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Hydrogenation and Ring Opening of Aromatic and Naphthenic Hydrocarbons Over Noble Metal (Ir, Pt, Rh)/Al_2O_3 Catalysts

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Abstract The hydrogenation and ring opening of model hydrocarbons and of naphtha was studied over commercial noble metal (Ir, Pt, Rh)/Al_2O_3 catalysts. The experiments were performed in a fixed bed reactor at temperatures between 220 and 350 °C and pressures of 1.1 and 5.0 MPa, respectively. The product distribution was determined and the cetane number was calculated. The Pt catalyst is very active for hydrogenation of aromatics but does not catalyse the ring opening of naphthenes. The Ir and Rh catalysts are active for both hydrogenation of aromatics and ring opening of naphthenes. Experiments with toluene, *m*-xylene, propyl-benzene, and methylcyclohexane indicate that ring opening follows a selective mechanism, where the cleavage of bisecondary carbon bonds is favoured. This results in predominant formation of branched paraffins. The product distribution as well as cracking of long-chain hydrocarbons, which increase at temperatures above 260 °C, lead to an insignificant boost in the cetane number, as confirmed by experiments using real naphtha as feedstock.

Keywords Hydrogenation · Ring opening · Naphtha · Platinum · Iridium · Rhodium · Cetane number

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1 Introduction

In recent years, a lot of research dealing with ring opening reactions has been undertaken. In the majority of cases, the aim was to develop new routes for the production of high quality transportation fuels which fulfill new, more strict environmental regulations, e.g. a low aromatic content [1–4]. New routes for diesel oil production are also needed, if the demand for diesel increases in the next years. Until the year 2030, the predicted sales volume of diesel will double in comparison to the demand for gasoline [5]. In this context future drive systems are also important, which mix the most favourable characteristics of both petrol and diesel technology, e.g. the combined combustion system (CCS) of Volkswagen or the so-called Diesotto-technology of Mercedes [6, 7]. Hence, the conversion of naphtha into "light" diesel with a preferably high cetane number (CN) may then be an option.

This aim of a gasoline with a high CN can only be achieved by hydrogenation of the aromatics (present in raw naphtha) and subsequent ring opening of the naphthenes (Fig. 1). Aromatics have a very low cetane number, e.g. $CN_{toluene} = -5$, followed by the corresponding cycloalkanes, e.g. $CN_{methylcyclohexane} = 20$. Depending on the position of the side chain iso-paraffins can have both higher and lower cetane numbers than the corresponding naphthenes. For example, the CN of 2-methylhexane is 35 while the CN of 3-methylhexane is only 17. However, linear paraffins exhibit the highest cetane numbers (e.g. $CN_{n\text{-heptane}} = 53$). In general, the CN number of linear and branched paraffins grows with increasing chain length, and for naphthenes and aromatics with increasing length of side chains.

Ring opening reactions are also interesting to produce synthetic steam cracker feed from aromatic-rich pyrolysis gasoline, as investigated by Weitkamp et al. [8–10].

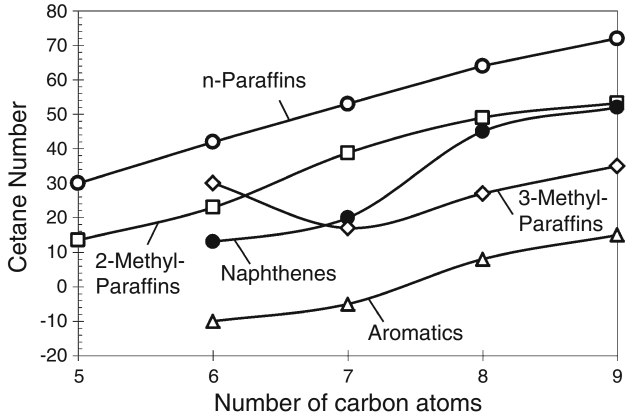

Fig. 1 Cetane number of different hydrocarbons versus the number of carbon atoms

All the above mentioned cases follow the approach to use (sometimes poorly marketable) aromatics as feedstock for conversion into valuable intermediates/products.

Before aromatic hydrocarbons can be ring opened to paraffins they have to be completely hydrogenated to their corresponding naphthenes [8]. Hydrogenation of aromatics is well described in the literature [11–14], and it is known that group-VIII metals (Pt, Pd, Rh…) are suitable catalysts for hydrogenations [12].

In principle, ring opening of naphthenic hydrocarbons can be achieved catalytically by cracking on solid acidic catalysts, hydrocracking on bifunctional catalysts or hydrogenolysis on noble metals.

On solid acid catalysts (e.g. zeolites), ring opening of naphthenes is achieved by a protolytic cracking mechanism via carbenium intermediates. Due to side reactions and consecutive cracking reactions these catalysts are not appropriate to yield high cetane products [2].

Already in 1953, Mills et al. [15] proposed a mechanism for the hydrocracking of naphthenes over a bifunctional catalyst based on experiments with cyclohexane, cyclohexene, methylpentane, and methylpentene. The mechanism proposes three steps [2, 15]: At first, cyclic hydrocarbons are dehydrogenated to cyclic olefins on a metal site. Secondly, the olefins are protonated on the acid site, which leads to formation of carbenium ions, which are either cracked or skeletally isomerised. The olefins formed after isomerisation are desorbed from the acid site and finally hydrogenated on the metal site. This mechanism and the intermediates were confirmed by Weisz and Swegler [16].

