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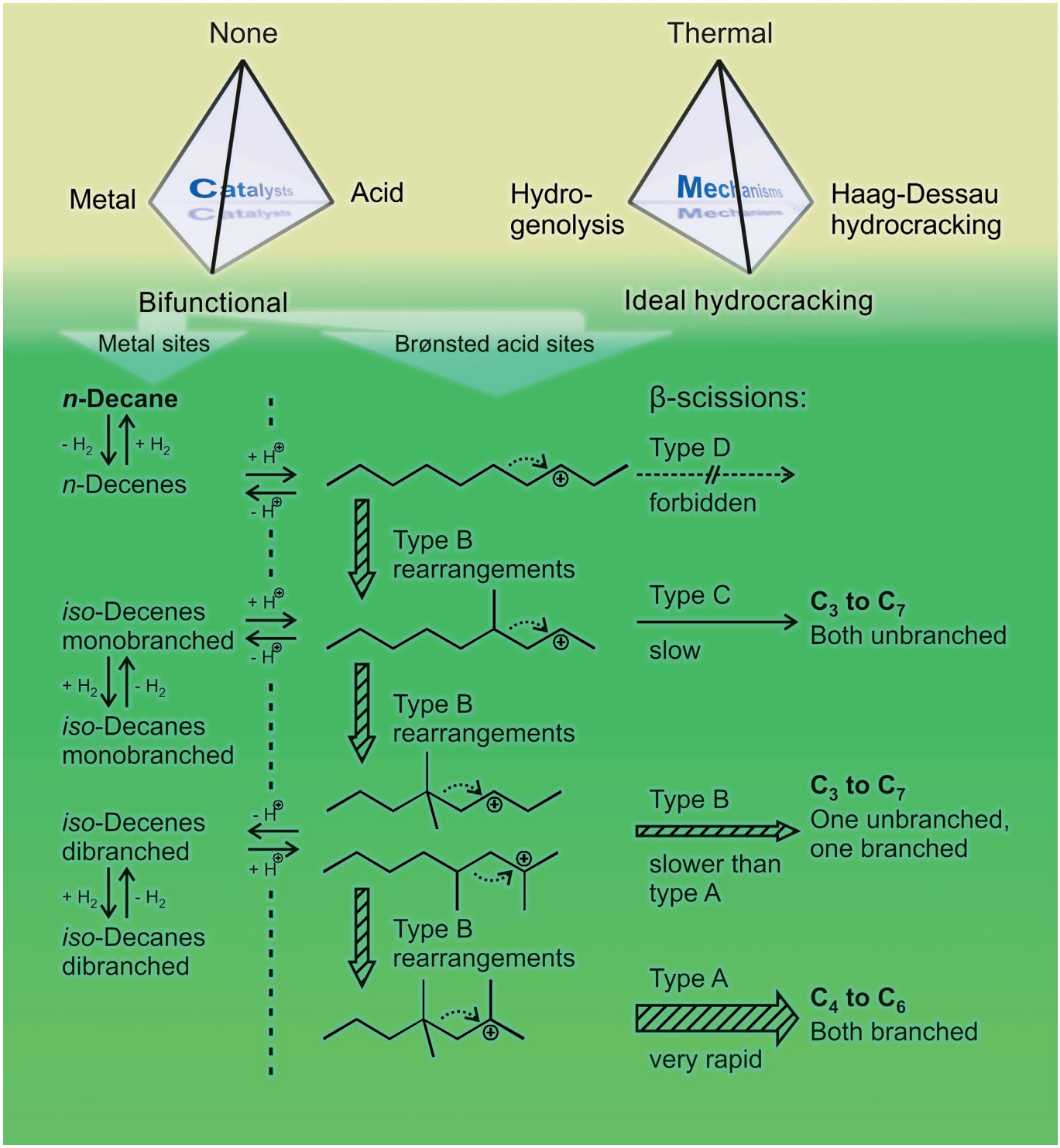
Catalytic Hydrocracking—Mechanisms and Versatility of the Process**

Jens Weitkamp*[a]



Hydrocracking of saturated hydrocarbons can proceed by means of four distinctly different mechanisms. On bifunctional catalysts comprising hydrogenation/dehydrogenation and Brønsted acid sites alkenes and carbocations occur as intermediates. The current mechanistic views of bifunctional hydrocracking of long-chain *n*-alkanes are discussed in detail with emphasis on the now widely accepted concept of ideal hydrocracking. Other mechanisms are hydrogenolysis and Haag–Dessau hydrocracking which proceed, respectively, on monofunctional metallic and acidic catalysts. Even without a catalyst, thermal hydrocracking occurs in chain reactions via radicals. The chemistry of hydrocracking naphthenes on bifunctional catalysts resembles that of alkanes. A peculiarity, however, is the pronounced reluctance of cyclic carbenium ions to undergo endocyclic β-scissions. The effect manifests itself in the so-called paring reaction, which, in turn, forms the basis for measuring the Spaciousness Index for characterizing the effective pore width of zeolitic catalysts. Hydrocracking on bifunctional catalysts is among the very important processes in modern petroleum refining. It is primarily used for converting heavy oils into diesel and jet fuel. Besides, hydrocracking is appreciated for its pronounced versatility: numerous process variants exist which help to meet specific requirements in refineries or petrochemical plants. Two recent developments are briefly discussed in this review, viz. the conversion of surplus aromatics, e.g., in pyrolysis gasoline, into a synthetic feedstock for steam crackers, and quality enhancement of diesel fuel by selective ring opening of polynuclear aromatics.

1. Introduction

Hydrocracking denotes a stoichiometry in which one or more carbon–carbon bonds in the reactant, typically a hydrocarbon, are broken, and the free valencies thereby created are saturated by hydrogen. Hydrocracking can proceed by means of four distinctly different mechanisms, depending on the nature of the catalyst:

1) Bifunctional catalysts comprise a hydrogenation/dehydrogenation component, often a noble metal, and a Brønsted acid component.[1–4] The main function of the metal is to dehydrogenate saturated reactant molecules to alkenes and to hydrogenate olefinic intermediates desorbed from the acid sites. There, skeletal rearrangements and carbon–carbon bond scissions occur, probably via carbocations as reactive species. Mass transfer between both types of sites is viewed to happen by diffusion of alkenes.[5] Such a pathway will be referred to in this article as *bifunctional hydrocracking*. A special case, which will be discussed in some detail, is ideal hydrocracking.[6–8]

2) Carbon–carbon bond cleavage followed by hydrogenation of the fragments may also occur on metals, that is, monofunctional catalysts. For such a hydrocracking mechanism the term *hydrogenolysis* is customary.[9–12]

3) The generic term for cracking on monofunctional acidic catalysts is "catalytic cracking". As shown by Haag and Dessau[13,14] and confirmed by others,[15–17] two mechanisms must be discerned for catalytic cracking, viz. classical bimolecular cracking via carbenium ions and non-classical monomolecular cracking via carbonium ions. Under conditions where the latter mechanism is operative (also called Haag–Dessau cracking), molecular hydrogen can be activated on Brønsted acid sites, e.g., for hydrogenating ethene[18] or hydrocracking of *n*-heptane.[19] We will refer to such a hydrocracking on monofunctional acidic catalysts as *Haag–Dessau hydrocracking*.

4) Finally, even in the absence of a catalyst, *thermal hydrocracking* (or hydropyrolysis) can be achieved at temperatures of 500 to 600 °C and elevated hydrogen pressures.[20] It proceeds through a chain reaction involving radicals as intermediates.

Hydrocracking on bifunctional catalysts is of prime importance in modern petroleum refining.[21,22] With a worldwide process capacity of 265×10^6 t a^{-1}, as of the end of the year 2010,[23] it is primarily operated for converting heavy vacuum gas oil (VGO) into diesel and jet fuel, in some cases also gasoline, and appreciated by refiners for its flexibility and versatility.

Flexibility means the broad range of product yields that can be achieved in an existing VGO hydrocracker,[24] thereby enabling a refinery to respond efficiently to fluctuations in the market needs. Versatility refers to the numerous process variants, each meeting specific requirements in an oil refinery or a petrochemical complex. Examples are, beside the manufacture of transportation fuels from VGO, mild hydrocracking of VGO or distillation residues,[25] for example for making high-quality feedstocks to fluid catalytic cracking, dewaxing of lube oils or middle distillates by shape-selective hydrocracking,[26] the manufacture of high-quality diesel fuel from Fischer–Tropsch wax as the last process step in the gas-to-liquid route,[27,28] or the production of feedstocks to steam crackers for the manufacture of light alkenes.[29] Finally, since bifunctional catalysts are also used in the skeletal isomerization of light gasoline and heavier petroleum fractions (dewaxing by isomerization) and in reforming of heavy naphtha, the catalytic chemistry of these refinery processes is closely related to that of bifunctional hydrocracking.

The objectives of this review are threefold: First, the chemistry of bifunctional hydrocracking of long-chain *n*-alkanes will be discussed with emphasis on the concept of ideal hydrocracking. Next, the fundamentals of probing the effective pore widths of zeolites by a shape-selective test reaction, viz. hydro-

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cracking of butylcyclohexane, will be developed. Finally, two relatively recent examples for the versatility of hydrocracking will be briefly addressed, viz. hydrocracking of surplus aromatics, e.g., in pyrolysis gasoline, into a synthetic steam cracker feed consisting of ethane, propane, and *n*-butane and ring opening of polynuclear aromatics for enhancement of the quality of diesel fuel.

2. Ideal Hydrocracking of Long-Chain *n*-Alkanes

Real feedstocks to industrial hydrocrackers are complex mixtures of individual hydrocarbons, viz. alkanes, naphthenes, and aromatics. For mechanistic studies, such oils must be simulated by model hydrocarbons, for instance an *n*-alkane. As will be shown below, the chain length of such a model *n*-alkane must not be too low to ensure that the results are meaningful for hydrocracking of real oils.

2.1. Salient features of ideal hydrocracking

Hydrocracking on bifunctional catalysts is mechanistically related to catalytic cracking on monofunctional acidic catalysts. In particular, the key step of carbon–carbon bond cleavage in both cases occurs while the hydrocarbon is adsorbed on an acid site. On the other hand, there are pronounced differences between both reactions, for example: i) hydrocracking occurs under high hydrogen pressure, and the products are usually fully saturated; ii) hydrocracking often proceeds at temperatures around 250 °C, whereas much higher temperatures are required for catalytic cracking; iii) there is usually no catalyst deactivation in hydrocracking, whereas carbonaceous deposits form during catalytic cracking which deactivate the catalyst; iv) the cracked products formed from an *n*-alkane are branched to a significantly higher extent in catalytic cracking than in hydrocracking and, especially, in ideal hydrocracking.

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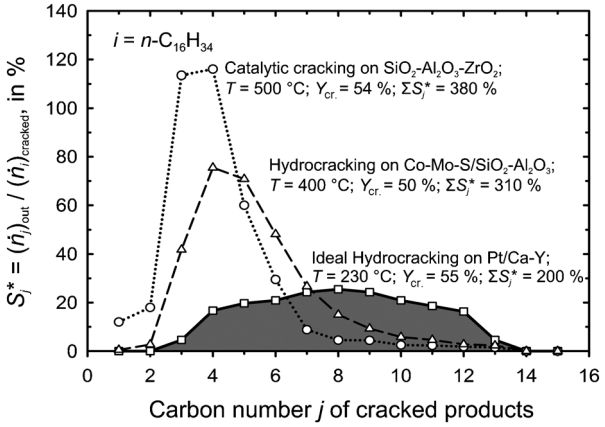

Figure 1. Molar distributions of the cracked or hydrocracked products from *n*-hexadecane, after Refs. [8, 30]. Typical results for three catalysts with no (SiO_2-Al_2O_3-ZrO_2),[31] a weak (sulfided Co-Mo-S/SiO_2-Al_2O_3),[6] and a strong (Pt/Ca-Y zeolite)[8] hydrogenation/dehydrogenation component are depicted for approximately the same yield of cracked or hydrocracked products ($Y_{cr.} \approx 50\,\%$). S_j^* is the modified cracking or hydrocracking selectivity defined as the molar amount of hydrocarbons with *j* carbon atoms formed divided by the molar amount of *n*-hexadecane converted to cracked or hydrocracked products.

