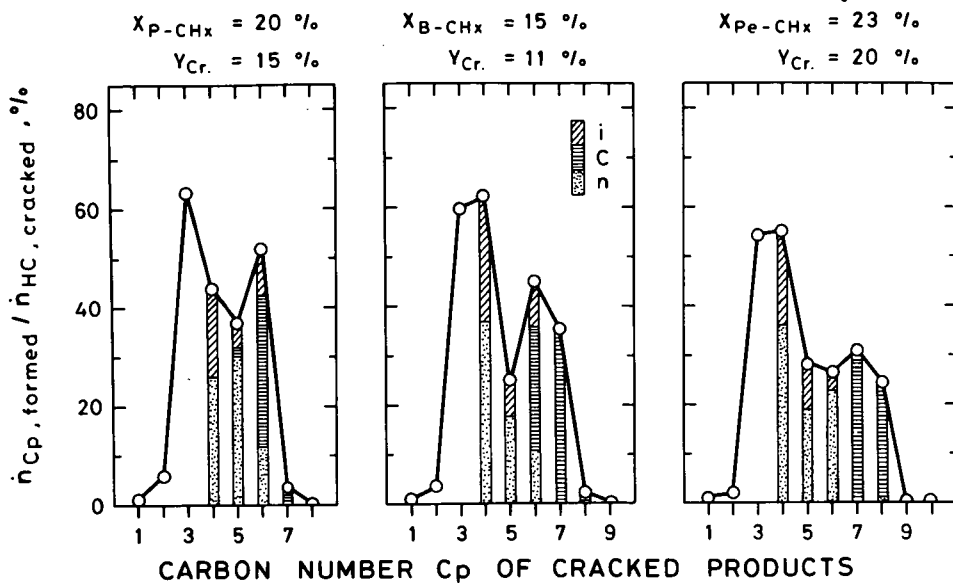


Fig. 5. Selectivities of hydrocracking on Pd/HZSM-5 zeolite (P-CHx: T = 260 °C; B-CHx: T = 250 °C; Pe-CHx: T = 260 °C).

much more C_3 and C_{m-3} are formed than on Pd/LaY. In principle, both these results have been found earlier in hydrocracking of alkanes on Pt/HZSM-5 [11]. Another feature of hydrocracking in 0.27 Pd/HZSM-5 is the formation of some methane and ethane. To account for their occurrence, either hydrogenolysis on Pd or ionic cleavage via non-classical cycloalkylcarbonium ions [13] can be invoked. From the facts that these same products do not form on 0.27 Pd/LaY (Fig. 3) which contains the same amount of Pd, and that there are more moles of C_2 than C_1 [13], one might favor the second possibility.

However, in the present context, the most striking result is that B-CHx and Pe-CHx indeed hydrocrack with a much lower selectivity than on Pd/LaY: Not only are the valleys at C_5 or C_5+C_6 much less pronounced, but many more individual hydrocarbons occur in the cracked products. Note, for example, that starting from B-CHx, the molar *i*-butane/*n*-butane ratio is around 0.7 compared to ca. 20 on Pd/LaY. A low *i*-butane/*n*-butane ratio of 0.8 has also been reported for hydrocracking of cyclodecane on Pt/HZSM-5 [14]. It is unlikely that the preferred formation of *n*-butane over *i*-butane in Pt/ or Pd/HZSM-5 is due to product shape selectivity since the diffusion coefficients of these two isomers in a pentasil type zeolite were shown to differ only slightly from each other [15]. Rather, the loss of selectivity in Pd/HZSM-5 as compared to Pd/LaY (or any other large pore catalyst)

probably results from the fact that the bulky precursors required for type A β -scissions cannot be formed in the pentasil type channels. Hence, even with B-CHx or Pe-CHx type B and/or type C β -scissions [11] take place in Pd/HZSM-5 as sketched in Fig. 6. The same principal conclusion was arrived at in a study on hydrocracking C₉ through C₁₆ alkanes on Pt/HZSM-5. Moreover, this postulated pathway accounts for the independent finding that, in Pd/HZSM-5 (see Fig. 1), P-CHx is hydrocracked essentially as fast as Pe-CHx: C₉ naphthenes, due to their relatively low carbon number, are principally excluded from exocyclic type A β -scissions. But if this route is forbidden on account of steric constraints, then all C₉ through C₁₁ naphthenes are forced to undergo type B and/or type C β -scissions.