The ring opening of naphthenic hydrocarbons can also occur on noble metal catalysts without acidic sites (hydrogenolysis). Galperin et al. [17] inhibited the activity of the acid sites of a bifunctional platinum catalyst by addition of potassium. They showed that the catalyst acted then like a monofunctional metallic catalyst, which enabled a high selectivity for ring opening products. The group of Gault et al. [18] carried out experiments on the ring opening of methylcyclopentane over platinum catalysts. They presented a correlation between the metal dispersion on the catalyst surface and the product distribution as well as the reaction mechanism. It was shown that the product distribution was non-selective on 0.2 % Pt/Al_2O_3 with highly dispersed particles. The possible ring opening products *n*-hexane, 2-methylpentane, and 3-methylpentane were formed with the same probability. When using 10 % Pt/Al_2O_3 with low dispersed metal particles, the ring was only opened between bisecondary (non-substituted) carbon atoms leading predominantly to the formation of 2-methylpentane (78 %) and not of *n*-hexane. Hence, Gault proposed three different reaction mechanisms. First, the non-selective mechanism (also known as the multiplet mechanism). Here methylcyclohexane is supposed to adsorb planar on the metal surface. The bisecondary and tertiary–secondary bonds are broken with the same probability. The second mechanism proposed is called the selective mechanism (dicarbene mechanism), where the hydrocarbon adsorbed perpendicularly on the metal surface via two adjacent bisecondary carbon atoms. Due to steric hindrance the tertiary–secondary bonds are not cleaved. A third mechanism, the "partially selective" mechanism, which competes with the dicarbene mechanism, was proposed to explain the product distribution, where mainly bisecondary, but sometimes also tertiary–secondary bonds are broken. The methyl group and a methylene group in α-position interact with a metal site forming a metallocyclobutane intermediate. This results in cleavage of tertiary–secondary bonds [2].

Other research groups showed that the size of metal particles is less important when using iridium or rhodium. But these metals have higher activity and selectivity to cleave the bisecondary bonds of the C_5-ring [2, 3]. Furthermore it was shown by Resasco et al. [19] that the dispersion of metal particles is less important for the reaction mechanism taking place by converting 1,2- and 1,3-dimethylcyclohexane over different Iridium catalyst. However, they showed the type of support influences the ring opening mechanism strongly.

In this work, hydrogenation and ring opening reactions over commercial noble metal catalysts (Ir, Pt, Rh) were studied with different model aromatic and naphthenic hydrocarbons as well as with "real" naphtha. Beside the kinetics, the impact on the cetane number was analysed.

2 Experimental

All experiments were carried out in a continuously operated fixed bed reactor (Fig. 2), designed to operate at

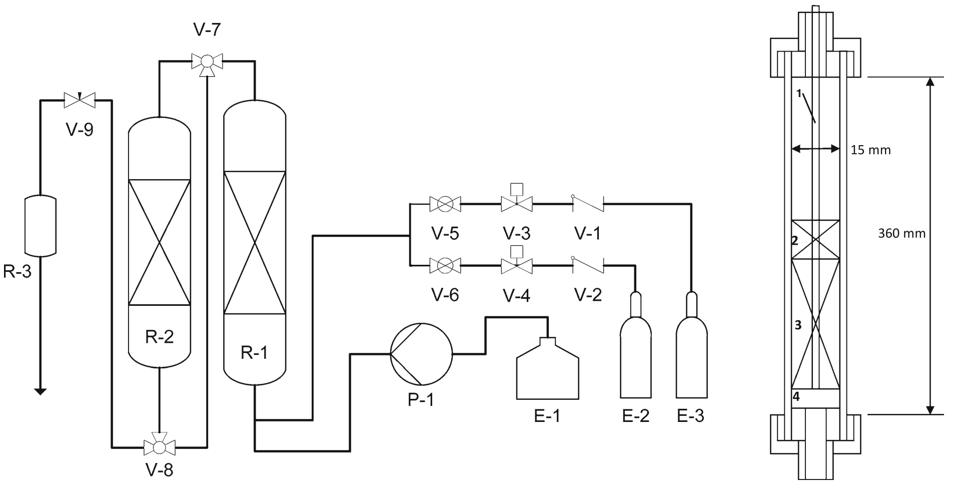

Fig. 2 Flow diagram of the experimental plant (*left*) and cross section of the fixed bed reactor (*right*)

E-1	Educt tank	V-5/6	Stop valve	1	Thermal element
E-2	Gas bottle N_2	V-7/8	Three-way valve	2	Catalyst bed
E-3	Gas bottle H_2	V-9	Needle valve	3	Inert bed (glass beads)
P-1	Educt pump	R-1	Vaporizer	4	Frit
V-1/2	Check valve	R-2	Fixed bed reactor		
V-3/4	Mass flow controller	R-3	Sampling		

temperatures up to 450 °C and pressures up to 6.0 MPa. The set-up is subdivided into three units, the vaporizer (45 mm inner diameter, 460 mm length), the fixed bed reactor (15 mm inner diameter, 360 mm length), and the sampling/analysis. Each part is separately heated and temperature controlled. The lab-scale plant is supplied with hydrogen and nitrogen via two mass flow controllers [5 to 100 l/h (STP)]. Nitrogen is needed to check on leak tightness and to flush the set-up with inert gas after experimental usage. A high pressure pump feeds the liquid hydrocarbon, and the combined stream of the hydrocarbon and of hydrogen enters the vaporizer where the hydrocarbon evaporates. Afterwards the gas mixture streams into the reactor containing the catalyst fixed bed. The catalyst bed is placed in the middle of the reactor to achieve almost isothermal conditions. Hence, the reactor is half-filled with glass beads (inert bed), on which the catalyst particles are placed. Running the experiments without catalyst cracking or conversion of the hydrocarbons was not observed. Thus a blind activity of the reactor can be excluded. The reactor is equipped with a metal frit (90 μm) to avoid discharge and deposit of glass beads or catalyst material into the pipework. Downstream the reactor, the pressure is reduced to standard pressure by a needle valve. Both gaseous and liquid samples are analysed using a gas chromatograph (Perkin Elmer, CLARUS 500) equipped with a PONA-column (100 m in length, 0.25 mm inner diameter, 0.5 mm film thickness) and a Flame Ionization Detector. The gas chromatographic (GC) raw data are interpreted by using ARNEL DHA Software.

The cetane number was calculated based on the product analysis simply with the individual mass content as weighting coefficient, whereby only hydrocarbons with 6 or more carbon atoms were taken into account.