Another striking difference is seen from Figure 1 (note that, throughout this article, *i* stands for the reactant or its carbon number, while *j* is the carbon number of the cracked or hydrocracked products): hydrocracking on Pt/Ca-Y zeolite gives a distribution curve which is fully symmetrical around $j = i/2 = 8$ and a ΣS_j^* of 200 %.

Both findings indicate a pure primary hydrocracking selectivity, i.e., one carbon–carbon bond in the reactant is cleaved, whereupon the hydrocracked products are desorbed, before a second carbon–carbon bond is broken. In other words, there exists an efficient mechanism of desorption of the primary products from the acid sites. Note also that neither C_1 (and C_{15}) nor C_2 (and C_{14}) are formed. C_3 and C_{13} do occur in the product, albeit in molar amounts that are much lower than those of the C_4 to C_{12} fragments. The bell- (or volcano-) shaped molar distribution curves with no C_1 and C_2 and little C_3 are all salient features of ideal hydrocracking. Such curves are generally observed on bifunctional catalysts with a strong hydrogenation/dehydrogenation activity and sufficiently large pores, i.e., in the absence of shape selectivity effects.

An entirely different distribution curve is obtained for catalytic cracking on the monofunctional acidic catalyst at nearly the same yield of cracked products: the vast majority of product hydrocarbons are in the range from C_3 to C_6, i.e., extensive secondary cracking of the primary fragments must have taken place (also, some C_1 and C_2 fragments occur which could be due to some superimposed thermal or Haag–Dessau[13,14] cracking at the high reaction temperatures required). Hydrocracking on the Co-Mo-S/SiO_2-Al_2O_3 catalyst with a weak hydrogenation/dehydrogenation component shows an intermediate behavior between the extreme cases Pt/Ca-Y and SiO_2-Al_2O_3-ZrO_2.

Coonradt and Garwood were the first to fully recognize the fundamental differences between catalytic cracking and hydro-

cracking on catalysts with a strong hydrogenation/dehydrogenation component.[32] In fact, hydrocracking had long been misunderstood as being merely a variant of catalytic cracking with hydrogenation reactions superimposed. Coonradt and Garwood also pointed out the wide span in types of products attainable from one and the same feed on various bifunctional catalysts.[32] These differences do not only pertain to the degree of secondary hydrocracking, but also to another selectivity feature of high industrial relevance: Long-chain ($i \geq 8$) *n*-alkanes cannot be isomerized to a significant extent on monofunctional acidic catalysts. By contrast, bifunctional catalysts with a strong hydrogenation/dehydrogenation component allow one to achieve very high selectivities of skeletal isomers at low and moderate conversions.

A typical example is shown in Figure 2 in which *n*-tridecane was converted on Pt/Ca-Y zeolite under a hydrogen pressure of 4.0 MPa.[33] Up to a conversion of approximately 40% at 230 °C skeletal isomerization to *iso*-tridecanes is the sole reaction. It is only upon further raising the temperature and conversion that hydrocracking starts. The yield of *iso*-tridecanes then passes through a maximum, which is as high as 66%. As the temperature and conversion are further increased, the yield of *iso*-tridecanes rapidly falls to zero indicating that the *iso*-tridecanes are more and more consumed by hydrocracking. Figure 2 strongly suggests that skeletal isomerization and hydrocracking of the long-chain *n*-alkane are consecutive reactions.

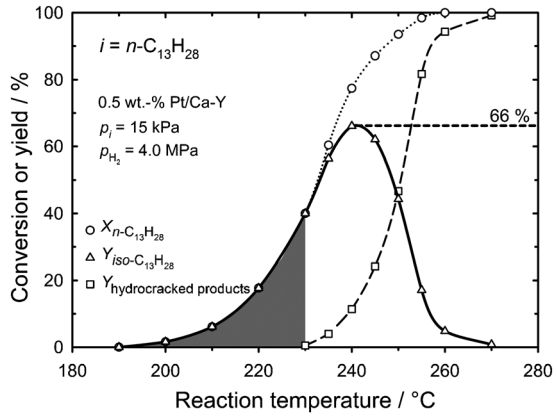

Figure 2. Isomerization and hydrocracking of *n*-tridecane on Pt/Ca-Y zeolite.[33] *X* and *Y* denote, respectively, the conversion and yield.

The term "ideal hydrocracking" was coined for catalytic systems, which allow one to convert an *n*-alkane (n-C_iH_{2i+2}) with a sufficiently high carbon number ($i \gtrsim 12$), at will and simply by varying the severity of the reaction, into skeletal isomers (*iso*-C_iH_{2i+2}, as shown in Figure 2), hydrocracked products C_jH_{2j+2} ($3 \leq j \leq i-3$) with a pure primary hydrocracking selectivity (see Figure 1 for Pt/Ca-Y) or, eventually, hydrocracked products with an ever more pronounced preponderance of the light fragments.[6–8] It has been repeatedly demonstrated, e.g., for the hydroconversion of *n*-hexadecane on Pt/SiO_2-Al_2O_3,[32] of *n*-dodecane on Pt/Ca-Y zeolite,[4] or of *n*-dodecane on Pt/ultrastable Y zeolite,[34] that the characteristic bell-shaped S_j* curves hold for a very wide range of yields of hydrocracked products, as long as these are below 100%. If non-symmetrical S_j* curves, i.e., more lighter hydrocarbons are desired, these can easily be achieved with the same catalyst simply by increasing the severity of hydrocracking beyond the point where $Y_{cr.}$ reaches 100%. Ideal hydrocracking catalysts, therefore, enable a maximal product flexibility in an existing industrial hydrocracker. This allows the refiner to run the plant with maximal yield of diesel fuel, jet fuel, or gasoline, in response to the needs of the market.[24] A catalytic cracker (fluid catalytic cracking, FCC), by contrast, inevitably and invariably produces light gasoline hydrocarbons (see S_j* curve for SiO_2-Al_2O_3-ZrO_2 in Figure 1) and does so without offering much product flexibility.

The products of ideal hydrocracking of a long-chain *n*-alkane consist again of alkanes in the carbon-number range of $3 \leq j \leq i-3$.[4,7] Both *n*- and *iso*-alkanes are formed. Figure 3 shows that i) branched alkanes dominate in all carbon number fractions *j*, ii) the content of branched alkanes formed from a given *n*-alkane reactant increases with increasing carbon number *j*, but iii) the content of branched alkanes in a given product fraction *j* is independent of the carbon number *i* of the feed. iv) It is, furthermore, clearly seen that an exception from rule iii is the carbon number fraction $j = i-3$ formed by splitting off propane. This particular fraction is unusually rich ($\approx$90%) in branched alkanes. All these selectivity features hold for a very broad range of yields of hydrocracked products up to approximately 80% or more. In Figure 3, no discrimination was made between *iso*-alkanes with one, two, or more branches. More detailed distributions of the *iso*-alkanes formed from, e.g., *n*-dodecane on Pt/Ca-Y zeolite have been published:[4] The *iso*-alkanes consist mainly of monobranched isomers and significantly smaller amounts of dibranched isomers, while tribranched isomers are absent. A deeper discussion of all these

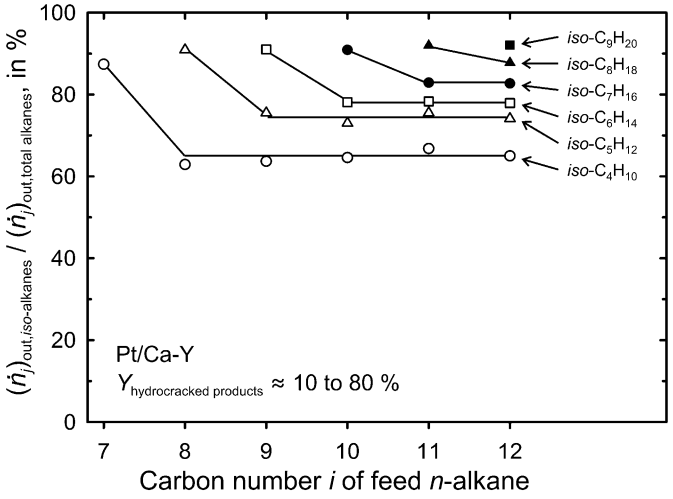

Figure 3. Ideal hydrocracking of *n*-alkanes n-C_iH_{2i+2} with $7 \leq i \leq 12$. Content of branched alkanes *iso*-C_jH_{2j+2} with $4 \leq j \leq (j-3)$ in the hydrocracked products.[7]

selectivity features of ideal hydrocracking has been conducted.[35,36] They are consistent with skeletal isomerization preceding carbon–carbon bond cleavage, as independently inferred from the highly selective isomerization of *n*-C_iH_{2i+2} at low to moderate conversion (see Figure 2).

Summing up, ideal hydrocracking

- proceeds on bifunctional catalysts with a strong hydrogenation/dehydrogenation component;
- enables product selectivities in the conversion of model hydrocarbons or heavy oils that are farthest away from those encountered in catalytic cracking on monofunctional acidic catalysts;
- offers an utmost degree of product flexibility in the conversion of heavy oils;
- allows skeletal isomerization of long-chain *n*-alkanes with high selectivities and yields of *iso*-alkanes;
- allows a pure primary hydrocracking selectivity of long-chain alkanes with bell-shaped carbon-number distributions of the hydrocracked products.

The concept of ideal hydrocracking is nowadays widely accepted,[28,37–41] as it helps rationalizing numerous features not only of bifunctional hydrocracking, but also of catalytic cracking and skeletal isomerization of hydrocarbons.

2.2. The mechanism of ideal hydrocracking

The classical mechanism for the conversion of an *n*-alkane on a bifunctional catalyst is depicted in Figure 4.[5,32,42,43] The reactant is dehydrogenated on the metal sites to the mixture of *n*-alkenes, *n*-C_iH_{2i}. These desorb from the metal sites and diffuse to Brønsted acid sites where they are protonated to the secondary alkylcarbenium ions, *n*-$C_iH_{2i+1}^+$. Carbenium ions are reactive intermediates which can undergo a number of conversions, such as skeletal rearrangements and carbon–carbon bond rupture. The latter is generally viewed to proceed through β-scission which will be discussed in detail in Section 2.3. The fragments of β-scission are a smaller alkylcarbenium ion and an alkene. In the case of β-scission of *n*-$C_iH_{2i+1}^+$ a primary carbenium ion would be formed, which is energetically unfavorable. The *n*-alkylcarbenium ions hence undergo skeletal rearrangements exclusively, whereby monobranched alkylcarbenium ions, *iso*-$C_iH_{2i+1}^+$, are formed. If there is an efficient mechanism of desorption from the acid sites, monobranched alkenes, *iso*-C_iH_{2i}, are released and diffuse to metal sites where they are hydrogenated to monobranched alkanes, *iso*-C_iH_{2i+2}. These are the primary products observed at low conversions.[33] As the conversion is increased, consecutive reactions occur at the acid sites, in particular, a second branching rearrangement leading to dibranched *iso*-$C_iH_{2i+1}^+$, which are again desorbed as dibranched *iso*-alkenes and appear, upon hydrogenation at the metal sites, in the product as dibranched *iso*-alkanes *iso*-C_iH_{2i+2}. Upon increasing the conversion further, tribranched alkylcarbenium ions form in a third rearrangement step at the acid sites. As the rate of β-scission increases strongly with the degree of branching, these tribranched cations *iso*-$C_iH_{2i+1}^+$ are not desorbed, even not in ideal bifunctional catalysis, they rather undergo β-scission into an alkylcarbenium ion $C_jH_{2j+1}^+$ and an alkene $C_{(i-j)}H_{2(i-j)}$. Neither C_1 nor C_2 hydrocarbons are formed, because this would require the energetically very unfavorable primary carbenium ions CH_3^+ and $C_2H_5^+$, respectively, as intermediates.

