Preparation of a high-quality synthetic steamcracker feedstock from methylcyclohexane on acidic zeolite H-ZSM-5: influence of the hydrogen partial pressure

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Abstract

With the advent of the European Auto Oil Program and comparable legislation in other parts of the world, the aromatics content of gasoline has to be reduced considerably. Therefore, new outlets for surplus aromatics have to be found and, thus, the preparation of a synthetic steamcracker feed consisting mainly of ethane, propane and *n*-butane from cycloalkanes (which can easily be obtained from surplus aromatics) could become a useful process option. In this work, the influence of the hydrogen partial pressure (0.6–10 MPa) on the product composition is studied during the conversion of methylcyclohexane on acidic zeolite H-ZSM-5 at 250–400 °C. Deactivation by coking and aromatics formation can be suppressed by hydrogen partial pressures of 4 MPa and higher. On the other hand, upon increasing the hydrogen partial pressure, increasing amounts of isoalkanes are formed, partially at the expense of the desired *n*-alkanes. Best catalytic results, i.e. high yields of small linear alkanes, stable with time-on-stream, are, thus, obtained at medium pressures between 4 and 6 MPa. Mechanistically, these changes in the catalytic behavior observed with increasing pressure can be rationalized by: (i) an enhanced incorporation of molecular hydrogen into the hydrocarbons and (ii) a decreasing contribution of the so-called oligomeric cracking.
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1. Introduction

New environmentally driven legislation calls for a massive diminution of the aromatics content in motor gasoline in many regions of the world [1–3]. As a consequence, large amounts of aromatics are likely to be available by around 2005 [4,5]. We have recently disclosed a novel catalytic route for converting surplus aromatics together with hydrogen into a high-quality synthetic steamcracker feedstock consisting of ethane, propane and *n*-butane [6]. It has also been shown that one can choose between two principal process variants, namely the direct hydroconversion of aromatics on bifunctional forms of the zeolites, e.g. Pd/H-ZSM-5 [7], and a two-stage process in which the aromatics are first hydrogenated into the corresponding cycloalkanes by conventional technology, whereupon the latter are further hydroconverted into the mixture of ethane, propane and *n*-butane using monofunctional acidic forms of the zeolites, e.g. H-ZSM-5 [8]. We moreover demonstrated that by far the best catalysts for the conversion of cycloalkanes

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are medium-pore zeolites with a three-dimensional pore system, i.e. zeolites ZSM-5 (MFI) and ZSM-11 (MEL) [9]. High, stable yields of light alkanes can, furthermore, only be achieved in the presence of a high excess of hydrogen [5,8]. So far, however, the influence of the hydrogen partial pressure has not been investigated systematically. The influence of the hydrogen pressure on cracking reactions over monofunctional, acidic zeolite catalysts has been studied in the past for the conversion of alkanes [10–15] and aromatics [16–18]. Beside the earlier work from our group [5,8,9,19,20], cycloalkanes have mainly been converted as such [21,22] or in an excess of nitrogen [23–26]. Very few studies only were addressing the conversion of cycloalkanes in an excess of hydrogen [27–29]. In this work, the influence of the hydrogen partial pressure on the hydroconversion of methylcyclohexane on acidic zeolite H-ZSM-5 was studied in the wide range between 0.6 and 10 MPa. Otherwise, the conditions were chosen in such a manner that they are industrially relevant; in particular, reaction temperatures up to 400 °C were applied where a complete conversion of methylcyclohexane is achieved.

2. Experimental section

2.1. Catalyst preparation and characterization

Zeolite ZSM-5 was synthesized hydrothermally according to a template-free procedure reported earlier [30]. Its ammonium form was prepared by a two-fold ion exchange: 10 g Na-ZSM-5 were suspended in 500 g of an aqueous ammonium nitrate solution (1 mol/cm^3). The suspension was stirred at 80 °C for 4 h. Afterwards, the catalyst was removed by filtration and washed with demineralized water. The ion exchange was then repeated, the catalyst was separated again, washed thoroughly with demineralized water, dried at 80 °C, and hydrated at room temperature over a saturated aqueous solution of calcium chloride. The aluminum content of the catalyst and the relative mass of the dry catalyst, as determined by AES/ICP (Plasma 400, Perkin-Elmer) and thermogravimetry (TG-DTA 92, Setaram), amounted to $n_{Al}/(n_{Si} + n_{Al}) = 4.8\%$ ($n_{Si}/n_{Al} = 20$) and $m_{catalyst, dry}/m_{catalyst} = 92\%$, respectively. Scanning electron microscopy (SEM, CAMSCAN 44) revealed

an average crystal size of 1.5 μm × 0.5 μm × 0.5 μm. The crystallinity and phase purity of the zeolite were proven by X-ray diffraction (Siemens D5000).