The catalysts used are commercially available. The platinum catalyst (0.3 wt% Pt on Al_2O_3, HDMAX800, Süd Chemie) is of cylindrical shape (4.5 mm length and diameter). The iridium catalyst (1 % Ir on Al_2O_3, Alfa Aesar) is spherical with a core-shell structure (0.5 mm shell thickness). The Rhodium catalyst (0.5 % Rh on Al_2O_3, Alfa Aesar) is cylindrical and also has a core-shell structure (0.5 mm shell thickness). Further properties of the catalysts are listed in Table 1. Before usage the catalysts were reduced for 2 h in H_2 at 250 °C.

Toluene ($\geq$99.7 % purity), ethylbenzene (99 % purity), propylbenzene (98 % purity), cyclohexane (99.9 % purity), and methylcyclohexane (99 % purity) were obtained from Sigma Aldrich. *m*-Xylene ($\geq$99 %) was purchased from Merck. All hydrocarbons were used without further purification. Naphtha (boiling range 30–230 °C) was provided by the MiRO Refinery (Karlsruhe, Germany). Due to the sulphur content of 600 ppm, the naphtha was desulfurized (hydrotreated) before usage to avoid catalyst poisoning (350 °C; H_2-pressure: 5.0 MPa; catalyst: NiMo/Al_2O_3, Süd Chemie). After desulfurization the S-content was less than 10 ppm. H_2 (purity grade 3.0) and N_2 (purity grade 5.0) were purchased from Riessner Gase.

3 Results and Discussion

At first, hydrogenation and ring opening reactions were studied with model substances. The results with iridium,

Table 1 Physical properties of the catalysts used in this work

Catalyst	HDMax 800 (Süd Chemie)	Ir/Al_2O_3 (Alfa Aesar)	Rh/Al_2O_3 (Alfa Aesar)
Composition	0.3 wt% Pt, Al_2O_3	1.0 wt% Ir, Al_2O_3	0.5 wt% Rh, Al_2O_3
Apparent density	1,260 kg/cm^3	1,100 kg/m^3	1,650 kg/m^3
Surface area (BET)	185 m^2/g	140 m^2/g	100 m^2/g
Porosity	68 %	72 %	60 %
Geometry	Cylindrical; length and diameter: 4.5 mm	Spherical; diameter: 5 mm, iridium shell: 0.5 mm	Cylindrical; length and diameter: 4 mm, Rh shell: 0.5 mm

rhodium and platinum as catalysts are shown in Sect. 3.1. Secondly, "real" naphtha was converted over the Pt and Ir catalysts (Sect. 3.2).

3.1 Experiments with Model Substances

3.1.1 Hydrogenation of Aromatics Over Pt/Al_2O_3

It is well known that platinum catalyses the hydrogenation of aromatics. Several research groups also claim that it is possible to ring open naphthenes over platinum catalysts [3, 17]. However, the results on the conversion of different aromatics over the platinum catalyst used here clearly indicate that ring opening is not possible. All aromatics are completely converted to the corresponding naphthenes, but a consecutive ring opening was not detected, and even at the highest temperature of 420 °C and long residence times (90 g s/cm^3) only the corresponding naphthenes were found as products. Even the direct usage of naphthenes as feedstock did not lead to a ring opening over the Pt-catalyst.

At a high modified residence time (=ratio of total mass of catalyst to the volumetric flow rate at reaction conditions) of e.g. 2 g s/cm^3, the conversion of the model aromatics toluene, ethylbenzene, propylbenzene, and *m*-xylene to the corresponding naphthenes is almost complete even at 200 °C. Fig. 3 depicts the conversion versus temperature (Fig. 3) at a very short residence time of 0.28 g s/cm^3 in a temperature range from 200 to 420 °C. At about 300 °C the reaction shifts from the regime of kinetic control to the regime of control by thermodynamics, i.e. the equilibrium limits the conversion, which then decreases with increasing temperature.

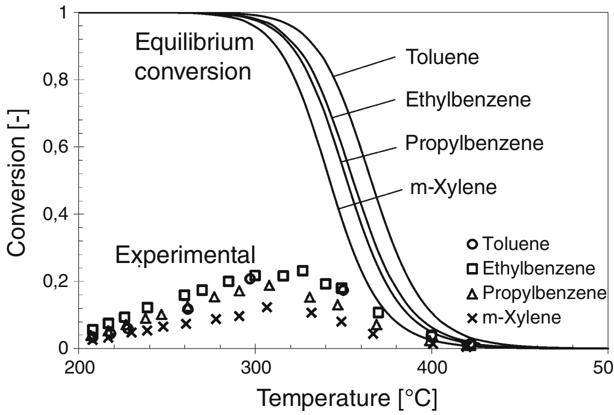

Fig. 3 Hydrogenation of different aromatics over Pt/Al_2O_3 (1.1 MPa; $n_{hydrogen}/n_{aromatic} = 15$; modified residence time: 0.28 g s/cm^3)

3.1.2 Ring Opening of Cyclohexane and Methylcyclohexane Over Ir/Al_2O_3 and Rh/Al_2O_3

In contrast to the Pt catalyst, ring opening takes place, if the Ir catalyst is used. In Fig. 4 (right), the conversion of cyclohexane over Ir/Al_2O_3 and the selectivities of the different products are depicted. In order to increase the conversion, the temperature was raised successively from 220 to 320 °C. At temperatures lower than 240 °C, the conversion of cyclohexane is less than 10 % and the selectivity to *n*-hexane is higher than 90 % (Fig. 4, left). With raising temperatures the conversion of cyclohexane increases while the selectivity to *n*-hexane decreases mainly via further cracking to short chain hydrocarbons. At 320 °C, nearly complete cyclohexane conversion (97 %) is reached, but the remaining selectivity of *n*-hexane is only 2 %. The main products are then methane, ethane, and propane (subsequently referred to as C_1 to C_3) with a selectivity of 94 %. In the medium temperature range between 250 and 280 °C, linear and branched butane and pentane as well as 2- and 3-methylpentane are also formed as intermediates (in Fig. 4 referred to as C_4 to C_6, except *n*-hexane), which are further cracked at T > 280 °C. These results show that the ring opening of cyclohexane only leads dominantly to *n*-hexane at a low degree of conversion, i.e. here at temperatures below 250 °C. At higher temperatures the paraffinic hydrocarbons are cracked over Ir/Al_2O_3 and the formation of C_1 to C_3 hydrocarbons increases drastically.