If the carbon number of the reactant is sufficiently high ($i \gtrsim 12$), the products of the primary β-scission can react further into one of two directions (Figure 4): In case there is an efficient mechanism of their desorption, they will be desorbed as alkenes, which will be hydrogenated on the metal and appear in the product as alkanes with a bell-shaped molar carbon number distribution (Figure 1 for Pt/Ca-Y zeolite). This is the case of ideal hydrocracking. Alternatively, if there is no rapid desorption of the primary cracked products, the largest fragments will undergo a secondary β-scission and appear in the product mainly as light alkanes. The result is a non-symmetrical molar carbon number distribution already at modest yields of hydrocracked products (Figure 1 for Co-Mo-S/SiO_2-Al_2O_3). In the extreme case of catalytic cracking (Figure 1 for SiO_2-Al_2O_3-ZrO_2), desorption of the cracked products from the acid sites is particularly slow and probably rate controlling, so high reaction temperatures are required, and severe secondary cracking occurs all the way down to C_3 to C_6 fragments.

Ideal hydrocracking is, therefore, readily understood as a special case of classical bifunctional catalysis with a rapid desorption of the primary products formed at the acid sites. The question then arises as to *why* the presence of a highly active dehydrogenation/hydrogenation component can enhance the rate of this desorption so markedly? According to Coonradt and Garwood's model,[32] the decisive quantity is the steady-state concentration of long-chain alkenes *n*-C_iH_{2i} formed from the reactant *n*-alkane. If there is a highly active dehydrogenation/hydrogenation component, the steady-state concentration of *n*-alkenes will essentially assume the equilibrium value, and this is considered to be high enough for rapidly displacing the alkylcarbenium ions from the acid sites through competitive adsorption/desorption. In this case, the chemical steps at the acid sites, i.e., skeletal rearrangements and β-scissions, are

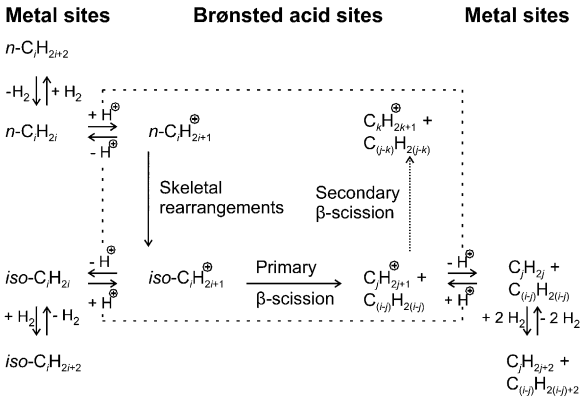

Figure 4. Classical mechanism of isomerization and hydrocracking of an *n*-alkane on a bifunctional catalyst comprising metal sites for dehydrogenation/hydrogenation and Brønsted acid sites.[5,32,42,43]

probably rate- and selectivity-controlling for the overall reaction. This is the case of ideal bifunctional catalysis.

In a complex reaction network as shown in Figure 4, the dehydrogenation/hydrogenation activity threshold, beyond which ideal bifunctional catalysis is attained, depends on several factors, inter alia on the concentration and strength of the Brønsted acid sites and the length of the diffusion paths of the olefinic intermediates, i.e., the average distance between both types of catalytic sites.[5] As a brief notion of this situation it is sometimes stated that, for ideal bifunctional catalysis to occur, the two catalyst functions must be "in balance".[38,39]

A characteristic feature of the classical bifunctional mechanism sketched in Figure 4 is the mass transfer between both types of catalytic sites by diffusion of alkenes. It should be mentioned that precisely this feature has occasionally been questioned. Using various arguments, some authors have instead been advocating mechanistic models in which an important role is ascribed to hydrogen spillover from the metal to the acid sites. In these views, the essential, if not exclusive locus of hydrocarbon conversion is believed to be an acid site, and the spilt-over hydrogen coming from a metal site helps to generate alkylcarbenium ions from the feed *n*-alkane, to desorb the products of carbocation reactions from the acid sites, and/or to avoid the build-up of carbonaceous deposits with the concomitant catalyst deactivation. For example, a model was advanced by Roessner and Roland[44] and Roland et al.[45] in which two coexisting hydrogen species spill over to the acid sites, of which one is a neutral hydrogen atom and the other a positively charged ion. Modified spillover models were proposed, inter alia, by Ebitani et al.[46] and by Fujimoto's group.[47–49]

In another approach based primarily on computational studies and put forward by Kazansky's[50–52] and van Santen's[53] groups, the hydrocarbon adsorbates, e.g., on a zeolite surface, were mainly described as alkoxide species with a considerable degree of covalent bonding to the framework oxygens. In this adsorbed state, hydrocarbon reactions like β-scissions were proposed to occur in a concerted manner, thereby avoiding the intermediacy of primary carbenium ions. Evidence against such a mechanism has later been presented by Denayer et al.[54] and Thibaut et al.,[55,56] especially in cases where alkanes with long hydrocarbon chains were involved.

Independent evidence for the classical mechanism has been presented by a direct observation of olefinic intermediates (C_jH_{2j} or $C_{(i-j)}H_{2(i-j)}$ in Figure 4) leading to the hydrocracked products C_jH_{2j+2} and $C_{(i-j)}H_{2(i-j)+2}$, respectively. This is difficult because the equilibrium concentrations of alkenes $n_{C_jH_{2j}}/n_{C_jH_{2j+2}}$ are very low at the low reaction temperatures (ca. 250 to 300 °C) and high hydrogen pressures (typically around 2 to 5 MPa) applied in experimental studies of ideal hydrocracking. In hydrocracking of *n*-dodecane on a Pd/Ca-Y zeolite, no alkenes at all were detected in the flame ionization detector of the gas chromatograph at reaction temperatures between 300 and 400 °C, for which the yield of hydrocracked products was 100% (see Figure 5). Above 400 °C alkenes appeared in concentrations that were of the same order of magnitude as the calculated equilibrium values. The alkenes observed in this high-temperature region can be attributed to the establishment of the alkenes/alkanes equilibria. Interestingly, light alkenes also appeared under conditions for which the yield of hydrocracked products was below 100%, i.e., under conditions where C_{12} alkanes were still present. At 250 °C, for which the yield of hydrocracked products was as low as 3.6%, i.e., more than 96% of the hydrocarbon mixture consisted of *n*-dodecane and *iso*-dodecanes, the alkene concentrations were four to five orders of magnitude higher than the equilibrium values. This finding can only be understood, if the alkenes/alkanes equilibria of the hydrocracked products are assumed to be approached from the side of the alkenes, and this hydrogenation appears to be impeded by the presence of large amounts of *n*-dodecane and *iso*-dodecanes.[57]

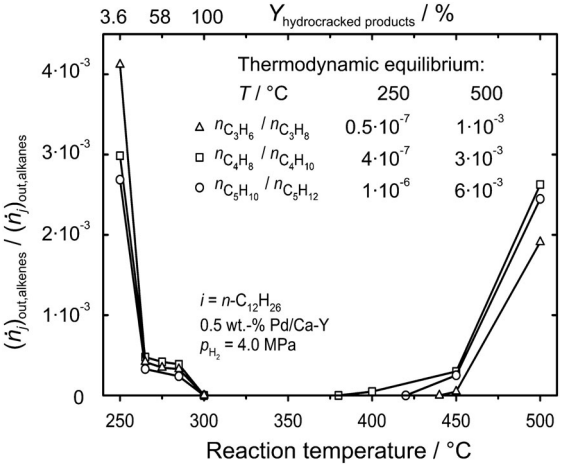

Figure 5. Experimental and equilibrium concentrations of alkenes C_jH_{2j} ($j = 3$, 4, and 5) in hydrocracking of *n*-dodecane on a Pd/Ca-Y zeolite catalyst.[57]

2.3. Ideal bifunctional catalysis as a tool for studying carbocation reactions

It is likely that, in ideal bifunctional catalysis, the chemical steps at the acid sites, i.e., skeletal rearrangements and β-scissions of alkylcarbenium ions (cf. Figure 4), are rate- and selectivity-controlling.[7,28,40] If so, measuring the detailed product selectivities during the hydroconversion of alkanes, especially of long-chain alkanes, on ideal bifunctional catalysts by means of high-resolution capillary gas chromatography can furnish much insight into the chemistry of alkylcarbenium ions. The information gained from such experiments may nicely supplement the one obtained from studying carbocation reactions in liquid superacids.

Before we discuss the mechanism of carbon–carbon bond rupture of alkylcarbenium ions through β-scission, we will throw a look at the skeletal rearrangements that precede β-scission (see Figure 4). It is customary and useful to distinguish between type A and type B rearrangements. In type A rearrangements, the amount of branching in the carbenium ion remains constant, just their positions change. In type B rearrangements, by contrast, the amount of branching increases or decreases. Type A rearrangements were generally found to be

much faster than those of type B.[58,59] Whereas type A rearrangements are generally viewed to occur through a sequence of classical alkyl and hydride shifts, type B rearrangements are believed to proceed via non-classical protonated cyclopropanes (PCPs). Evidence for the PCP mechanism emerged both from the isomerization of *n*-pentane and ^{13}C-labelled *n*-butane in HF-SbF_5[60] and from the selectivities of isomerization of the homologous *n*-alkanes with 8 to 15 carbon atoms on an ideal bifunctional zeolite catalyst.[33]

A similar classification, which is also currently widely accepted, has been introduced for β-scissions of alkylcarbenium ions (Figure 6).[61,62] Type A β-scissions, so named because they are

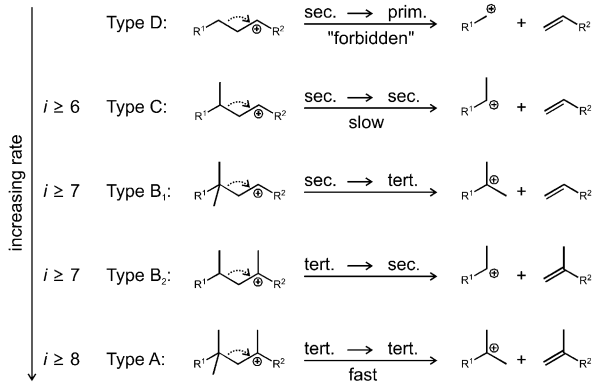

Figure 6. Classification of β-scission reactions of alkylcarbenium ions.[61,62]

by far the fastest, both start and end up in a tertiary carbenium ion. For type A β-scissions to occur, at least eight carbon atoms and three branchings in an α,γ,γ-arrangement are required. In type B β-scissions, a secondary carbenium ion reacts to give a tertiary one (type B_1) or vice versa (type B_2). Type B_1 and type B_2 β-scissions require a minimum of seven carbon atoms and two branches arranged in the γ,γ- and α,γ-positions, respectively. Type C β-scissions start from a secondary and give again a secondary carbenium ion. At least six carbon atoms and one branching in the γ-position are required. For the sake of completeness, type D β-scissions should also be considered. They would start from a secondary carbenium ion and give a primary carbenium ion. Buchanan et al. extended this classification to type E β-scissions, which start from a primary and lead to a tertiary carbenium ion or vice versa.[63] In ideal hydrocracking which typically occurs at mild temperatures of approximately 250 °C, type D and type E β-scissions probably do not play a role at all, due to the high energy content of the primary carbenium ions involved.

Note that the relative rates of β-scissions strongly decrease from type A to type D. Together with the two types of rearrangement reactions and the desorption of carbenium ions as alkenes from the acid sites, the following qualitative order of decreasing rates is likely to govern the chemistry of alkylcarbenium ions:[40]

$$r_{\text{type A β-scission}} > r_{\text{type A rearrangement}} > r_{\text{desorption}} > r_{\text{type B rearrangement}} \approx r_{\text{type B}_1\ \beta\text{-scission}} \approx r_{\text{type B}_2\ \beta\text{-scission}} > r_{\text{type C β-scission}} \gg r_{\text{type D β-scission}}$$

The mechanism of ideal hydrocracking of a long-chain *n*-alkane can now be discussed in a much more detailed manner, e.g., for *n*-decane as the reactant. Figure 7 is an enlarged view of the left-hand half of Figure 4 and starts with a member of the secondary decyl cations. Its type D β-scission would lead to a primary carbenium ion, which is forbidden at the mild reaction conditions, in line with the total absence of methane and ethane in the hydrocracked products.