2.2. Catalytic experiments

Before use, the zeolites were pretreated in a flow of 100 cm^3/min nitrogen at 400 °C and atmospheric pressure for 12 h. The catalytic experiments were performed in a stainless-steel, flow-type apparatus with a fixed-bed saturator (filled with chromosorb (Macherey & Nagel) and methylcyclohexane (purity > 99.5%, Fluka)) and a fixed-bed reactor. Hydrogen (purity > 99.999%) was used as co-feed. The mass of the dry catalyst (particle size between 0.2 and 0.3 mm) and the weight hourly space velocity (*WHSV*) of methylcyclohexane amounted to 500 mg and 0.68 h^{-1}, respectively. This corresponds to a weight to flow ratio (W/F_{M-CHx}) of 144 g h/mol. The reaction temperature and the hydrogen partial pressure were varied, respectively, between 250 and 400 °C and between 0.6 and 10 MPa. The partial pressure of methylcyclohexane at the reactor inlet was kept constant at 65 kPa. To achieve this at various hydrogen pressures, the saturator temperature had to be adjusted between 72 and 86 °C. Product analysis was achieved by capillary gas chromatography using a PONA column (Hewlett-Packard). For each pressure a fresh catalyst sample was used. During conversion at 4 MPa and higher pressures, constant conversions and yields were achieved within 8 h time-on-stream. Therefore, the experiments at various temperatures were performed with the same catalyst sample. In contrast, at 0.6 and 2 MPa a slight deactivation and yield decrease with time-on-stream were observed and, thus, at these hydrogen partial pressures, data were taken at 400 °C only. The results given for these pressures hold for a time-on-stream of 30 min.

3. Results

Upon increasing the temperature from 250 to 400 °C, typical S-shaped curves are obtained for the conversion of methylcyclohexane (cf. Fig. 1). At hydrogen partial pressures between 4 and 10 MPa, the influence of the pressure on the conversion is not very pronounced, though a slight maximum seems to exist
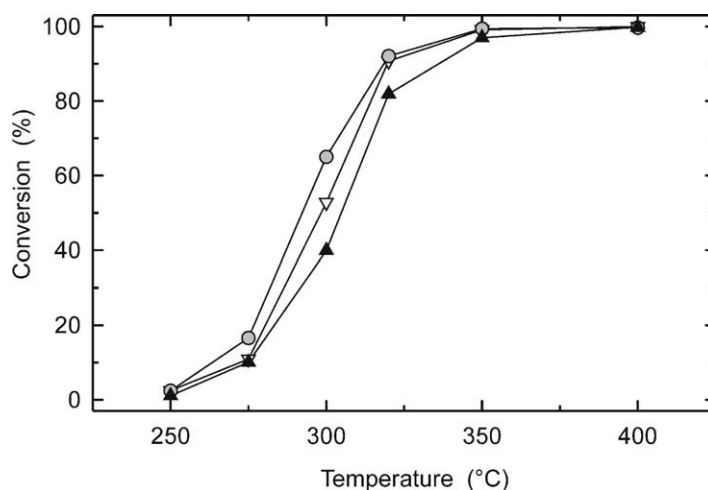
Fig. 1. Temperature dependency of the conversion of methylcyclohexane on zeolite H-ZSM-5 at hydrogen partial pressures of ($\triangledown$): 4 MPa, ($\bigcirc$): 6 MPa, and ($\blacktriangle$): 10 MPa.

at 6 MPa: at 300 °C, the conversion increases from 53% at 4 MPa to 65% at 6 MPa, but then decreases considerably to 40% at 10 MPa (Fig. 1). At 400 °C, total conversion is achieved irrespective of the hydrogen pressure (cf. Table 1). For hydrogen pressures of 4 MPa and above, constant conversions and yields are observed at all temperatures during at least 8 h time-on-stream. In contrast, at 0.6 and 2 MPa the yields of the desired C_{2+}-n-alkanes decrease slightly at 400 °C between 30 and 300 min time-on-stream to 96 and 98% of their values after 30 min, respectively (see Table 1, bottom row). At these relatively low hydrogen pressures, the initially white catalysts are dark gray after methylcyclohexane conversion (as opposed to the catalysts used at pressures of 4 MPa or above which only show a light grayish touch). From this we conclude that the yield decrease is due to coke formation. Clearly, on shape-selective zeolite catalysts such as H-ZSM-5, coke formation is efficiently suppressed by sufficiently high hydrogen partial pressures.

At temperatures below 300 °C, isomers of methylcyclohexane (ethylcyclopentane and dimethylcyclopentanes) are the dominant products, irrespective of the hydrogen pressure. With increasing temperature,

Table 1
Conversion of methylcyclohexane on zeolite H-ZSM-5 at 400 °C and various hydrogen partial pressures

p_{H_2} (MPa)	0.6	2	4	6	8	10
$X_{M\text{-}CHx}$ (%)	100	99.9	100	99.7	99.7	99.8
$Y_{methane}$ (%)	2.1	2.6	3.7	3.7	3.5	3.3
Y_{ethane} (%)	11.0	12.2	9.4	10.5	9.4	9.5
$Y_{propane}$ (%)	51.0	50.5	48.7	46.5	45.0	44.7
$Y_{n\text{-}butane}$ (%)	6.9	10.2	11.7	12.8	13.5	13.8
$Y_{C_{2+}\text{-}n\text{-}alkanes}$ (%)	69.2	73.7	70.8	70.8	69.2	69.1
$Y_{isoalkanes}$ (%)	9.3	15.8	22.9	24.5	27.0	27.4
$Y_{cycloalkanes}$ (%)	0.0	0.2	0.0	0.3	0.0	0.0
$Y_{aromatics}$ (%)	19.3	7.7	2.6	0.3	0.0	0.0
$Y_{n\text{-}butane}/Y_{butanes}$	0.48	0.47	0.42	0.42	0.41	0.40
$Y_{C_{2+}\text{-}n\text{-}alkanes, 300\,min}/Y_{C_{2+}\text{-}n\text{-}alkanes, 30\,min}$ [a]	0.96	0.98	1.00	1.00	0.99	0.99