The appearance of small amounts 2- and 3-methylpentane raises the question about the reaction mechanism

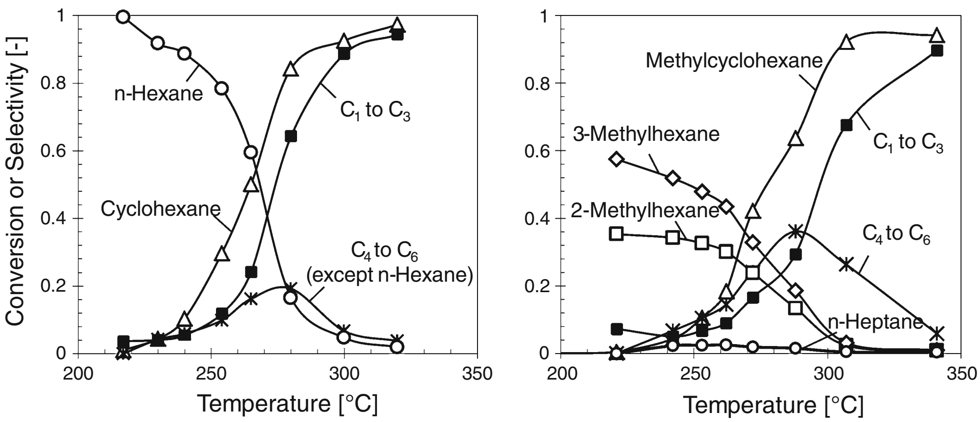

Fig. 4 Conversion of cyclohexane (*left*) and methylcyclohexane (*right*) over Ir/Al_2O_3 and the product selectivities (1.1 MPa; $n_{\mathrm{hydrogen}}/n_{\mathrm{hydrocarbon}} = 15$; modified residence time: 2 g s/cm^3)

occurring on the iridium catalyst. It is known that bifunctional catalysts with metal and acid sites contract the cyclohexane ring to form methylcyclopentane, which is subsequently ring opened to *n*-hexane but also 2- and 3-methylpentane [20]. Experiments with methylcyclopentane as feedstock over the iridium catalyst were carried out to get an indication about the reaction mechanism and the catalysts' acidity. The reaction conditions were equal to the ones listed in Fig. 4. The conversion of methylcyclopentane resulted in the formation of 2- and 3-methylpentane in a ratio of 2:1 but no *n*-hexane. This result shows that ring opening of cyclohexane over the iridium catalyst is not achieved by ring contraction but by direct opening on the metal site. Thus, acid sites on the iridium catalyst can be excluded.

To exclude temperature effects, the conversion of cyclohexane was also increased at a constant temperature (240 °C) by raising modified residence time successively from 2 to 8 g s/cm^3 (Fig. 5). For comparison, the result of the experiments discussed before at a constant residence time (2 g s/cm^3) but with varied temperature are also shown. At a conversion of about 30 %, in both cases the selectivity of *n*-hexane is about 80 %. Fig. 5 indicates that the selectivity to *n*-hexane is improved, if the conversion is enhanced by a higher residence time and not by increasing the temperature. For example at a conversion of 80 %, the *n*-hexane selectivity is still 61 % at 240 °C ($\tau = 8$ g s/cm^3) compared to only 16 % at 280 °C (2 g s/cm^3).

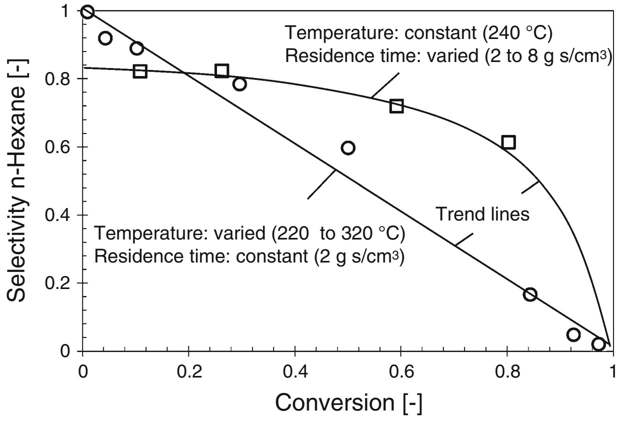

Fig. 5 Conversion of Cyclohexane over Ir/Al_2O_3 at constant temperature and at constant residence time (pressure: 1.1 MPa; $n_{\mathrm{hydrogen}}/n_{\mathrm{cylohexane}} = 15$)

A similar picture is obtained with methylcyclohexane as feedstock (Fig. 4, right), which was used to obtain informations on ring opening of 6-ring naphthenes with side chains. At temperatures below 260 °C and a corresponding low conversion of methylcyclohexane, the main products are 2-methylhexane (selectivity: 34 % at 240 °C) and 3-methylhexane (52 %) while C_1 to C_3 (5 %) and C_4 to C_6 hydrocarbons (HCs) (7 %) are formed to a very low extent. The selectivity to *n*-heptane is low (2 %) and remains below 3 % throughout the entire temperature range investigated. At higher temperatures (>240 °C), the conversion increases, and the selectivities to 2- and 3-methylhexane strongly decrease. The selectivity of C_4 to C_6 HCs passes a maximum at 290 °C (36 %) and then also drops. Hence, cracking of all these intermediates finally leads to C_1 to C_3 HCs (selectivity: 90 % at 340 °C).