The secondary decyl cation hence undergoes a type B rearrangement via protonated cyclopropanes. The resulting monobranched decyl cation can have three different fates: i) A desorption followed by hydrogenation to a monobranched *iso*-decane (see Figure 2 at mild conditions), ii) a second type B rearrangement to a dibranched decyl cation or iii) a type C β-scission leading to unbranched fragments with 3 to $i-3=7$ carbon atoms. The dibranched decyl cations have essentially the same options of consecutive reactions. Indeed, dibranched *iso*-decanes appear in the product at enhanced conversions. Instead of being desorbed, they can be cleaved, but this time in a type B β-scission leading to one branched and one unbranched moiety with 3 to $i-3=7$ carbon atoms. If, however, the dibranched decyl cations rearrange again, a tribranched decyl cation forms which inevitably shows the very rapid type A β-scission. This time, the fragments contain 4 to $i-4=6$ carbon atoms and are both branched.

Such a pathway by means of a triple type B rearrangement followed by type A β-scissions accounts for the formation of C_4 to C_{i-4} as the main hydrocracked products (Figure 1). Moreover, it explains the large amount of branched isomers in the hydrocracked products from a long-chain *n*-alkane (Figure 3), and it is consistent with the occurrence of monobranched and dibranched isomers of the feed *n*-alkane in significant yields at moderate conversions (Figure 2).

On the other hand, to account for the full spectrum of product hydrocarbons, one has to allow for some type B β-scissions

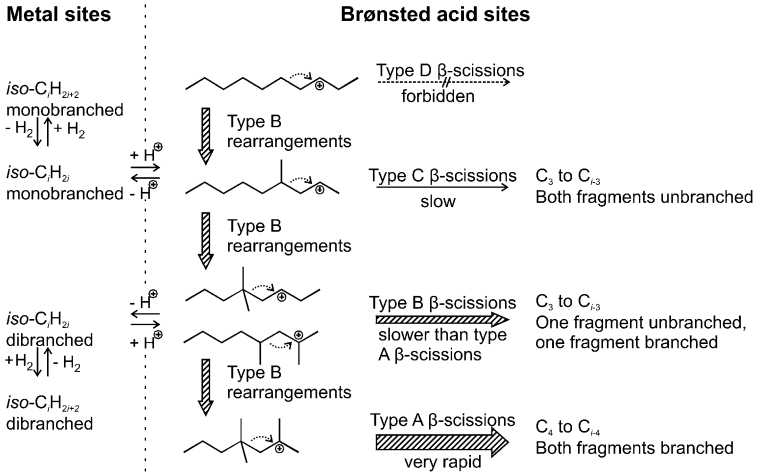

Figure 7. Proposed pathway of ideal hydrocracking of a long-chain *n*-alkane *n*-C_iH_{2i+2} on a bifunctional catalyst.

of dibranched carbenium ions and even some small contribution of type C β-scissions of monobranched carbenium ions, beside the mainstream pathway by means of type A β-scissions of tribranched carbenium ions (Figure 7). The type B β-scissions are needed to explain the formation of some C_3 and C_{i-3} fragments (no C_3 can be formed by means of type A β-scissions). At the same time, invoking the occurrence of some type B β-scissions gives a straightforward explanation for the fact that the carbon number fraction C_{i-3} formed by abstraction of C_3 is unusually rich (≈90%, see Figure 3) in branched alkanes. If, however, *all* C_3 were formed by type B β-scissions of dibranched carbenium ions, the content of branched alkanes in the fraction C_{i-3} would be expected to amount to 100% instead of the measured 90%. This small remaining deviation is readily accounted for by allowing some small contribution of type C β-scissions of monobranched carbenium ions.

There is independent evidence for such a pathway of ideal hydrocracking mainly by means of type A β-scissions of tribranched carbenium ions. These precursors of type A β-scissions are relatively bulky species. Although they can be readily formed inside the spacious pore system of zeolite Y, one would expect their formation to be severely hindered under conditions of shape-selective hydrocracking, e.g., in a catalyst based on zeolite ZSM-5. If so, the main reaction path inside such a catalyst would be through type B β-scissions, which start from less bulky, dibranched precursors (Figure 7). This would be expected to have far-reaching repercussions on the nature of the hydrocracked products. In Figure 8, the molar carbon number

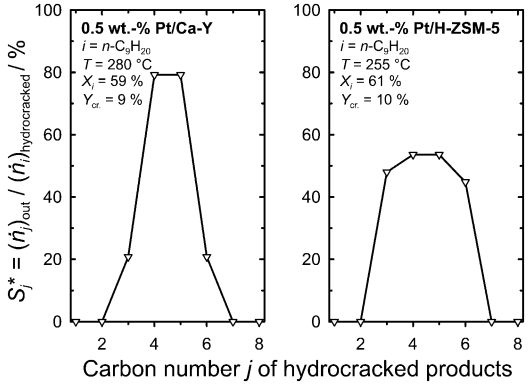

Figure 8. Carbon number distributions of the hydrocracked products from *n*-nonane on bifunctional catalysts based on a large-pore (Pt/Ca-Y) and a medium-pore (Pt/H-ZSM-5) zeolite.[61]

distributions in hydrocracking of *n*-nonane on a large-pore Pt/Ca-Y and a medium-pore Pt/ZSM-5 catalyst are compared at equal conversion and yield of hydrocracked products.[61]

On Pt/H-ZSM-5, C_3 and C_6 are no longer by-products occurring in minor quantities, but are now main hydrocracked products, as one would expect in a route by means of type B β-scissions (see Figure 7). It is exactly the same mechanistic effect as the one that is exploited in industrial fluid catalytic cracking, when H-ZSM-5 is added as a co-catalyst to ultrastable zeolite Y to enhance the yield of propene.

Bearing in mind that type A and type B β-scissions of alkylcarbenium ions require at least eight and seven carbon atoms, respectively, one would predict a pronounced dependence of the rate of hydrocracking on the carbon number of the feed in the range C_6 to C_8. Figure 9 shows the results of converting

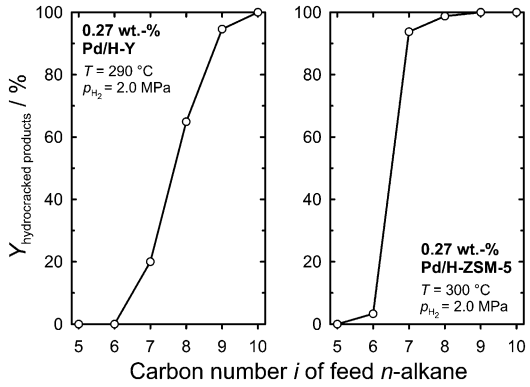

Figure 9. Yields of hydrocracked products from *n*-alkanes with five to ten carbon atoms on a large-pore (left) and a medium-pore (right) zeolite catalyst. For a given catalyst, the reaction conditions are identical for all six *n*-alkane reactants.[64]

the pure *n*-alkanes with five to ten carbon atoms under identical conditions on a large-pore and a medium-pore zeolite catalysts.[64] Plotted against the carbon number of the feed *n*-alkane are the yields of hydrocracked products. The curve for the shape-selective Pd/H-ZSM-5 catalyst shows a very steep jump between *n*-hexane and *n*-heptane, in-line with the conjecture that type B β-scission is the predominating cracking mechanism in this medium-pore zeolite. The curve for the large-pore zeolite is less steep, but the essential result is that the large jump now occurs between *n*-heptane and *n*-octane.

It should be mentioned that, in the early 1990s, Sie proposed a modified mechanism for acid-catalyzed cracking of carbon–carbon bonds.[65] Based on the now generally accepted view that type B *isomerizations* proceed via non-classical protonated cyclopropanes, he suggested a route for cracking via similar intermediates with cyclic structures and non-classical bonds. However, even though almost 20 years elapsed since the proposal of Sie's mechanism, it has failed to receive widespread acceptance, and has been recently severely questioned by Berner and East on theoretical grounds.[66] These same authors also undertook ab initio molecular dynamics simulations of cracking of alkylcarbenium ions, and their results seem to give independent support for the classical mechanism outlined in the present paper over Kazansky's/van Santen's concerted mechanism[50] and Sie's[65] non-classical mechanism.[66]

3. Hydrocracking of Naphthenes

3.1. Low rates of β-scissions of endocyclic carbon–carbon bonds

Hydrocracking of naphthenes on bifunctional catalysts follows reaction paths, which resemble those of alkanes. There is, how-

ever, one significant difference: carbon–carbon bonds, that are part of the naphthenic ring, show a remarkable reluctance to undergo β-scission. This was nicely demonstrated by Brouwer and Hogeveen[67] who studied the type A β-scissions of the aliphatic 2,4,4-trimethylpentyl cation and its alicyclic counterpart, the 2,4,4-trimethylcyclopentyl cation in the superacid FSO_3H-SbF_5-SO_2ClF. Although the former cation underwent β-scission readily at −73 °C, the analogous naphthenic carbenium ion did not react at all, even not at the much higher temperature of 0 °C.

These same authors advanced a good explanation of the effect (Figure 10):[67,68] In the aliphatic carbenium ion, there is free rotation around the α-bond, and in the most stable conformation the vacant *p*-orbital at the positively charged carbon atom and the β-bond to be broken are ideally coplanar. Hence,

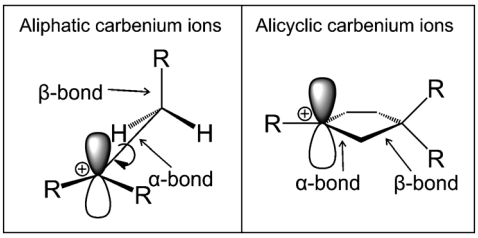

Figure 10. The role of orbital orientation for the easiness of β-scissions of alkylcarbenium ions, after Brouwer and Hogeveen.[67,68]

there is a very efficient orbital overlap in the transition state of β-scission, and the reaction proceeds smoothly. A completely different orbital orientation is encountered in the alicyclic carbenium ion: Now, the β-bond forms part of a ring, and it is fixed in a position perpendicular or near-perpendicular to the vacant *p*-orbital. Hence, there is minimal orbital overlap in the transition state, and β-scission proceeds sluggishly, if at all. The effect is expected to be more pronounced in five-membered rings due to their planarity, but it is also present, maybe to a lesser extent, in six-membered rings.

The low rate of cleavage of endocyclic carbon–carbon bonds has strong repercussions on the course of hydroconversion of naphthenes on bifunctional catalysts. For example, the comparative hydroconversion of 2-methylheptane and ethylcyclohexane was studied on a Pd/La-Y zeolite in the temperature range of 200 to 300 °C.[69] Both C_8 hydrocarbons were equally reactive, and the alkane behaved essentially as shown for *n*-tridecane in Figure 2: Mono- and dibranched isomers (but no tribranched ones) were formed up to moderate conversions, at elevated conversions hydrocracking occurred. The naphthene, by contrast, did give large amounts of trimethylcyclopentanes, and essentially no ring opening was observed up to very high conversions above 95%. This is a key result which supports the pathway shown in Figure 7 by suggesting that tribranched alkylcarbenium ions are formed from an alkane feed at the acid sites, but once formed they disappear by means of the very fast type A β-scission. With a naphthenic feed, the tribranched cycloalkylcarbenium ions do not undergo a rapid type A β-scission, instead they are desorbed from the acid sites and appear in the product as tribranched isomers of the naphthenic ethylcyclohexane feed.