[a] Ratio of the yields of the desired n-alkanes with two or more carbon atoms after 300 and 30 min time-on-stream, respectively.
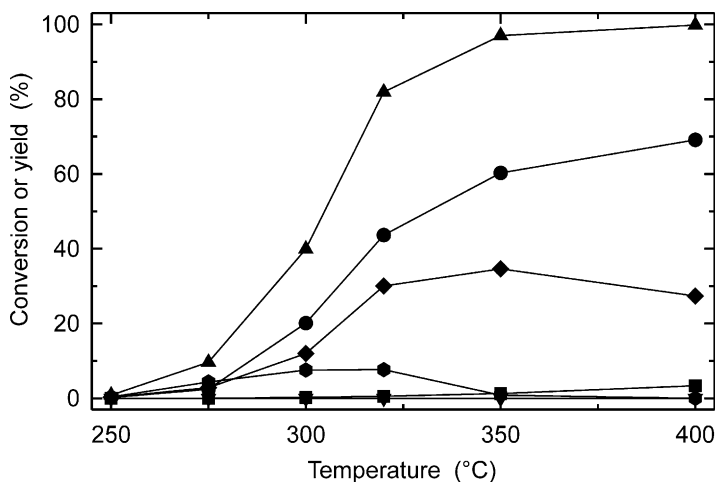
Fig. 2. Temperature dependency of the conversion and yields during the reaction of methylcyclohexane on zeolite H-ZSM-5 at a hydrogen partial pressure of 10 MPa (▲): X_{M-CHx}, (●): $Y_{C_{2+}-n-alkanes}$, (◆): $Y_{isoalkanes}$, (■): $Y_{methane}$, (⬟): $Y_{cycloalkanes}$, (▼): $Y_{aromatics}$).

ring opening and consecutive cracking reactions become more important. Therefore, the yields of the desired C_{2+}-*n*-alkanes (cf. Section 4.1) and that of methane (a very undesirable product) increase monotonously with increasing temperature, while the yields of cycloalkanes and isoalkanes pass through maxima (cf. Fig. 2).

The hydrogen partial pressure has a very pronounced effect on the selectivity to aromatics in the reaction product: it decreases drastically with increasing hydrogen partial pressure (cf. Fig. 3 and Table 2). At 400 °C, the selectivity to aromatics is 19.3% at 0.6 MPa, while no aromatics at all are formed at 8 and 10 MPa. No alkenes are detected irrespective of the hydrogen pressure, which clearly reveals that molecular hydrogen is incorporated into the hydrocarbons on monofunctional zeolites, as it has been observed earlier [8,10,12–16,18,31]. This is especially
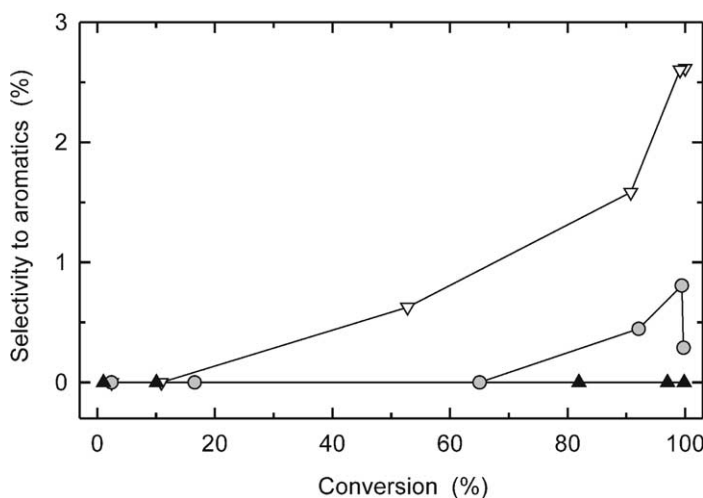

Fig. 3. Dependency of the selectivity to aromatics on the conversion of methylcyclohexane over zeolite H-ZSM-5 at hydrogen partial pressures of (▽): 4 MPa, (◎): 6 MPa, and (▲): 10 MPa.

Table 2

Conversion of methylcyclohexane on zeolite H-ZSM-5 at 400 and 275 °C, respectively, and various hydrogen partial pressures

p_{H_2} (MPa)	X_{M-CHx} (%)	$S_{cycloalkanes}$ (%)	$S_{aromatics}$ (%)	$Y_{methane}/$ $Y_{acyclic\ comp.}$	$Y_{C_{2+}-n\text{-}alkanes}/$ $Y_{acyclic\ comp.}$	$Y_{isoalkanes}/$ $Y_{acyclic\ comp.}$	$n_{butanes}/$ $n_{propane}$
$T = 400\,°C$							
0.6	100	0.0	19.3	0.027	0.86	0.12	0.21
2	99.9	0.2	7.7	0.028	0.80	0.17	0.32
4	100	0.0	2.6	0.038	0.73	0.24	0.43
6	99.7	0.3	0.3	0.037	0.72	0.25	0.50
8	99.7	0.0	0.0	0.035	0.70	0.27	0.56
10	99.8	0.0	0.0	0.034	0.69	0.27	0.58
$T = 275\,°C$							
4	10.9	32.7	0.0	0.008	0.62	0.37	0.87
6	16.6	29.3	0.0	0.006	0.54	0.46	0.91
10	10.1	42.3	0.0	0.006	0.45	0.55	0.96

the case at elevated hydrogen partial pressures (cf. Section 4.3).