This results show that the ring opening of cyclohexane and methylcyclohexane to the corresponding paraffins with the same carbon number is only possible at low temperatures. The selectivity decreases with increasing conversion, but to a lower extent, if the residence time and not the temperature is increased to achieve a higher conversion without loosing product quality (Fig. 5).

The experiments with methylcyclohexane also give a hint about the mechanism responsible for the product distribution of ring opened naphthenes with a side chain. Depending on where the ring is cleaved, three products are possible to be formed: 2-methylhexane, 3-methylhexane and *n*-heptane. If the mechanism is non-selective the three products would be formed with the same probability. As the product spectrum shows an 8:11:1 distribution of 2-methylhexane, 3-methylhexane, and *n*-heptane (Fig. 5) it is obvious that the mechanism is selective. This implies that mainly bisecondary bonds are cleaved according to the dicarbene mechanism. But the appearance of small amounts of *n*-heptane in the product spectrum shows that also tertiary-secondary bonds are broken. This leads to the conclusion that at least to a minor extent also the partially selective mechanism proceeds resulting in the formation of *n*-heptane via metallocyclobutane intermediates.

In summary, it can be stated that the ring opening of naphthenes with a side chain over the iridium catalyst predominantly forms branched paraffins, which is a drawback regarding the Cetane number (Fig. 1). Conversion of methylcyclohexane (CN = 20) mainly leads to 2-methylhexane (CN = 35) and 3-methylhexane (CN = 17). Only 5 % of *n*-heptane (CN = 53) is formed. Hence, the average CN only increases from 20 to 26 (Fig. 6).

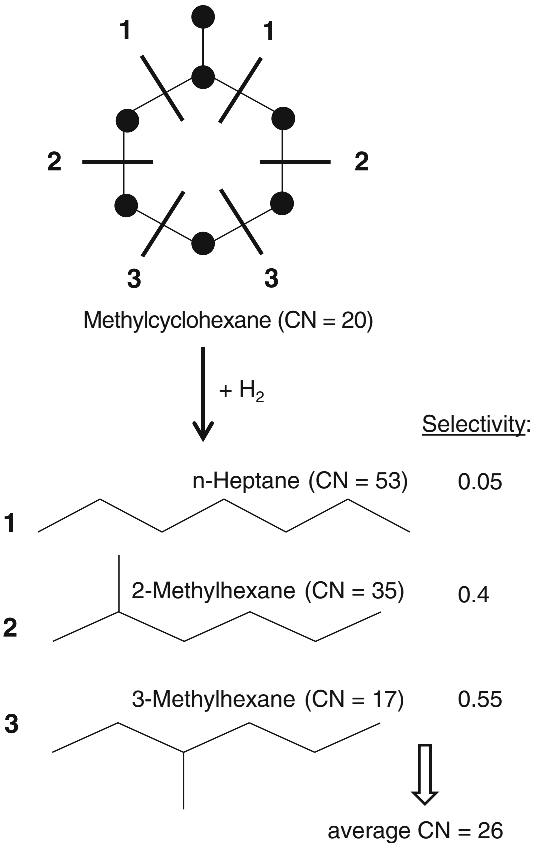

Fig. 6 Product distribution after the cleavage of bisecondary (*2* and *3*) and tertiary–secondary (*1*) bonds of the methylcyclohexane ring over Ir/Al_2O_3

Based on the results shown in Fig. 4 the reaction rates (r_m in mol kg_{cat}^{-1} s^{-1}) of the conversion of cyclohexane and methylcyclohexane were calculated.

The solution of the power law reaction rate approach (with τ as modified residence time = ratio of total mass of catalyst to the volumetric flow rate at reaction conditions)

$$-\frac{dc_i}{d\tau} = r_m = k(T)c_i^m c_{H_2}^n \qquad (1)$$

leads to the following equation for the reaction rate constant k(T)

$$k(T) = \frac{(1-X)^{1-m} - 1}{(m-1)c_{i,in}^{(m-1)} c_{H_2}^n \tau} \qquad (2)$$

X is the conversion of the hydrocarbon, $c_{i,in}$ the initial hydrocarbon concentration, and c_{H2} the constant hydrogen concentration (high surplus).

In the area of low conversions (T < 260 °C), the rate constant k(T) is in agreement with Arrhenius' law:

$$k(T) = k_0 e^{-\frac{E_A}{RT}} \qquad (3)$$

It was proven by respective calculations, that internal and external mass transfer limitations are not present in this temperature range. The values for the activation energy E_A, the pre-exponential factor k_0, and the reaction orders m and n are listed in Table 2. The reaction orders for hydrogen and for the hydrocarbon were experimentally determined by varying separately the respective feed concentration (Table 2). The Arrhenius plot is shown in Fig. 7. Due to different reaction orders of hydrogen, and thus different units of k, Fig. 7 depicts the reaction rate (and not k) versus the reciprocal temperature in order to compare the activity of the Ir catalyst for conversion (ring opening) of cyclohexane and methylcyclohexane. The activation energy is similar in both cases (around 200 kJ/mol, Table 2). Hence, the rates differ by a constant factor, whereby the activity to convert cyclohexane is (at 1.1 MPa) by a factor of three higher. Interestingly (although the reason is still an open question), the rate of ring opening of methylcyclohexane is slightly enhanced with increasing hydrogen concentration ($r_{MCH} \sim c_{H2}^{0.5}$), whereas for cyclohexane this is reverse and the rate decreases ($r_{CH} \sim 1/c_{H2}$).