3.2. The paring reaction

If the naphthenic model hydrocarbon contains a sufficiently high number of carbon atoms ($i \geq 10$), it still shows the same reluctance to open the ring, but it can escape into another type of reaction: The carbocations at the acid sites undergo a series of skeletal type A and type B rearrangements (including contractions and enlargements between six- and five-membered rings), until an α,γ,γ-tribranched structure is reached, which can undergo the very rapid type A β-scission in the *alkyl side-chain*. For C_{10} naphthenes, there are three such structures which are depicted in Figure 11. Their type A β-scissions lead to fragments, which, upon desorption from the acid sites and hydrogenation at the metal sites, end up as *iso*-butane and methylcyclopentane exclusively.

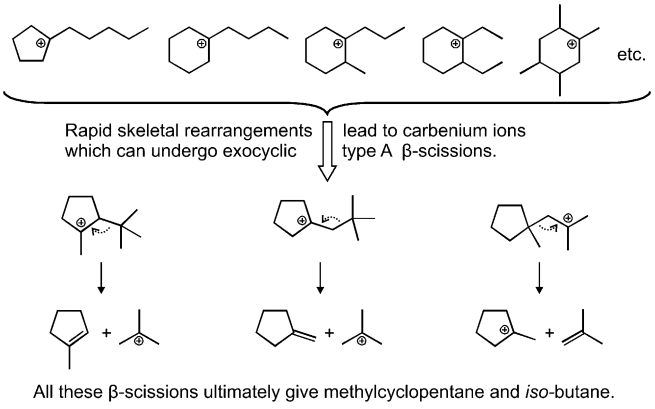

Figure 11. The paring reaction:[70–72] Hydrocracking of C_{10} naphthenes with any arbitrary structure (five examples are shown) involves a series of skeletal rearrangements until a carbon skeleton is reached which allows an *exocyclic* type A β-scission. In all cases, hydrocracking leads to *iso*-butane and methylcyclopentane.

In fact, the selective formation of *iso*-butane and methylcyclopentane in hydrocracking of C_{10} naphthenes with arbitrary structure was discovered about 50 years ago by Chevron researchers using a NiS/SiO_2-Al_2O_3 catalyst.[70,71] They coined the term "paring reaction" which is meant to express that, with a reactant like tetramethylcyclohexane, the *tert*.-butyl group is by no means preformed; it rather appears that the methyl groups are pared or peeled off and released as *iso*-butane, while the naphthenic ring remains intact. Later, the same selectivities were found in hydrocracking of C_{10} naphthenes using bifunctional zeolite catalysts.[64,72] As shown in Figure 12, the carbon number distribution of the hydrocracked products from a C_{10} naphthene is M-shaped with pronounced maxima at C_4 and C_6. This is in sharp contrast to the bell-shaped carbon number distribution obtained in ideal hydrocracking of the *n*-alkane with the same carbon number which is also depicted in Figure 12.

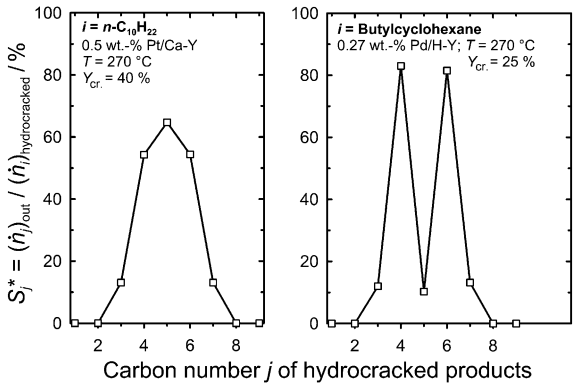

Figure 12. Carbon number distributions of the hydrocracked products from *n*-decane (bell-type curve) and butylcyclohexane (M-type curve) on bifunctional zeolite catalysts.[64,72]

Although *iso*-butane (ca. 95% of the C_4 fraction) and methylcyclohexane (ca. 95% of the C_6 fraction) are strongly dominating the hydrocracked products from butylcyclohexane, other hydrocarbons are formed in small amounts as well. These are mainly propane, *n*-butane, *iso*-pentane, cyclohexane and C_7 hydrocarbons. It has been shown[64,72,73] that the occurrence of these minor by-products can be readily accounted for by invoking a small contribution of type B, possibly even a very small contribution of type C β-scissions in the alkyl side chains of C_{10} cycloalkylcarbenium ions. This is in complete analogy to the postulated mechanism of ideal hydrocracking of long-chain *n*-alkanes (see Figure 7).

Summing up, the unifying mechanistic principle in bifunctional hydrocracking of alkanes and naphthenes is their tendency to undergo, as the main pathways, type A β-scissions of tribranched alkylcarbenium ions and exocyclic type A β-scissions of tribranched cycloalkylcarbenium ions, respectively. It should be stressed that alkanes with less than eight carbon atoms and naphthenes with less than ten carbon atoms are excluded from these most favorable hydrocracking routes. They hence escape into various other reactions and peculiar hydrocracking mechanisms, which must not be generalized to larger hydrocarbons, as they occur in the feedstock to a real hydrocracker. We, therefore, recommend that, in model hydrocarbon studies on catalytic hydrocracking, an alkane with $i \geq 8$ or a naphthene with $i \geq 10$ be used, if the results are of interest in the general context of hydrocracking heavy oils.

3.3. The Spaciousness Index

The tribranched precursors of type A β-scissions governing the chemistry of hydrocracking are relatively bulky species which can be readily accommodated inside the spacious pore system of zeolite Y. In a shape-selective environment, however, for example in the pores of zeolite ZSM-5, the spatially demanding tribranched carbenium ions cannot be formed, with the consequence that the mechanism escapes into type B and type C β-scissions, as already discussed in Section 2.3 (Figures 8 and 9) for hydrocracking of *n*-alkanes. A similar shift in the mechanism happens, if hydrocracking of a C_{10} naphthene is conducted in zeolite catalysts with decreasing pore width. As a consequence, e.g., in hydrocracking of butylcyclohexane, *iso*-butane and methylcyclopentane gradually lose their role as strongly predominating product hydrocarbons and, concomitantly, the selectivity shifts to other fragments. A careful scrutiny of the selectivities of hydrocracking butylcyclohexane in a variety of zeolite catalysts with known pore widths revealed that the yield ratio of *iso*-butane and *n*-butane correlates well with the pore width of the zeolite. As the numerical value of this yield ratio increases with increasing space inside the pores, it was named the "Spaciousness Index" (SI),[73,74]

$$SI \equiv \frac{Y_{iso-\text{butane}}}{Y_{n-\text{butane}}}$$

in hydrocracking of a C_{10} naphthene, preferentially butylcyclohexane or pentylcyclopentane. SI is measured on a Brønsted acid form of the zeolite modified with a small amount of a noble metal, typically 0.1 to 0.5 wt.% of palladium or platinum.

In Figure 13 SI values for a number of common zeolites are given.[74–76] Clearly, SI is most appropriate for characterizing the pore width of 12-membered ring zeolites, for these the span of SI values ranges from ca. 3 to 21. It, hence, ideally supplements similar indices, viz. the Constraint Index introduced by Frilette et al.[77] and the Refined or Modified Constraint Index proposed by Martens et al.,[78] which are suitable for probing the pore width of 10-membered ring zeolites.

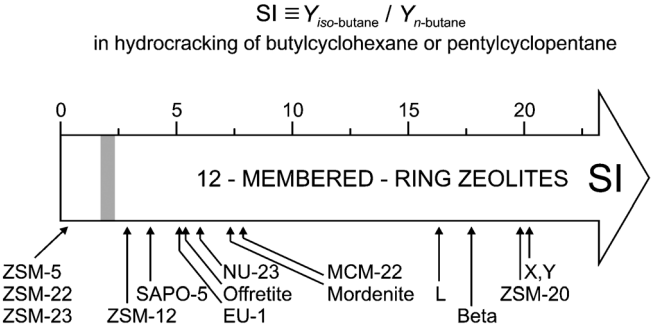

Figure 13. Spaciousness Indices of various zeolites.[74–76]

The Spaciousness Index has proven to be useful for a number of applications, for example for probing the pore width of zeolites with unknown structure or for detecting the effect of coke deposition during a catalytic reaction or any other modification of the zeolite on the effective pore width. It is easily determined and very user-friendly since i) there is no catalyst deactivation during its determination, ii) a product analysis for *iso*- and *n*-butane suffices, which is very easy and can be completed quickly, and iii) SI is, in a very broad range, independent of the conversion of the C_{10} naphthene and the yield of hydrocracked products. The last-mentioned feature is particularly advantageous in the routine application, as there is no prescribed conversion or yield to be attained in the catalytic experiment; hence, a tedious search for appropriate experimental conditions is often superfluous. These and other fea-

tures of the Spaciousness Index have been discussed in more detail in the literature.[79,80]

4. Hydrocracking of One-Ring Aromatics into a Synthetic Steamcracker Feed

Aromatic hydrocarbons, preeminently benzene and *para*-xylene, are important base chemicals used in numerous industrial syntheses.[81] Moreover, even larger amounts of aromatics are spent in motor gasoline where they are the main contributors to the required high octane numbers. On the other hand, aromatics in gasoline can also bring about undesired effects. For example, as their hydrogen content is low, their combustion necessarily results in elevated carbon dioxide emissions and, under certain engine conditions, their combustion can be accompanied by the occurrence of the carcinogenic benzene in the exhaust gas. The ecology-driven clean-fuel legislation therefore aims, inter alia, at lowering the aromatics content of gasoline. In 2005 the EU, for example, set the maximal aromatics content of gasoline to 35 vol.%, and a further mandated reduction in the future cannot be excluded.

In such a case, the hydrocarbon markets may be faced with a surplus of aromatics, and options have to be made available to the refining and petrochemical industries for either cutting down the production of aromatics or converting excess aromatics into valuable products. The two dominating processes for producing aromatic hydrocarbons are catalytic reforming of heavy gasoline and steam cracking of light naphtha (i.e., the C_5 and C_6 fraction from petroleum). The significance of catalytic reforming in modern petroleum refining is unlikely to decrease markedly, as it co-produces large amounts of hydrogen in an environmentally friendly manner, and this hydrogen is indispensable for the manufacture of ever cleaner fuels. The objective of steam cracking of light naphtha is to produce the base chemicals ethene and propene, their combined yields being typically around 50%. Among the by-products are hydrogen (about 3%) and around 20 to 25% of an aromatics-rich fraction referred to as "pyrolysis gasoline". Today, pyrolysis gasoline, after a selective hydrogenation, is mostly returned to a refinery where it is blended into motor gasoline.

As an alternative, a new hydrocracking process has been envisaged, by which the aromatics-rich pyrolysis gasoline is selectively hydrocracked into a mixture of ethane, propane, and *n*-butane.[82] These light alkanes are excellently suited for being recycled into the steam cracker where they react in high yields to ethene and propene. The net effect of such an operation would be a noticeable saving of light naphtha for making the same amount of ethene and propene.

Two process options have been identified for the new hydrocracking of pyrolysis gasoline:[81] in the so-called one-stage route, the aromatics-rich pyrolysis gasoline is directly converted with hydrogen on a bifunctional zeolite catalyst, such as Pd/H-ZSM-5 at a temperature of ca. 400 °C and a hydrogen pressure of approximately 6.0 MPa. Under these conditions the combined yields of ethane, propane and *n*-butane ("C_{2+}-*n*-alkanes") from various aromatic model hydrocarbons were found to be between 70 and 95%.[83] In the two-stage route, the aromatics in the pyrolysis gasoline are first hydrogenated to the corresponding naphthenes on a conventional hydrogenation catalyst. In a second stage, these naphthenes are hydrocracked on a monofunctional acidic zeolite catalyst, again at about 400 °C and a hydrogen pressure of 6.0 MPa.