Cleavage of *endocyclic* carbon-carbon bonds is a very slow reaction in large pore zeolites [9]. With C₆ through C₈ naphthenes, this effect was found to be less pronounced in pentasils [4]. It is reasonable, then, to anticipate (Fig. 6, bottom) that ring opening routes contribute to the mechanism of hydrocracking in Pd/HZSM-5. This is one way to explain the formation of, e.g., i-butane and n-hexane (see Fig. 6). Such a pathway is not in contradiction with the low yields of ring opening products (cf. Fig. 1) on Pd/HZSM-5 since the aliphatics formed by ring opening can undergo consecutive cleavage prior to leaving the intracrystalline channel system.

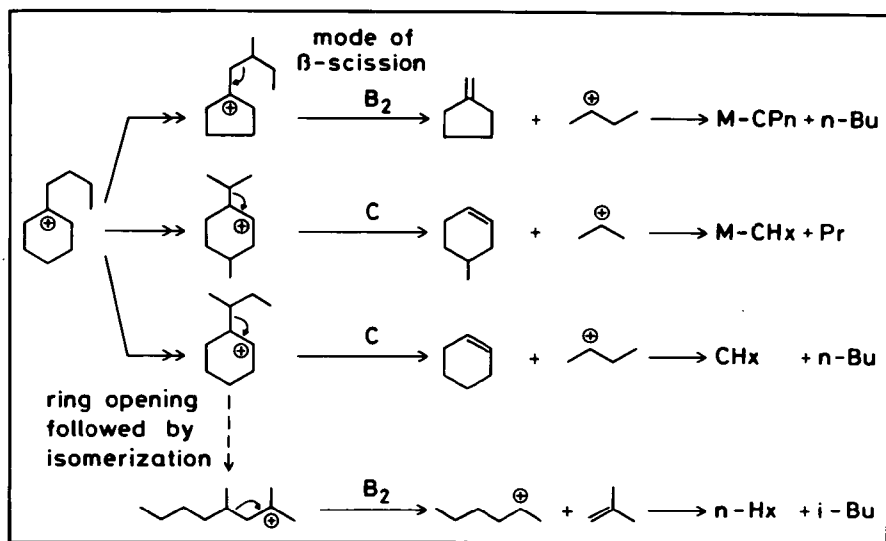


Fig. 6. Exocyclic type B and type C β -scissions [9,11] of cycloalkyl-carbenium ions with 10 carbon atoms and hydrocracking via ionic ring opening (probable mechanisms of cleavage in Pd/HZSM-5).

CONCLUSIONS

This study reveals that catalytic reactions may proceed *less selectively in a medium pore zeolite* as compared to a large pore zeolite. Hydrocracking of butylcyclohexane is an example. The phenomenon can be rationalized if one takes into account that the most selective mode (type A) of ionic β -scission starts from very bulky intermediates. We propose hydrocracking of butylcyclohexane as another [2] test reaction the selectivity of which might furnish rapid information on the effective pore width of zeolites with unknown structures.

It has been pointed out earlier [1,8] that model *alkanes* with at least eight carbon atoms should be employed to allow for the most favorable ionic pathways of hydrocracking in large pore zeolites. It is now shown that this critical carbon number is even higher for *naphthenes*. For mechanistic studies we recommend model naphthenes with at least ten carbon atoms.

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SYMBOLS AND ABBREVIATIONS

F_i	feed rate	$\text{mol}\cdot\text{h}^{-1}$
m	carbon number of feed	
\dot{n}	molar flux	$\text{mol}\cdot\text{h}^{-1}$
P_i	partial pressure	Pa
p	carbon number of cracked products	
T	temperature	$^{\circ}\text{C}$
W	mass of dry catalyst	g
X_i	conversion	
Y_i	yield	

B	butyl	Pe	pentyl	HC	hydrocarbon
Bu	butane	Pn	pentane	i	iso-alkanes
E	ethyl	Pr	propane	Iso.	isomerization
Hx	hexane			n	normal alkane
M	methyl	C	cyclo	Ro.	ring opening
P	propyl	Cr.	hydrocracking	TtPA	tetrapropylammonium

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