The ring opening of cyclohexane was also studied over a rhodium catalyst (0.5 % Rh/Al_2O_3, cylindrical shape,

Table 2 Kinetic data of cyclohexane and methylcyclohexane conversion (ring opening) over Ir/Al_2O_3 (1.1 MPa; $n_{hydrogen}/n_{hydrocarbon} = 15$; modified residence time: 2 g s/cm^3)

	E_A in kJ	k_0	Reaction order H_2 (m)	Reaction order hydrocarbon (*n*)
Cyclohexane	204	1.7×10^{19} $mol^{1.5}/m^{1.5}$ kg s	−1	0.5
Methylcyclohexane	197	4.8×10^{14} m^3/kg s	0.5	0.5

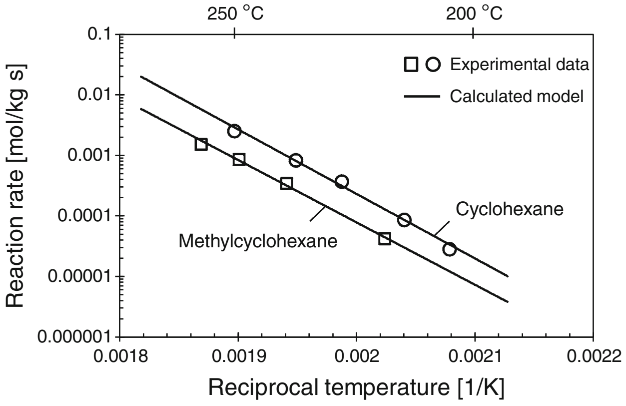

Fig. 7 Arrhenius plot of cyclohexane and methylcyclohexane ring opening over Ir/Al_2O_3 (200–260 °C, 1.1 MPa; $n_{\text{hydrogen}}/n_{\text{hydrocarbon}} = 15$; modified residence time: 2 g s/cm^3)

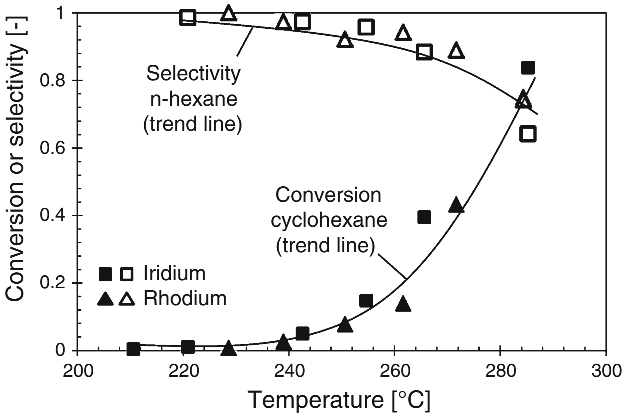

Fig. 8 Conversion of cyclohexane over 0.5% Rh/Al_2O_3 and 1.0 % Ir/Al_2O_3 and the selectivity of *n*-hexane (5 MPa; $n_{\text{hydrogen}}/n_{\text{cylohexane}} = 15$, modified residence time: 30 g s/cm^3 (Rh) and 15 g s/cm^3 (Ir); note that the residence time related to the mass of the noble metal is constant

4.5 mm in height and diameter, purchased from Alfa Aesar). Neither the conversion of cyclohexane nor the selectivity of *n*-hexane is influenced by the type of noble metal (Fig. 8), if the residence time related to the mass of the noble metal is kept constant. Thus, it can be assumed that the results shown here, which were mainly performed over iridium, could also be achieved by using a similar rhodium based catalyst.

3.1.3 Conversion of Aromatics Over Ir/Al_2O_3

The conversion of toluene, propylbenzene, and *m*-xylene over Ir/Al_2O_3 was studied at temperature from 220 to 280 °C. In all three cases the hydrogenation to the corresponding naphthenes is very fast, and almost complete conversion of the aromatics is reached even at the lowest temperature of 220 °C (Fig. 9).

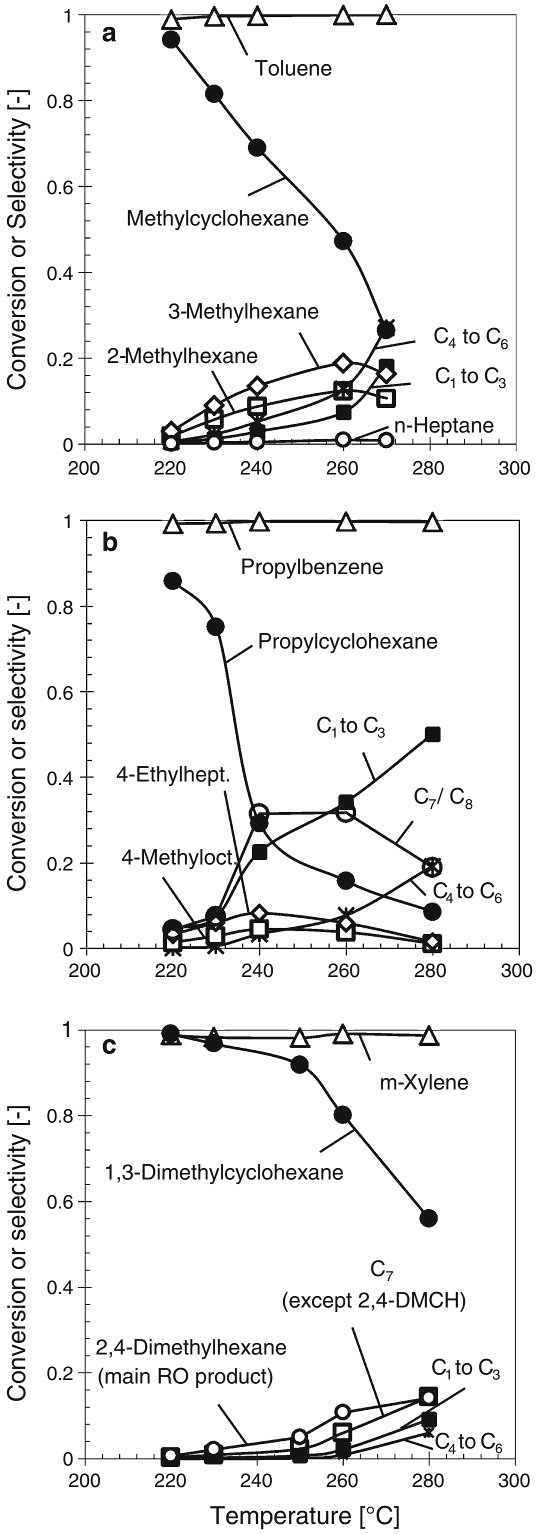

Fig. 9 Conversion of toluene (**a**), propylbenzene (**b**) and *m*-xylene (**c**) over Ir/Al_2O_3 and product selectivities (1.1 MPa; $n_{\text{hydrogen}}/n_{\text{hydrocarbon}} = 50$, modified residence time: 2 g s/cm^3)