The best suited zeolite for the second stage seems to be H-ZSM-5.[84] Typical results obtained on such a catalyst with methylcyclohexane as model hydrocarbon are depicted in Figure 14. It can be seen that at 400 °C methylcylohexane is

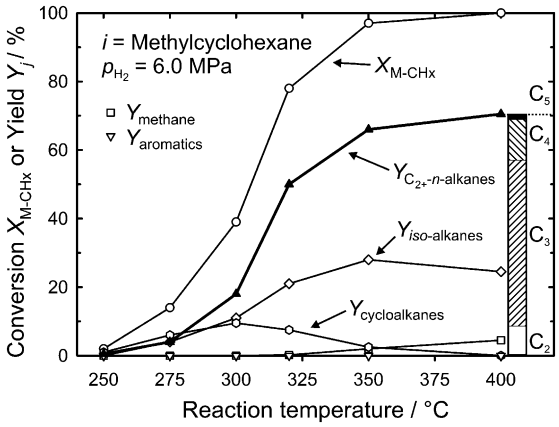

Figure 14. Product yields in the hydrocracking of methylcyclohexane on zeolite H-ZSM-5.[82b]

completely converted, namely into the desired C_{2+}-*n*-alkanes with propane as the main product, some 25% of *iso*-alkanes (mostly *iso*-butane), and ca. 5% methane. *Iso*-alkanes are somewhat less desired than *n*-alkanes, as they tend to give lower yields of alkenes in the steam cracker. Methane is a very undesired product, because its formation consumes significant amounts of hydrogen, and it is inert in the steam cracker.

The catalytic chemistry in the second process stage is particularly interesting. Under the typical reaction conditions, large amounts of hydrogen (ca. 2 moles per mole of methylcyclohexane fed) are incorporated into the hydrocracked products,[85] even though the catalyst does not contain a metal component. At first glance, this capability of metal-free H-ZSM-5 zeolite to activate molecular hydrogen may be astonishing, but it is in agreement with a few literature reports on the use of zeolite H-ZSM-5 as a catalyst in other hydrocarbon reactions under similar reaction conditions.[18,19] In fact, using the so-called "cracking mechanism ratio" (*CMR*) introduced by Wielers et al.,[86] evidence has been obtained for a significant contribution of Haag–Dessau hydrocracking on zeolite H-ZSM-5 at $T=$ 400 and $P_{H_2}=6.0$ MPa.[81] Its salient feature is a direct attack of the proton of the Brønsted acid site on C-C or C-H σ-bonds.[13–17] It was fortuitously found that the highest contribution of Haag–Dessau hydrocracking and the highest yields of the desired C_{2+}-*n*-alkanes are achieved, if the H-ZSM-5 catalyst is modified with ultra-low amounts of a noble metal, e.g., 10 to 100 wt.-ppm of palladium.[87]

Since the discovery of this new ring opening chemistry, a number of groups have been looking at various aspects related to the catalytic conversion of pyrolysis gasoline into a synthetic steam cracker feed, either through the direct or the two-stage route.[88–94] It remains to be seen, whether this catalytic chemistry is getting economically viable, if and when a more far-reaching reduction of the aromatics content in gasoline will be mandated by legislation. In any event, the conversion of surplus aromatics is an impressive example for the versatility of catalytic hydrocracking, and the same holds true for another potential application that is briefly discussed in the subsequent Section.

5. Selective Ring Opening of Multi-Ring Naphthenes Derived from Polynuclear Aromatics

For various reasons, polynuclear aromatic hydrocarbons (PAHs) are particularly undesired components of diesel fuel. They possess poor ignition properties in the engine and, correspondingly, very low cetane numbers (*CN*s). Moreover, they contribute to unfavorable cold-flow properties and a too high density of the fuel. They are generally considered to be precursors in the formation of soot and particular matter during the combustion, and their low hydrogen content ($n_H/n_C < 1$) brings about relatively high carbon dioxide emissions per heating value. With this in mind, the content of PAHs in diesel fuel has been limited in many regions of the world, e.g., to 8 wt.% in the European Union, and an even more stringent legislation is under discussion. To meet the pertinent specifications, certain refinery streams, which are notoriously rich in PAHs, such as the so-called light cycle oil from fluid catalytic crackers or middle distillate fractions from cokers, can in some instances not fully be blended into commercial diesel fuel.

One way for solving the problems created by PAHs in diesel fuel consists in their hydrogenation to the corresponding multi-ring naphthenes followed by their selective ring opening, as shown in Figure 15 for the PAH naphthalene. Ring opening is a special case of hydrocracking for which an endocyclic carbon–carbon bond in a naphthene is to be broken. It is evident from Figure 15 that a mere ring hydrogenation of naphthalene to decalin brings about a significant improvement of both the cetane number and the cold-flow properties (expressed in a simplified manner as the melting points of the pure hydrocarbons), but the gain in cetane number is insufficient for the requirements of commercial diesel fuel (*CN* ≈ 50). It is only after the opening of a single ring to alkylated one-ring naphthenes or, even better, the opening of both rings to open-chain decanes that the required cetane numbers and cold-flow properties are reached. The reaction network finally shows that the desired ring-opening products are intermediates which can undergo consecutive hydrocracking to alkanes (see Section 2) or naphthenes (the paring reaction, see Section 3) with less than 10 carbon atoms. This degradation of the carbon number is highly undesired, since it is equivalent to a loss of hydrocarbons in the boiling range of diesel fuel. The terms "selective ring opening" or, synonymously, "selective hydrodecyclization" therefore refer to a ring opening reaction under retention of the carbon number, and with as little as possible hydrocracking to light hydrocarbons.

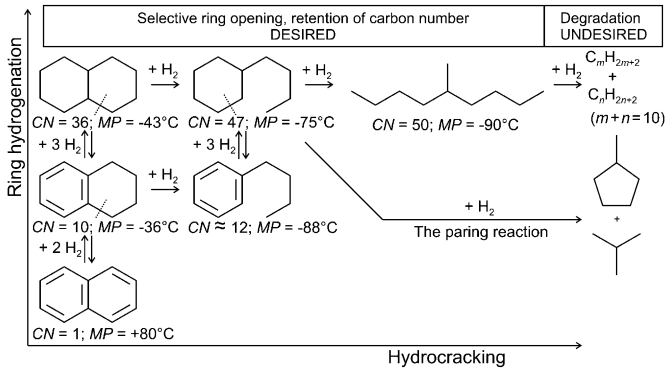

Figure 15. Reaction network for complete ring hydrogenation of a polynuclear aromatic hydrocarbon into the corresponding multi-ring naphthene followed by selective ring opening.[97] *CN*: Cetane number; *MP*: Melting point. The values for the cetane numbers were taken from Ref. [95].

With the popularization of the diesel passenger car, since about the year 2000, and the ever increasing consumption of diesel fuel, a number of groups have initiated investigations into the selective catalytic ring opening. Reviews covering this work are available in the literature.[95–97] For the most part, decalin or tetralin were used as model hydrocarbons, and the catalysts employed can be broadly classified into monofunctional acidic zeolites, such as H-Y, H-Beta, and H-mordenite,[98,99] and bifunctional versions of the same zeolites modified with about 1 to 2 wt.% of a noble metal, often platinum or iridium.[98,100–104] The performance of monofunctional zeolites generally turned out to be unsatisfactory, since the maximal yields of ring opening products were low (less than 20%), at elevated conversions too high amounts of light hydrocarbons were made, and the catalysts deactivated while on-stream, owing to the build-up of carbonaceous deposits. Bifunctional zeolite catalysts were more promising in that they did not deactivate, and the maximal yields of ring opening products were higher (up to ≈30%, in one exceptional case a yield of ring opening products as high as 60% has been claimed for decalin hydroconversion on Ir/H-Beta[104]). The literature on hydrogenolytic ring opening on noble metals is very scarce, but one report deserves particular attention, as it provides a wealth of mechanistic information concerning the hydrogenolysis of one- and two-ring naphthenes on various noble metals, especially on iridium.[105]

Although this first-generation literature on selective catalytic ring opening has furnished a large body of relevant and most interesting information, it has also left unanswered various important questions. For example, the ring opening products from decalin or tetralin were usually reported to consist of C_{10} naphthenes with a single ring.[100–104] By contrast, extremely scant information is available concerning the formation or not of open-chain decanes. In a few reports the occurrence of decane isomers was qualitatively mentioned.[104,106,107] In just one paper quantitative yields of open-chain decanes formed in the hydroconversion of decalin on a Pt,Ir/H-Y zeolite were given: their maximum yield was reported to be 4%.[108] It was

only very recently that improved analytical procedures for the separation and identification of the multi-component reaction products were described.[109] Using these procedures it was demonstrated that significantly higher yields of open-chain decanes than previously reported can be achieved in the hydroconversion of decalin on typical bifunctional catalysts, namely up to 12% on a highly lanthanum-exchanged Pt/La-X zeolite catalyst.[109] Even much higher yields of open-chain decanes between 30 and 40% were attained in the ring opening of decalin on low-acidity bifunctional catalysts, such as Ir/Na,H-Y and Pt/Na,H-Y zeolites (Y_{OCDs} = 31% and 39%, respectively).[110] It was, moreover, shown recently that the quantitative distribution of the hydrocracked products with one to nine carbon atoms is a very valuable source of information concerning the ring opening mechanisms that are operative on a given catalyst. Figure 16 shows distribution curves obtained

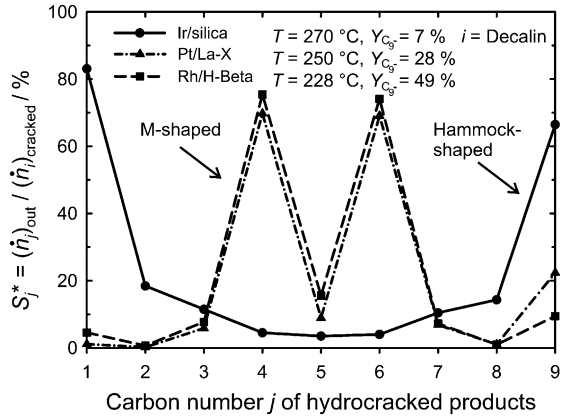

Figure 16. Carbon number distributions of the hydrocracked products from decalin on two bifunctional zeolite catalysts (Pt/La-X and Rh/H-Beta) and on Ir/silica with a non-acidic support.[111]

for ring opening of decalin on two bifunctional zeolite catalysts, viz. Pt/La-X and Rh/H-Beta, and one Ir/silica catalyst with a non-acidic carrier. On the two former catalysts, M-type distribution curves are found that are strong evidence for a cationic hydrocracking mechanism resembling the one of the paring reaction (Figure 12, right-hand part).[111] By contrast, a completely different curve with a strong preponderance of C_1 and C_9 is found on Ir/silica. This curve, for which the term "hammock-type" was coined,[111] is indicative for a hydrogenolytic mechanism on iridium. It remains to be seen to what extent the ring opening catalysts can be improved in the years to come. This is one of the key questions for the viability of a commercial ring opening process for upgrading aromatics-rich middle distillate streams into premium diesel fuel. Furthermore, ring opening of polynuclear aromatics is an excellent example for the versatility of catalytic hydrocracking and its potential for solving upcoming problems within the future fuels and aromatics markets.

Summary and Outlook

Hydrocracking is the generic term for hydrocarbon reactions in which at least one carbon–carbon bond is broken and the free valencies thereby formed are saturated by hydrogen. Such a stoichiometry can be achieved by means of four fundamentally different mechanisms the relative contributions of which depend on the nature of the catalyst: *Bifunctional hydrocracking* proceeds on catalysts comprising both a hydrogenation/dehydrogenation and a Brønsted acid component. Alkenes and carbocations are involved as intermediates. For hydrocracking on monofunctional metallic catalysts, the term *hydrogenolysis* is customary. Likewise, hydrocracking on monofunctional acidic catalysts can be achieved under certain reaction conditions, we suggest the term *Haag–Dessau hydrocracking* for the pertinent mechanism. Finally, *thermal hydrocracking* can occur even without a catalyst at high temperatures and hydrogen pressures.