Only a minor effect of the hydrogen partial pressure on the selectivity to cycloalkanes (mainly ethyl-cyclopentane and dimethylcyclopentanes) is observed: at low conversions, slightly higher selectivities to cycloalkanes are observed at 4 and especially at 10 MPa than at 6 MPa (cf. Fig. 4). This minimum at 6 MPa correlates well with the maximum of the conversion at the same pressure (see Fig. 1), revealing a slightly higher cracking activity of the catalyst at medium hydrogen partial pressures.

The hydrogen partial pressure has also a remarkable influence on the composition of the ring opening and cracking products: increasing the pressure from 4 to 10 MPa significantly increases the selectivities to isoalkanes (see Fig. 5) with a concomitant decrease of the selectivities to the more desired n-alkanes with two and more carbon atoms (C_2-n-alkanes, cf. Fig. 6). This effect is superimposed by the strongly decreasing formation of aromatics with increasing hydrogen partial pressure (cf. Fig. 3 and Table 1) and the minimum of the selectivities to cycloalkanes at 6 MPa at low conversion (cf. Fig. 4). Therefore,
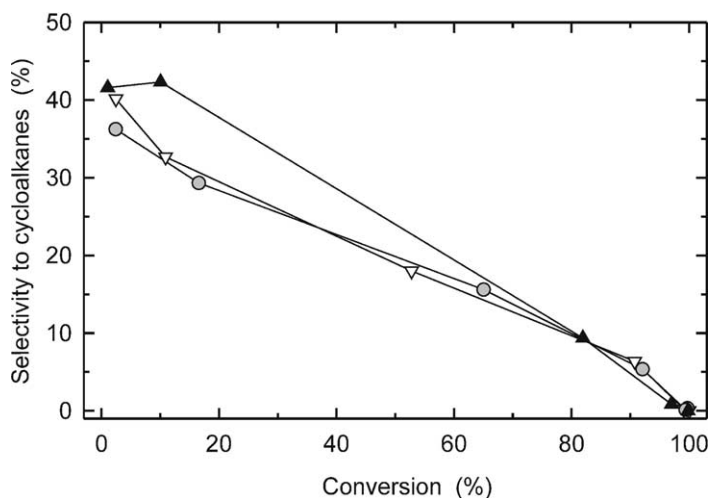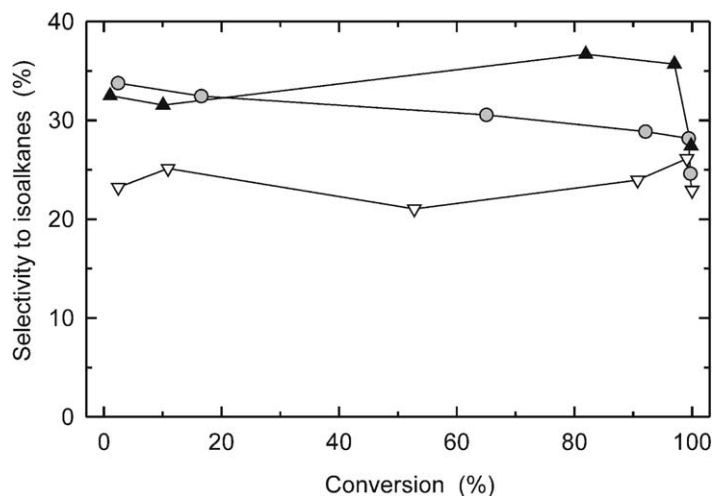

Fig. 4. Dependency of the selectivity to cycloalkanes on the conversion of methylcyclohexane over zeolite H-ZSM-5 at hydrogen partial pressures of ($\triangledown$): 4 MPa, (◉): 6 MPa, and (▲): 10 MPa.

Fig. 5. Dependency of the selectivity to isoalkanes on the conversion of methylcyclohexane over zeolite H-ZSM-5 at hydrogen partial pressures of ($\triangledown$): 4 MPa, ($\bigcirc$): 6 MPa, and ($\blacktriangle$): 10 MPa.

with increasing hydrogen partial pressure, the yield of C_{2+}-n-alkanes at 400 °C passes through a maximum at 2 MPa (much lower yield of aromatics than at 0.6 MPa, cf. Table 1). At low conversion, less isoalkanes are formed at 10 MPa than at 6 MPa (cf. Fig. 5) because of the higher selectivities to cycloalkanes in this case. To sort out these effects, the ratios of the yields of methane, C_{2+}-n-alkanes and isoalkanes to

the yield of acyclic hydrocarbons are calculated in Table 2. In this way, the change in the composition of ring-opened and cracked products becomes obvious: at 400 °C, the ratio between the relative yields of C_{2+}-n-alkanes and of isoalkanes (mainly isobutane) decreases from 7.2 at 0.6 MPa to 2.6 at 10 MPa. At 275 °C, this ratio decreases from 1.7 at 4 MPa to 0.8 at 10 MPa.
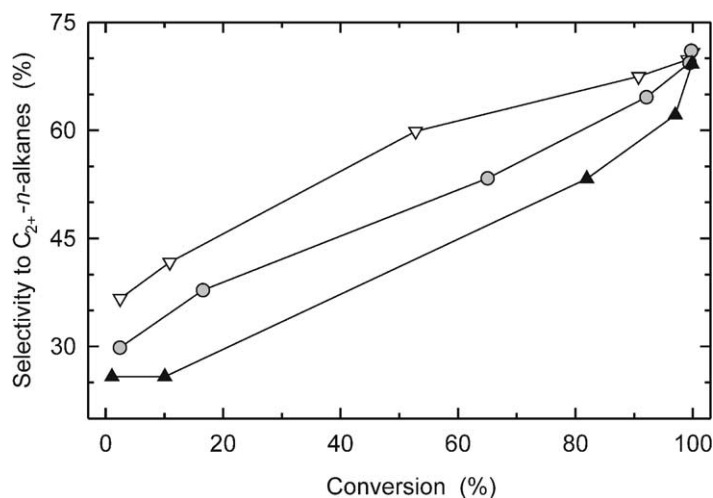