In case of toluene (Fig. 9a), the primary product at 220 °C is methylcyclohexane, which is subsequently ring opened mainly to 2- and 3-methylhexane. As expected in respect to initial fast hydrogenation of toluene, the distribution of ring opening products is equal to the results of the conversion of methylcyclohexane. Again, cracking reactions at temperatures higher than 240 °C predominantly lead to formation of C_1 to C_6 hydrocarbons.

The conversion of propylbenzene (Fig. 9b) leads initially to the formation of propylcyclohexane, which is ring opened subsequently. The expected products *n*-nonane, 4-methyloctane, and 4-ethylheptane are formed in a ratio of 1:10:20. This fits in the theory that ring opening over iridium follows the dicarbene mechanism, where mainly the bisecondary bonds are cleaved leading to the formation of branched hydrocarbons. At 240 °C, the formation of C_7/C_8 and C_1 to C_3 hydrocarbons escalates. Propylcyclohexane is split into ethane and methylcyclohexane, which is subsequently ring opened to 2- and 3-methylhexane. Unfortunately, the yield of C_9 ring opening products is therefore <15 %. To avoid side chain cleavage of the naphthenes temperatures below 240 °C are necessary.

In Fig. 9c, the conversion of *m*-xylene over Ir/Al_2O_3 is depicted. The hydrogenation to 1,3-dimethylcyclohexane (1,3-DMCH) is very fast, but compared to methyl- and propylcyclohexane the ring opening of 1,3-DMCH to paraffins is slower. Even at 280 °C 1,3-DMCH is still the main product with a selectivity of 55 %. The distribution of the three possible ring opening products 4-methylheptane, 2-methylheptane, and 2,4-dimethylhexane is 1:4:30. As expected, the main ring opening product is 2,4-dimethylhexane, showing that the 1,3-DMCH is opened predominantly in bisecondary positions.

Figure 10 summarizes the reactions and the product selectivities obtained in with the different aromatic hydrocarbons with Ir/Al_2O_3 as catalyst. In the best case, i.e. if cracking is negligible, the increase of the cetane number is relatively high for benzene (from −10 to 42), toluene (−5 to 26), and *m*-xylene (1 to 29), but rather low for propylbenzene (15 to 16).

3.2 Hydrogenation and Ring Opening of Aromatic and Naphthenic Compounds of Naphtha

The composition of the naphtha used here before and after conversion over platinum and iridium catalysts at temperatures between 250 and 290 °C and the resulting cetane numbers are listed in Table 3. For hydrogenation over Pt/Al_2O_3 the cetane number raised only from 32 to 34. This marginal increase is due to the composition of the feed. The used naphtha already contains almost 60 % paraffins, which are the target product, and 32 % naphthenes, which are not ring opened over the platinum catalyst. Only the aromatics, which are present to a small extent (9 %), are nearly completely converted to their corresponding naphthenes. Thus, the cetane number of low aromatic but high paraffinic and naphthenic feed stocks cannot be significantly changed by using a catalyst, which is only active for aromatic hydrogenation.

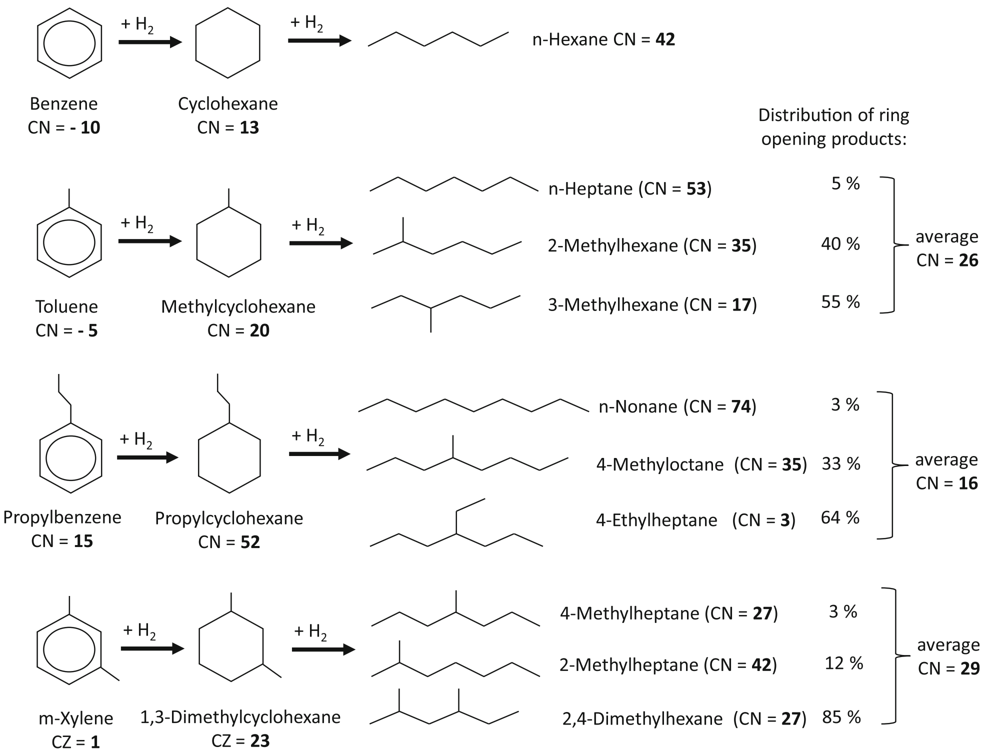

Fig. 10 Reaction paths of aromatic hydrogenation and ring opening over Ir/Al_2O_3 (and Rh/Al_2O_3)