Much attention has been devoted in this review to the mechanism of bifunctional hydrocracking because it is most relevant for the industrial refinery process, which is used on a large scale to convert heavy vacuum gas oil into high-quality transportation fuels. Emphasis was placed in this discussion to the now widely accepted concept of ideal hydrocracking of long-chain *n*-alkanes. It proceeds on bifunctional catalysts with a strong hydrogenation/dehydrogenation activity, typically platinum or palladium. As salient features, it enables skeletal isomerization of long-chain *n*-alkanes with high selectivities and yields and primary hydrocracking selectivities with bell-shaped carbon number distributions of the hydrocracked products. It appears that in ideal hydrocracking all elementary steps at the metal sites, mass transfer of alkenes between both types of catalytic sites, and desorption of carbenium ions from the acid sites are fast compared to the chemical rearrangement and β-scission steps of alkylcarbenium ions at the acid sites. The latter are hence rate and selectivity controlling, and measuring the detailed distributions of the isomerized and hydrocracked products may furnish a wealth of information concerning the chemistry of carbocation reactions. Such studies can nicely supplement results gained in the study of carbocation chemistry in liquid superacids. A long-chain *n*-alkylcarbenium ion, for example, experiences three skeletal isomerizations, and the triply branched *iso*-alkylcarbenium ion undergoes a very rapid so-called type A β-scission. Besides, there is a minor contribution of type B and even type C β-scissions of, respectively, dibranched and monobranched *iso*-alkylcarbenium ions.

Bifunctional hydrocracking of naphthenes follows essentially the same mechanistic pathways as alkanes. There is, however, one important difference stemming from a pronounced reluctance of cyclic carbenium ions to undergo cleavage of endocyclic carbon–carbon bonds: This mechanistic peculiarity brings about drastic differences in the distribution of the hydrocracked products when using an alkane and a naphthene with the same carbon number as reactants. The peculiar product distributions obtained in hydrocracking of naphthenes have been known since about 50 years under the term "paring reaction". More recently, it has been found that in hydrocracking of

a C_{10} naphthene, such as butylcyclohexane, on bifunctional zeolite catalysts, the selectivity is strongly influenced by its pore width. Based on this finding, the Spaciousness Index has been defined as the yield ratio of *iso*- and *n*-butane, which is by now a valuable tool for characterizing the pore width of nanoporous materials.

Besides its capability to produce clean, hydrogen-rich transportation fuels from heavy oils, catalytic hydrocracking is appreciated for its versatility. Even now, several process variants are in operation, which meet specific requirements in an oil refining or a petrochemical plant. Examples are mild hydrocracking of vacuum gas oil to be converted by fluid catalytic cracking, dewaxing of lube oil by shape-selective hydrocracking, or the conversion of Fischer–Tropsch wax into premium diesel and jet fuel. Two more recent developments are briefly discussed in this article, viz. hydrocracking of surplus aromatics, e.g., in pyrolysis gasoline, into a synthetic steam cracker feed consisting of ethane, propane and *n*-butane, and selective ring opening of polynuclear aromatics in diesel fuel. The former process seems to be ready for industrial application, but the hurdle to be overcome is probably the cost of the relatively large amounts of hydrogen consumed. A further mandated reduction of the aromatics content in motor gasoline could, however, change the situation and make the process economically more attractive. Particular mention deserves the second stage of the two-stage route in which naphthenes are selectively hydrocracked on a monofunctional shape-selective catalyst, viz. H-ZSM-5.[84] Mechanistically, this is one of the rare examples of Haag–Dessau hydrocracking, which clearly deserves more intense research activities in the future. The field of selective ring opening of multi-ring naphthenes made by complete hydrogenation of polynuclear aromatics appears to be less mature, but worldwide efforts are being undertaken with the aim of finding improved catalysts which enable enhanced yields of ring opening products. The current state of the art has been documented in the recent literature.[95–111] From a mechanistic point of view, this ring opening catalysis is particularly interesting, as it seems to involve elements of both bifunctional hydrocracking and hydrogenolysis on metals.

Keywords: bifunctional catalysis · carbenium ions · hydrocracking · paring reaction · spaciousness index

[1] J. W. Ward in *Preparation of Catalysts III* (Eds.: G. Poncelet, P. Grange, P. A. Jacobs), *Studies in Surface Science and Catalysis*, *Vol. 16*, Elsevier, Amsterdam, **1983**, pp. 587 – 616.
[2] J. Scherzer, A. J. Gruia, *Hydrocracking Science and Technology*, Marcel Dekker, New York, **1996**, pp. 13 – 72.
[3] C. Marcilly, *Acido-Basic Catalysis—Application to Refining and Petrochemistry, Vol. 2*, Editions Technip, Paris, **2006**, pp. 689 – 717.
[4] H. Schulz, J. Weitkamp, *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 46 – 53.
[5] P. B. Weisz in *Advances in Catalysis, Vol. 13* (Eds.: D. D. Eley, P. W. Selwood, P. B. Weisz), Academic Press, New York, London, **1962**, pp. 137 – 190.
[6] H. Pichler, H. Schulz, H. O. Reitemeyer, J. Weitkamp, *Erdöl Kohle Erdgas Petrochem.* **1972**, *25*, 494 – 505.
[7] J. Weitkamp in *Hydrocracking and Hydrotreating* (Ed.: J. W. Ward), *American Chemical Society Symposium Series*, *Vol. 20*, American Chemical Society, Washington, D. C., **1975**, pp. 1 – 27.
[8] J. Weitkamp, *Erdöl Kohle Erdgas Petrochem.* **1978**, *31*, 13 – 22.
[9] F. G. Gault in *Advances in Catalysis, Vol. 30* (Eds.: D. D. Eley, H. Pines, P. B. Weisz), Academic Press, New York, London, **1981**, pp. 1 – 95.
[10] J. R. Anderson in *Advances in Catalysis, Vol. 23* (Eds.: D. D. Eley, H. Pines, P. B. Weisz), Academic Press, New York, London, **1973**, pp. 1 – 90.
[11] J. H. Sinfelt in *Advances in Catalysis, Vol. 23* (Eds.: D. D. Eley, H. Pines, P. B. Weisz), Academic Press, New York, London, **1973**, pp. 91 – 119.
[12] J. H. Sinfelt, *Catal. Rev.* **1970**, *3*, 175 – 205.
[13] W. O. Haag, R. M. Dessau in *8th International Congress on Catalysis, Vol. 2*, Verlag Chemie, Weinheim, **1984**, pp. 305 – 316.
[14] W. O. Haag, R. M. Dessau, R. M. Lago in *Chemistry of Microporous Crystals* (Eds.: T. Inui, S. Namba, T. Tatsumi), *Studies in Surface Science and Catalysis*, *Vol. 60*, Kodansha, Tokyo, and Elsevier, Amsterdam, **1991**, pp. 255 – 265.
[15] H. Krannila, W. O. Haag, B. C. Gates, *J. Catal.* **1992**, *135*, 115 – 124.
[16] S. Kotrel, H. Knözinger, B. C. Gates, *Microporous Mesoporous Mater.* **2000**, *35 – 36*, 11 – 20.
[17] J. Weitkamp, M. Hunger in *Introduction to Zeolite Science and Practice, 3rd ed.* (Eds.: J. Čejka, H. van Bekkum, A. Corma, F. Schüth), *Studies in Surface Science and Catalysis*, *Vol. 168*, Elsevier, Amsterdam, **2007**, pp. 787 – 835.
[18] J. Kanai, J. A. Martens, P. A. Jacobs, *J. Catal.* **1992**, *133*, 527 – 543.
[19] J. Meusinger, A. Corma, *J. Catal.* **1995**, *152*, 189 – 197.
[20] K. Hedden, J. Weitkamp, *Ger. Chem. Eng.* **1985**, *8*, 271 – 181.
[21] J. A. R. van Veen, J. K. Minderhoud, L. G. Huve, W. H. J. Stork in *Handbook of Heterogeneous Catalysis, Vol. 6*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2778 – 2808.
[22] C. Marcilly, *Acido-Basic Catalysis—Application to Refining and Petrochemistry, Vol. 2*, Editions Technip, Paris, **2006**, pp. 666 – 717.
[23] W. R. True, L. Koottungal, *Oil Gas J.* **2010**, *108* (46), 50 – 59.
[24] K. Hedden, J. Weitkamp, *Chem. Eng. Technol.* **1975**, *47*, 505 – 513.
[25] J. Scherzer, A. J. Gruia, *Hydrocracking Science and Technology*, Marcel Dekker, New York, **1996**, pp. 215 – 222.
[26] C. Marcilly, *Acido-Basic Catalysis—Application to Refining and Petrochemistry, Vol. 2*, Editions Technip, Paris, **2006**, pp. 719 – 727.
[27] T. J. Remans, G. Jenzer, A. Hoek in *Handbook of Heterogeneous Catalysis, Vol. 6*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3004 – 3008.
[28] C. Bouchy, G. Hastoy, E. Guillon, J. A. Martens, *Oil Gas Sci. Technol.* **2009**, *64*, 91 – 112.
[29] J. Scherzer, A. J. Gruia, *Hydrocracking Science and Technology*, Marcel Dekker, New York, **1996**, pp. 238 – 242.
[30] J. Weitkamp, S. Ernst in *Guidelines for Mastering the Properties of Molecular Sieves* (Eds.: D. Barthomeuf, E. G. Derouane, W. Hölderich), *NATO ASI Series B: Physics*, *Vol. 221*, Plenum Press, New York, London, **1990**, pp. 343 – 354.
[31] B. S. Greensfelder, H. H. Voge, G. M. Good, *Ind. Eng. Chem.* **1949**, *41*, 2573 – 2584.
[32] H. L. Coonradt, W. E. Garwood, *Ind. Eng. Chem. Proc. Des. Dev.* **1964**, *3*, 38 – 45.
[33] J. Weitkamp, *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 550 – 558.
[34] M. Steijns, G. Froment, P. Jacobs, J. Uytterhoeven, J. Weitkamp, *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 654 – 660.
[35] J. A. Martens, P. A. Jacobs, J. Weitkamp, *Appl. Catal.* **1986**, *20*, 239 – 281.
[36] J. A. Martens, P. A. Jacobs, J. Weitkamp, *Appl. Catal.* **1986**, *20*, 283 – 303.
[37] G. E. Giannetto, G. R. Perot, M. R. Guisnet, *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 481 – 490.
[38] T. F. Degnan, C. R. Kennedy, *AIChE J.* **1993**, *39*, 607 – 614.
[39] J. W. Thybaut, C. S. L. Narasimhan, J. F. Denayer, G. V. Baron, P. A. Jacobs, J. A. Martens, G. B. Marin, *Ind. Eng. Chem. Res.* **2005**, *44*, 5159 – 5169.
[40] C. Marcilly, *Acido-Basic Catalysis—Application to Refining and Petrochemistry, Vol. 1*, pp. 223 – 238.
[41] K. P. de Jong, J. Zečevič, H. Friedrich, P. E. de Jongh, M. Bulut, S. van Donk, R. Kenmogne, A. Finiels, V. Hulea, F. Fajula, *Angew. Chem.* **2010**, *122*, 10272 – 10276; *Angew. Chem. Int. Ed.* **2010**, *49*, 10074 – 10078.
[42] G. A. Mills, H. Heinemann, T. H. Milliken, A. G. Oblad, *Ind. Eng. Chem.* **1953**, *45*, 134 – 137.
[43] P. B. Weisz, E. W. Swegler, *Science* **1957**, *126*, 31 – 32.