Fig. 6. Dependency of the selectivity to C_{2+}-n-alkanes on the conversion of methylcyclohexane over zeolite H-ZSM-5 at hydrogen partial pressures of ($\triangledown$): 4 MPa, ($\bigcirc$): 6 MPa, and ($\blacktriangle$): 10 MPa.
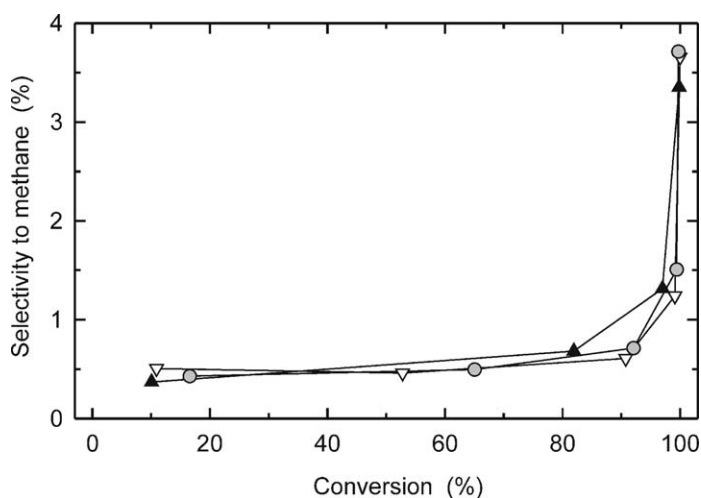
Fig. 7. Dependency of the selectivity to methane on the conversion of methylcyclohexane over zeolite H-ZSM-5 at hydrogen partial pressures of ($\bigtriangledown$): 4 MPa, ($\bigcirc$): 6 MPa, and ($\blacktriangle$): 10 MPa.

The strongly decreasing selectivities to C_{2+}-n-alkanes with increasing hydrogen partial pressure are mainly due to the decreasing selectivities to propane and n-butane over a wide range of conversions (cf. Table 3). Only at total conversion, i.e. at 400 °C, the inverse order occurs for n-butane (cf. Table 1). This is presumably caused by the negligible yields of aromatics and the lower cracking activity at high hydrogen partial pressures. In contrast, no clear trend can be observed in the formation of ethane. The slight maximum of its selectivity at medium hydrogen partial pressures (cf. Table 3) remains in the range of the experimental accuracy.

Table 3
Selectivities to light linear alkanes during the conversion of methylcyclohexane on zeolite H-ZSM-5 at various hydrogen partial pressures and two reaction temperatures

p_{H_2} (MPa)	4	6	10
$T = 275$ °C			
S_{ethane}	0.0	0.3	0.0
$S_{propane}$	28.3	28.1	20.9
$S_{n\text{-butane}}$	9.7	6.5	3.3
$S_{C_{2+}\text{-}n\text{-alkanes}}$	41.7	37.8	25.8
$T = 320$ °C			
S_{ethane}	1.4	1.6	1.2
$S_{propane}$	43.3	42.3	36.7
$S_{n\text{-butane}}$	18.3	16.6	12.6
$S_{C_{2+}\text{-}n\text{-alkanes}}$	67.5	64.6	53.3

The selectivity to methane behaves similar to the selectivity to ethane: at medium pressures a slight maximum of the methane formation can be observed at 400 °C (see Table 1), but over the whole range of conversions no clear trend can be perceived (cf. Fig. 7).

In Fig. 8, the product distributions during the conversion of methylcyclohexane at 300 °C, i.e. at a conversion around 50%, are given in more detail. Besides the increasing significance of isobutane formation with increasing hydrogen partial pressure, the molar ratio of butanes to propane increases considerably in the same order. This is mainly due to the low selectivities to isobutane at low hydrogen partial pressures and can also be observed at other temperatures, e.g. at 275 and 400 °C (cf. Table 2). Fig. 8 additionally reveals that the formation of hydrocarbons with 5, 6 and 8 carbon atoms decreases with increasing hydrogen partial pressure.

4. Discussion

4.1. Key parameters for obtaining a high-quality synthetic steamcracker feed

In steamcrackers, the product distribution is predominantly determined by the feedstock composition. The highest amounts of ethene and propene are formed
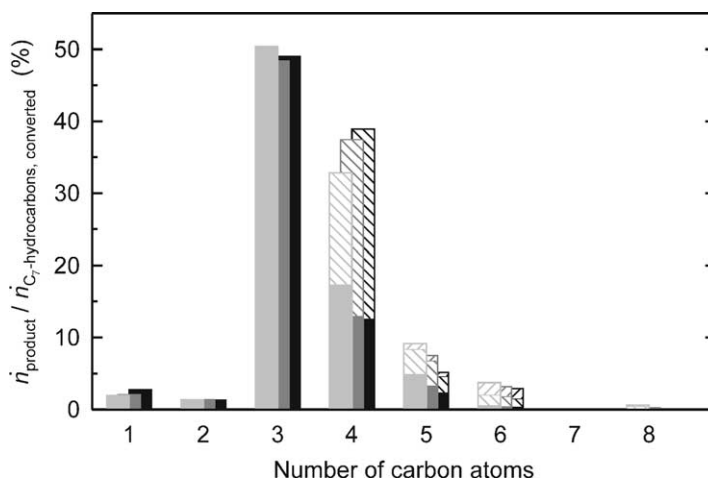
Fig. 8. Molar fractions of the products with n carbon atoms during the conversion of methylcyclohexane on zeolite H-ZSM-5 at 300 °C and 4 MPa (light gray), 6 MPa (dark gray), and 10 MPa (black). Forwards shading (⧅): cycloalkanes; backwards shading (⧄): isoalkanes; solid color: *n*-alkanes; hardly any aromatics are formed.