Table 3 Conversion of naphtha over platinum and iridium catalysts at different temperatures (5 MPa; $n_{hydrogen}/n_{naphtha} = 15$; modified residence time: 90 g s/cm^3)

	Catalyst	Fractions in wt%					CN
		n-Paraffins	*i*-Paraffins	C_5-naphthenes	C_6-naphthenes	Aromatics	
Feed (Naphtha)		25.4	33.8	13.8	18.2	8.8	32
250 °C	Pt/Al_2O_3	25.8	32.6	14.5	26.2	0.8	34
270 °C		25.7	32.4	14.6	26.4	0.8	34
290 °C		25.9	32.5	14.5	26.2	0.9	34
250 °C	Ir/Al_2O_3	25.8	48.2	7.5	18.2	0.3	32
270 °C		24.7	64.9	3.2	7.0	0.2	31
280 °C		15.1	79.4	2.3	2.9	0.3	28

Table 4 Carbon number distribution of naphtha before and after conversion over Ir/Al_2O_3

Number of carbon atoms	Naphtha	250 °C	270 °C	280 °C
C_1/C_2	0.0	0.6	4.4	8.2
C_3–C_5	9.4	14.8	23.9	27.6
C_6–C_8	**69.1 (76.4)**	**76.2 (90)**	**68.2 (95)**	**59.2 (92.2)**
C_9–C_{11}	**21.4 (23.6)**	**8.5 (10)**	**3.6 (5)**	**5.0 (7.8)**

Bold hydrocarbons used to calculate the cetane number, values in brackets indicate the content within the C_6 to C_{11} fraction, which is used to calculate the CN

To hydrogenate all aromatics and additionally ring open the resulting naphthenes (and the naphthenes already present in the feed), the naphtha was converted over Ir/Al_2O_3. Unfortunately, the CN remains constant (250 °C) or even decreases (280 °C) from 32 to 28 (Table 3). (Note that the CN was calculated for the fraction "C_6 and higher" only.) This negative effect on the cetane number can be attributed to three reasons:

Firstly, the reaction mechanism leads to an unfavourable product distribution. Even at the lowest temperature of 250 °C the aromatics are completely converted (content <0.3 %) and the content of 5-ring-naphthenes drops from 14 to 8 %. The fraction of 6-ring-naphthenes remains constant (18 %), but one has to consider that this fraction also contains the hydrogenated aromatics, which are not completely converted to paraffins at 250 °C. The fraction of *n*-paraffins remains unchanged while the fraction of *i*-paraffins increases from 33 to 48 %. As discussed in Sect. 3.1.2, the conversion of naphthenes over the Ir catalyst leads predominantly to a cleavage of bisecondary bonds, and hence mainly branched paraffins (with low CN) are formed. With rising temperature and conversion this effect is intensified. At 280 °C the residual content of 5- and 6-ring-naphthenes is low ($\leq$3 %) and iso-paraffins are dominant (79 %).

The second reason that leads to a low cetane number is the cracking of hydrocarbons taking place over Ir/Al_2O_3. Table 4 shows the carbon number distribution of the feed (naphtha) and the product after conversion over the Ir catalyst. The feed consists of 69 % C_6 to C_8 compared to 21 % C_9 to C_{11} HCs, i.e. 24 % within the C_6 to C_{11} fraction used to calculate the CN. With conversion over Ir/Al_2O_3 and rising temperatures the composition of the product is shifted to short-chained hydrocarbons. At 250 °C the fraction of C_6 to C_8 (within the C_6 to C_{11} fraction) increases to 90 % and is even higher for 270 and 280 °C. Hence, long chained hydrocarbons like C_9 to C_{11}, which have a fraction of more than 20 % in the feed, are almost completely cracked to shorter ones over the iridium catalyst, which decreases the cetane number (Fig. 1).

A drawback is also, that the fraction of C_3 and C_5 hydrocarbons increases from 9 % in the feed to 15 % at 250 °C and at 280 °C even to 28 %. C_1 and C_2 hydrocarbons (methane and ethane), which are very undesirable, are also formed at temperatures above about 270 °C.

Thirdly, the naphtha used here is already rich in paraffines (59 %, see Table 3). Thus, the conversion of the aromatics (only 9 %) and of the naphthenes (about 32 %) does not lead to an improvement of the CN compared to the expected case of a highly aromatic/naphthenic naphtha as feedstock.

4 Summary

The conversion of aromatics (toluene, propylbenzene, *m*-xylene) over Ir/Al_2O_3 and Rh/Al_2O_3 reveals that it is possible to perform hydrogenation of aromatics as well as ring opening of the corresponding naphthenes with one single catalyst. Full conversion by hydrogenation to naphthenes is already achieved at 220 °C. Hence, the consecutive ring opening of the naphthenes is the rate determining step. The distribution of the paraffinic products leads to the conclusion that the reaction follows the dicarbene mechanism. For a high conversion, unfavourable cracking takes place leading to short chain hydrocarbons, if the temperature is higher than about 240 °C. With Pt/Al_2O_3 as catalyst, only hydrogenation and not ring opening occurs.

With Ir/Al_2O_3 as catalyst, the achievable increase of the cetane number (CN) is high for benzene (from -10 to 42), toluene (-5 to 26), and *m*-xylene (1 to 29), but rather low for propylbenzene (15 to 16). Nevertheless, these values are still low compared to commercial diesel oils with CN of around 50. The reason is that mainly branched paraffines (with low CN) and - with the exception of benzene only to a small extent *n*-paraffines (high CN, selectivity < 5 %) are formed. If real naphtha is used as feedstock, the increase of CN may be low or even negligible, because cracking of long chain hydrocarbons (with high CN) takes place.

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