[44] F. Roessner, U. Roland, *J. Mol. Catal. A* **1996**, *112*, 401 – 412.
[45] U. Roland, T. Braunschweig, F. Roessner, *J. Mol. Catal. A* **1997**, *127*, 61 – 84.
[46] K. Ebitani, J. Tsuji, H. Hattori, H. Kita, *J. Catal.* **1992**, *135*, 609 – 617.
[47] K. Fujimoto, K. Maeda, K. Aimoto, *Appl. Catal. A* **1992**, *91*, 81 – 86.
[48] A. Zhang, I. Nakamura, K. Aimoto, K. Fujimoto, *Ind. Eng. Chem. Res.* **1995**, *34*, 1074 – 1080.
[49] K. Tomishige, A. Okabe, K. Fujimoto, *Appl. Catal. A* **2000**, *194 – 195*, 383 – 393.
[50] V. B. Kazansky, I. N. Senchenya, *J. Catal.* **1989**, *119*, 108 – 120.
[51] V. B. Kazansky in *Advanced Zeolite Science and Applications* (Eds.: J. C. Jansen, M. Stöcker, H. G. Karge, J. Weitkamp), *Studies in Surface Science and Catalysis*, *Vol. 85*, Elsevier, Amsterdam, **1994**, pp. 251 – 272.
[52] V. B. Kazansky, *Catal. Today* **1999**, *51*, 419 – 434.
[53] M. V. Frash, R. A. van Santen, *Top. Catal.* **1999**, *9*, 191 – 205.
[54] J. F. Denayer, G. V. Baron, G. Vanbutsele, P. A. Jacobs, J. A. Martens, *J. Catal.* **2000**, *190*, 469 – 473.
[55] J. W. Thybaut, G. B. Marin, G. V. Baron, P. A. Jacobs, J. A. Martens, *J. Catal.* **2001**, *202*, 324 – 339.
[56] J. W. Thybaut, C. S. L. Narasimhan, G. B. Marin, J. F. Denayer, G. V. Baron, P. A. Jacobs, J. A. Martens, *Catal. Lett.* **2004**, *94*, 81 – 88.
[57] J. Weitkamp, H. Schulz, *J. Catal.* **1973**, *29*, 361 – 366.
[58] D. M. Brouwer, H. Hogeveen in *Progress in Physical Organic Chemistry, Vol. 9* (Eds.: A. Streitwieser, Jr, R. W. Taft), Interscience Publishers, New York, **1972**, pp. 179 – 240.
[59] J. Weitkamp, H. Farag, *Acta Physica et Chemica* **1978**, *24*, 327 – 333.
[60] D. M. Brouwer, J. M. Oelderik, *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 721 – 736.
[61] J. Weitkamp, P. A. Jacobs, J. A. Martens, *Appl. Catal.* **1983**, *8*, 123 – 141.
[62] J. Weitkamp, S. Ernst, H. G. Karge, *Erdöl Kohle Erdgas Petrochem.* **1984**, *37*, 457 – 462.
[63] J. S. Buchanan, J. G. Santiesteban, W. O. Haag, *J. Catal.* **1996**, *158*, 279 – 287.
[64] J. Weitkamp, S. Ernst in *Catalysis 1987* (Ed.: J. W. Ward), *Studies in Surface Science and Catalysis*, *Vol. 38*, Elsevier, Amsterdam, **1988**, pp. 367 – 382.
[65] S. T. Sie, *Ind. Eng. Chem. Res.* **1992**, *31*, 1881 – 1889.
[66] G. M. Berner, A. L. L. East, *Can. J. Chem.* **2009**, *87*, 1512 – 1520.
[67] D. M. Brouwer, H. Hogeveen, *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 211 – 224.
[68] D. M. Brouwer in *Chemistry and Chemical Engineering of Catalytic Processes* (Eds.: R. Prins, G. C. A. Schuit), Sijthoff & Noordhoff, Alphen aan den Rijn, **1980**, pp. 137 – 160.
[69] J. Weitkamp, S. Ernst in *Catalysis by Acids and Bases* (Eds.: B. Imelik, C. Naccache, G. Coudurier, Y. Ben Taarit, J. C. Védrine), *Studies in Surface Science and Catalysis*, *Vol. 20*, Elsevier, Amsterdam, **1985**, pp. 419 – 426.
[70] C. J. Egan, G. E. Langlois, R. J. White, *J. Am. Chem. Soc.* **1962**, *84*, 1204 – 1212.
[71] G. E. Langlois, R. F. Sullivan in *Refining Petroleum for Chemicals* (Eds.: L. J. Spillane, H. P. Leftin), *Advances in Chemistry Series*, *Vol. 97*, American Chemical Society, Washington, D. C., **1970**, pp. 38 – 67.
[72] S. Ernst, J. Weitkamp in *Proceedings of the International Symposium on Zeolite Catalysis*, Siófok, Hungary, May 13 – 16, **1985**, pp. 457 – 466.
[73] J. Weitkamp, S. Ernst, *Catal. Today* **1994**, *19*, 107 – 149.
[74] J. Weitkamp, S. Ernst, R. Kumar, *Appl. Catal.* **1986**, *27*, 207 – 210.
[75] Y. Traa, J. Weitkamp in *Handbook of Porous Solids, Vol. 2* (Eds.: F. Schüth, K. S. W. Sing, J. Weitkamp), Wiley-VCH, Weinheim, **2002**, pp. 1015 – 1057.
[76] Y. Traa, S. Sealy, J. Weitkamp in *Molecular Sieves—Science and Technology, Vol. 5* (Eds.: H. G. Karge, J. Weitkamp), Springer, Berlin, Heidelberg, **2007**, pp. 103 – 154.
[77] V. J. Frillette, W. O. Haag, R. M. Lago, *J. Catal.* **1981**, *67*, 218 – 222.
[78] J. A. Martens, M. Tielen, P. A. Jacobs, J. Weitkamp, *Zeolites* **1984**, *4*, 98 – 107.
[79] J. Weitkamp, C. Y. Chen, S. Ernst in *Successful Design of Catalysts* (Ed.: T. Inui), *Studies in Surface Science and Catalysis*, *Vol. 44*, Elsevier, Amsterdam, **1989**, pp. 343 – 350.
[80] J. Weitkamp, S. Ernst, C. Y. Chen in *Zeolites: Facts, Figures, Future* (Eds.: P. A. Jacobs, R. A. van Santen), *Studies in Surface Science and Catalysis*, *Vol. 49*, *Part B*, Elsevier, Amsterdam, **1989**, pp. 1115 – 1129.
[81] a) J. Weitkamp, A. Raichle, Y. Traa, *Appl. Catal. A* **2001**, *222*, 277 – 297; b) A. Raichle, Y. Traa, J. Weitkamp, *Chem. Ing. Tech.* **2001**, *73*, 947 – 956.
[82] a) J. Weitkamp, H. Bischof, W. Döhler, J. Laege, F. Fuder, A. Raichle, Y. Traa (Deutsche BP AG), EP 1 228 168 B1, **2000**; b) J. Weitkamp, A. Raichle, Y. Traa, M. Rupp, F. Fuder, *Chem. Commun.* **2000**, 403 – 404.
[83] A. Raichle, Y. Traa, J. Weitkamp, *Catal. Today* **2002**, *75*, 133 – 139.
[84] A. Raichle, Y. Traa, J. Weitkamp, *Erdöl Erdgas Kohle* **2002**, *118*, 83 – 87.
[85] A. Raichle, Y. Traa, J. Weitkamp, *Appl. Catal. B* **2003**, *41*, 193 – 205.
[86] A. F. H. Wielers, M. Vaarkamp, M. F. M. Post, *J. Catal.* **1991**, *127*, 51 – 66.
[87] A. Raichle, Y. Traa, F. Fuder, M. Rupp, J. Weitkamp, *Angew. Chem.* **2001**, *113*, 1268 – 1272; *Angew. Chem. Int. Ed.* **2001**, *40*, 1243 – 1246.
[88] C. Ringelhan, G. Burgfels, J. G. Neumayr, W. Seuffert, J. Klose, V. Kurth, *Catal. Today* **2004**, *97*, 277 – 282.
[89] P. Castaño, B. Pawelec, J. L. G. Fierro, J. M. Arandes, J. Bilbao, *Appl. Catal. A* **2006**, *315*, 101 – 113.
[90] P. Cataño, B. Pawelec, A. T. Aguayo, A. G. Gayubo, J. M. Arandes, *Ind. Eng. Chem. Res.* **2008**, *47*, 665 – 671.
[91] P. Castaño, A. Gutiérrez, I. Villanueva, B. Pawelec, J. Bilbao, J. M. Arandes, *Catal. Today* **2009**, *143*, 115 – 119.
[92] P. Castaño, J. M. Arandes, M. Olazar, J. Bilbao, B. Pawelec, U. Sedrán, *Catal. Today* **2010**, *150*, 363 – 367.
[93] A. Cesana, L. Dalloro, F. Rivetti, R. Buzzoni, *OIL Gas Eur. Mag.* **2008**, 89 – 94.
[94] H. Molero, C. Galarraga, F. Feng, E. Hernandez, V. Birss, P. Pereira, *Catal. Lett.* **2009**, *132*, 402 – 409.
[95] R. C. Santana, P. T. Do, M. Santikunaporn, W. E. Alvarez, J. D. Taylor, E. L. Sughrue, D. E. Resasco, *Fuel* **2006**, *85*, 643 – 656.
[96] H. Du, C. Fairbridge, H. Yang, Z. Ring, *Appl. Catal. A* **2005**, *294*, 1 – 21.
[97] J. Weitkamp in *Handbook of Heterogeneous Catalysis, Vol. 7*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3133 – 3152.
[98] M. Santikunaporn, J. F. Herrera, S. Jongpatiwut, D. E. Resasco, W. E. Alvarez, E. L. Sughrue, *J. Catal.* **2004**, *228*, 100 – 113.
[99] D. Kubička, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, T. Salmi, D. Y. Murzin, *J. Catal.* **2004**, *222*, 65 – 79.
[100] D. Kubička, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, H. Karhu, T. Salmi, D. Y. Murzin, *J. Catal.* **2004**, *227*, 313 – 327.
[101] M. A. Arribas, A. Corma, M. J. Díaz-Cabañas, A. Martínez, *Appl. Catal. A* **2004**, *273*, 277 – 286.
[102] H. Ma, X. Yang, G. Wen, G. Tian, L. Wang, Y. Xu, B. Wang, Z. Tian, L. Lin, *Catal. Lett.* **2007**, *116*, 149 – 154.
[103] M. A. Arribas, P. Concepción, A. Martínez, *Appl. Catal. A* **2004**, *267*, 111 – 119.
[104] D. Kubička, M. Kangas, N. Kumar, M. Tiitta, M. Lindblad, D. Y. Murzin, *Top. Catal.* **2010**, *53*, 1438 – 1445.
[105] G. B. McVicker, M. Daage, M. S. Touvelle, C. W. Hudson, D. P. Klein, W. C. Baird, Jr., B. R. Cook, J. G. Chen, S. Hantzer, D. E. W. Vaughan, E. S. Ellis, O. C. Feeley, *J. Catal.* **2002**, *210*, 137 – 148.
[106] M. A. Arribas, J. J. Mahiques, A. Martínez in *Zeolites and Mesoporous Materials at the Dawn of the 21st Century* (Eds.: A. Galarneau, F. Di Renzo, F. Fajula, J. C. Védrine), *Studies in Surface Science and Catalysis*, *Vol. 135*, Elsevier, Amsterdam, **2001**, p. 303.
[107] R. Contreras, J. Ramírez, R. Cuevas-García, A. Gutiérrez-Alejandre, P. Castillo-Villalón, G. Macías, I. Puente-Lee, *Catal. Today* **2009**, *148*, 49 – 54.
[108] K. Chandra Mouli, V. Sundaramurthy, A. K. Dalai, *J. Mol. Catal. A* **2009**, *304*, 77 – 84.
[109] S. Rabl, A. Haas, D. Santi, C. Flego, M. Ferrari, V. Calemma, J. Weitkamp, *Appl. Catal. A* **2011**, *400*, 131 – 141.
[110] S. Rabl, D. Santi, A. Haas, M. Ferrari, V. Calemma, G. Bellussi, J. Weitkamp, *Microporous Mesoporous Mater.* **2011**, *146*, 190 – 200.
[111] a) J. Weitkamp, S. Rabl, A. Haas, D. Santi, M. Ferrari, V. Calemma in *Preprints of the Conference—The Future Role of Hydrogen in Petrochemistry and Energy Supply* (Eds.: S. Ernst, A. Lercher, J. Lichtscheidl, M. Marchionna, F. Nees, E. Santacesaria), DGMK Report 2010-3, DGMK, Hamburg, **2010**, pp. 77 – 86; b) *OIL GAS Eur. Mag.* **2011**, *37*, 94 – 98.

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