from C_{2+}-*n*-alkanes, which are, thus, a premium steamcracker feed, followed by isoalkanes and cycloalkanes. Aromatics and methane are virtually inert in the steamcracker [32]. Thus, during the preparation of a synthetic steamcracker feedstock, C_{2+}-*n*-alkanes are the most desired products; isoalkanes are still acceptable, but the formation of cyclic hydrocarbons and methane should be minimized. Our earlier work [5] revealed, that key parameters for obtaining high yields of C_{2+}-*n*-alkanes and for preventing the catalyst from deactivation are: (i) a medium-pore zeolite with the appropriate pore width, such as ZSM-5, (ii) a relatively high temperature around 400 °C, and (iii) elevated hydrogen partial pressure to prevent aromatics formation and catalyst deactivation.

With increasing hydrogen partial pressure, the yield of undesired aromatics decreases drastically. On the other hand, the yield of isoalkanes increases strongly, partially at the expense of the desired C_{2+}-*n*-alkanes (cf. Table 1). It follows that there is an optimum hydrogen partial pressure around 4–6 MPa.

4.2. Influence of the hydrogen partial pressure on the product composition

To rationalize the observations described in Section 3, the following three mechanisms proposed in the literature for cracking of hydrocarbons on acidic

catalysts have to be considered: (i) classical bimolecular cracking, (ii) classical oligomeric cracking, and (iii) non-classical Haag–Dessau cracking.

Classical cracking is considered to proceed via alkoxy species as intermediates and carbenium ions as transition states [33–35]. Skeletal isomerization reactions lead to highly branched isomers which are readily cracked via β-scission. On monofunctional acidic catalysts, the formation of the carbenium ions can only proceed via a spatially demanding bimolecular hydride transfer from a feed molecule to carbenium ions formed by isomerization or cracking reactions. Therefore, classical or bimolecular cracking is significantly hindered in medium-pore zeolites (such as H-ZSM-5, used in this study) compared to large-pore zeolites [26]. In cycloalkanes, endocyclic classical β-scission, i.e. ring opening, is much slower than exocyclic β-scission or β-scission of aliphatic carbenium ions [36]. This sluggishness of endocyclic β-scission has been attributed to an unfavorable orbital orientation in cyclic carbenium ions [36] or to a lower activation entropy for endocyclic compared to exocyclic or acyclic β-scission [37]. The dominant products of classical bimolecular cracking are, due to the preceding isomerization, propane and isobutane. Because of the instability of primary carbenium ions, neither methane nor ethane are formed.

As a special case of classical cracking, the term oligomeric cracking has been coined [38]. Oligomeric cracking comprises alkylation steps forming higher hydrocarbons and consecutive cracking steps [38]. Thereby, a large variety of products (mainly isoalkanes) with various carbon numbers are formed. Oligomeric cracking is often accompanied by catalyst deactivation. Taking into account the high stability of the tertiary butyl cation (compared to, e.g. the secondary butyl-2 cation or the propyl-2 cation [39]), an important reaction path in oligomeric cracking can be looked upon (see Scheme 1) as alkylation of the tertiary methylcyclohexyl cation by isobutene (or of a tertiary butyl cation by methylcyclohexene, cf., e.g. [23,26]) followed by skeletal rearrangements and *exocyclic* classical β-scissions. Scheme 1 shows that such a pathway results in a cycloalkane and a small alkane, e.g. in a C_8-cycloalkane plus propane, cyclo-

hexane plus isopentane or methylcyclopentane plus *n*-pentane.

While oligomeric cracking represents a variant of classical cracking, a completely different mechanism is non-classical or protolytic cracking via carbonium ions invoked by Haag and Dessau [40] to account for their results of *n*-hexane and isohexanes cracking on medium-pore acidic zeolites: alkanes [40] or cycloalkanes [9,26,27] are directly protonated on acidic sites forming adsorbed non-classical carbonium ions in the transition state [35]. Because alkenes are much better proton acceptors than alkanes, Haag–Dessau cracking is strongly favored by low alkene concentrations [40,41]. Since the activation energy of Haag–Dessau cracking is considerably higher than that of classical cracking, the contribution of Haag–Dessau cracking strongly increases with increasing temperature [40,41]. Small *n*-alkanes,
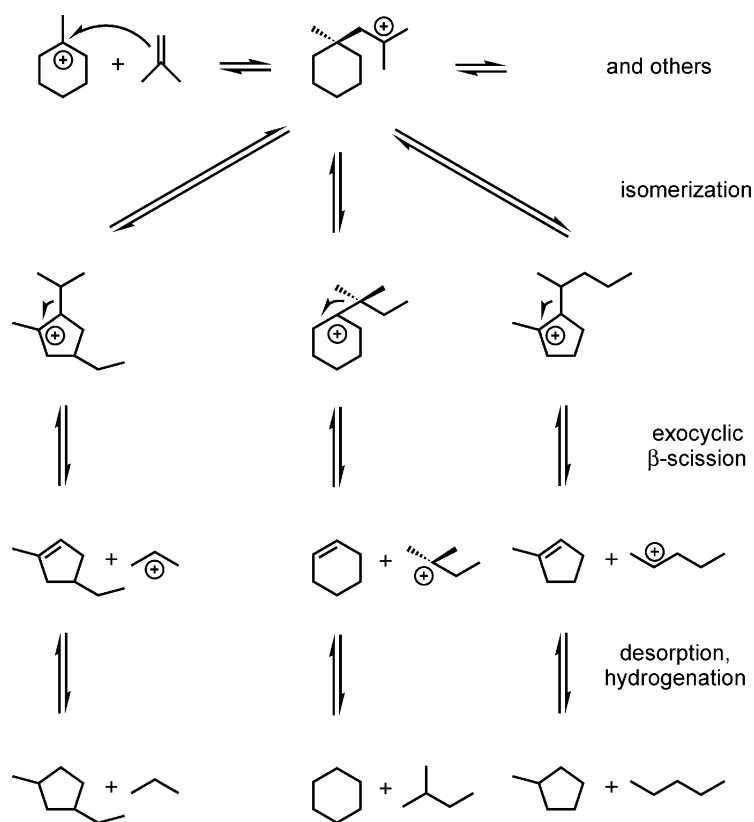
Scheme 1. Examples for oligomeric cracking reactions: alkylation of the methylcyclohexyl cation with isobutene and three examples for possible consecutive isomerization and exocyclic β-scission reactions.

including methane and ethane, are the main products of Haag–Dessau cracking, even during cracking of branched alkanes.

On the basis of these generally accepted mechanistic concepts, an attempt will be made to rationalize the experimental data described in Section 3. The contribution of non-classical Haag–Dessau cracking can be estimated from the selectivities to ethane and methane, i.e. products which are not formed during classical cracking. Neither the ethane selectivity (see Table 3) nor the methane selectivity (see Fig. 7) are significantly affected by the hydrogen partial pressure. From this we conclude that the contribution of Haag–Dessau cracking is nearly independent of the hydrogen pressure.

With regard to the effect of the hydrogen partial pressure on the methylcyclohexane conversion, a weak maximum can be made out at 6 MPa (see Fig. 1). This could be due to two opposing effects of molecular hydrogen on the availability of acidic sites for hydrocarbon conversion: the desorption of adsorbed carbenium ions is the rate-determining step (presumably at low hydrogen partial pressures), hydrogen will have a beneficial effect on the number of available acidic sites by enhancing the desorption of the carbenium ions in the form of saturated hydrocarbons [12,13,15]. This may be looked upon as a scavenging effect of molecular hydrogen. On the other hand, (especially at high hydrogen partial pressures), hydrogen could be adsorbed itself and, thus, block some of the acidic sites [11]. In this way, hydrogen-assisted desorption could bring about a decrease in the concentration of adsorbed carbenium ions and unsaturated species, in the rate of classical cracking and, hence, in the methylcyclohexane conversion [10,13].

A decreasing number of adsorbed carbenium ions and alkenes, such as the relatively stable tertiary butyl cation and isobutene are expected to slow down consecutive reactions of these ions, in particular, coke formation and oligomeric cracking. This is exactly what is observed upon increasing the hydrogen pressure. The slight deactivation occurring at $p_{H_2} = 0.6$ and 2 MPa ceases to exist at higher hydrogen partial pressures (cf. Table 1), and the experimental data indicate a decreasing contribution of oligomeric cracking with increasing hydrogen partial pressure: (i) Fig. 8 clearly reveals that an enhancement of the hydrogen partial pressure from 4 to 10 MPa remarkably

decreases the molar fraction of hydrocarbons with 5 (mainly n- and isopentane), 6 (mainly iso- and cycloalkanes), and 8 (cycloalkanes and few aromatics) carbon atoms. These hydrocarbons are typical products of oligomeric cracking (see Scheme 1); note that the alternative formation of C_5- and C_6-hydrocarbons by Haag–Dessau cracking of C_7-hydrocarbons is limited, since their molar fractions are much higher than those of the respective alkanes with 2 and 1 carbon atoms; (ii) with increasing hydrogen partial pressure, a considerably increasing molar ratio of butanes to propane is observed (cf. Fig. 8 and Table 2): at 275 °C and 10 MPa, a value close to unity (expected for simple β-scission of C_7 hydrocarbons) is observed. This can be accounted for by a decreasing contribution of consecutive oligomeric cracking starting, e.g. from the methylcyclohexyl cation and butenes (cf. Scheme 1); (iii) due to its high reactivity, isobutene is the main alkylation agent. With increasing hydrogen partial pressure, the molar fraction of its hydrogenation product isobutane increases (see Fig. 8). Simultaneously, the molar fraction of products of oligomeric cracking (mainly n-alkanes) decreases. We consider this as the main reason for the decreasing ratio between the relative yields of C_{2+}-n-alkanes and isoalkanes (Table 2, values in column 6 divided by values in column 7) observed upon increasing the hydrogen partial pressure.

4.3. Mechanistical aspects of the incorporation of hydrogen into hydrocarbons

Alkenes are initial products of both classical and Haag–Dessau cracking. Nevertheless, they are not observed in the product. This can be rationalized by two different reactions: (i) by hydrogen transfer between alkenes and cycloalkanes forming alkanes and aromatics (cf., e.g. [26], via bimolecular hydride transfer) and (ii) by the incorporation of molecular hydrogen into the products (cf., e.g. [13]). A good measure for the importance of these reactions is the ratio of the molar flows of dihydrogen transferred between various cracking products ($\dot{n}_{H_2, \text{transferred}}$) or incorporated into the products from molecular hydrogen ($\dot{n}_{H_2, \text{incorporated}}$) and the molar flow of methylcyclohexane fed ($\dot{n}_{M\text{-}CH_x, \text{fed}}$). Both values are calculated from the mass-based product composition using the mass fraction of aromatics and their hydrogen to
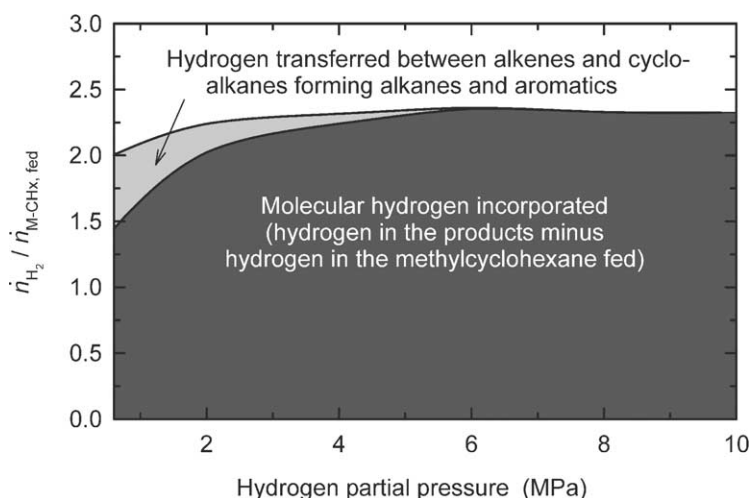
Fig. 9. Molar ratio of hydrogen transferred between hydrocarbons (light gray) or incorporated into the hydrocarbon products (dark gray) to methylcyclohexane fed during its conversion at 400 °C: dependency on the hydrogen partial pressure.

carbon mass ratio in the first case and the hydrogen to carbon mass ratio of the whole product in the second case, respectively.

It is evident from Fig. 9 that large amounts of hydrogen are incorporated into the hydrocarbon products. This is especially true at high hydrogen partial pressures: upon increasing p_{H_2} from 0.6 to 6 MPa, the molar ratio of consumed dihydrogen to methylcyclohexane fed increases from 1.5 to 2.3. Besides this incorporation of molecular hydrogen, some hydrogen transfer between hydrocarbons takes place at hydrogen partial pressures below 6 MPa (see Fig. 9). Interestingly, even at 0.6 MPa hydrogen incorporation clearly dominates: only about one hydrogen atom is transferred between hydrocarbons (excluding hydrogen transfer during the formation of coke deposits) per molecule of methylcyclohexane fed, while three hydrogen atoms are incorporated from molecular hydrogen.

This incorporation of molecular hydrogen into hydrocarbons on acidic zeolites lacking a hydrogenation/dehydrogenation component has been observed earlier [8,12–16,18,31]. The effect has been clearly confirmed even in the absence of iron impurities [16]. It appears that molecular hydrogen can be activated by the acid sites of the zeolite and/or by adsorbed carbenium ions and transferred to hydrocarbons [12,13, 15,18]. Kanai et al. [31] envisaged the hydrogenation

of ethene on acidic zeolites as the reverse reaction of non-classical Haag–Dessau cracking (cf. Section 4.2), i.e. addition of molecular hydrogen to a classical carbenium ion results in a non-classical carbonium ion which, upon proton abstraction, gives a saturated hydrocarbon. It is easily conceivable that such a mechanism of hydrogen incorporation is promoted by high hydrogen pressures.

5. Conclusions

On acidic zeolite H-ZSM-5, methylcyclohexane can be converted into a high-quality synthetic steamcracker feed consisting of ethane, propane and *n*-butane without producing significant amounts of the undesired methane. At 400 °C, yields of the desired C_{2+}-*n*-alkanes above 70% are achieved. Catalyst deactivation and the formation of undesired aromatics are absent at hydrogen partial pressures of about 4 MPa or higher. Too high hydrogen partial pressures are to be avoided, because they bring about increased yields of isoalkanes, partially at the expense of C_{2+}-*n*-alkanes. The resulting optimum in the hydrogen partial pressure lies between 4 and 6 MPa. Over the whole range of hydrogen partial pressures (0.6–10 MPa) studied, the yield of methane could be kept below 4%.

Mechanistic considerations show that the contribution of non-classical Haag–Dessau cracking is essentially constant during the conversion of methylcyclohexane at hydrogen partial pressures between 0.6 and 10 MPa. In contrast, all experimental results indicate that the contribution of the so-called oligomeric cracking (comprising an alkylation and a consecutive cracking step) is decreasing considerably with increasing hydrogen partial pressure. This is attributed to a lower concentration of reactive intermediates, such as isobutene, and is proposed to be mainly responsible for the strongly increasing yield of isoalkanes with increasing hydrogen partial pressure. The selectivities to aromatics decrease drastically with increasing hydrogen partial pressure, and no alkenes are observed under any reaction conditions in the products. Large amounts of molecular hydrogen (ca. 2 moles per mole methylcyclohexane fed) are incorporated into the products formed by ring opening and cracking, and this is consistent with prior reports by other groups who claimed an activation of molecular hydrogen on monofunctional acidic zeolites.

Acknowledgements

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