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Ring opening of decalin via hydrogenolysis on Ir/- and Pt/silica catalysts

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ABSTRACT

The catalytic conversion of cis-decalin was studied at a hydrogen pressure of 5.2 MPa and temperatures of 250–410 °C on iridium and platinum supported on non-acidic silica. The absence of catalytically active Brønsted acid sites was indicated by both FT-IR spectroscopy with pyridine as a probe and the selectivities in a catalytic test reaction, viz. the hydroconversion of n-octane. On iridium/silica, decalin hydroconversion starts at ca. 250–300 °C, and no skeletal isomerization occurs. The first step is rather hydrogenolytic opening of one six-membered ring to form the direct ring-opening products butylcyclohexane, 1-methyl-2-propylcyclohexane and 1,2-diethylcyclohexane. These show a consecutive hydrogenolysis, either of an endocyclic carbon-carbon bond into open-chain decanes or of an exocyclic carbon-carbon bond resulting primarily in methane and C₉ naphthenes. The latter can undergo a further endocyclic hydrogenolysis leading to open-chain nonanes. All individual C_{10} and C_9 hydrocarbons predicted by this "direct ringopening mechanism" were identified in the products generated on the iridium/silica catalysts. The carbon-number distributions of the hydrocracked products C₉- show a peculiar shape resembling a hammock and could be readily predicted by simulation of the direct ring-opening mechanism. Platinum on silica was found to require temperatures around 350-400 °C at which relatively large amounts of tetralin and naphthalene are formed. The most abundant primary products on Pt/silica are spiro[4.5]decane and butylcyclohexane which can be readily accounted for by the well known platinum-induced mechanisms described in the literature for smaller model hydrocarbons, namely the bond-shift isomerization mechanism and hydrogenolysis of a secondary-tertiary carbon-carbon bond in decalin.

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1. Introduction

A promising route for upgrading low-quality middle-distillate refinery streams with a high content of polynuclear aromatics into valuable blending cuts for diesel fuel is their hydrogenation to multi-ring naphthenes followed by selective ring opening to alkyl naphthenes with one remaining ring or open-chain alkanes. As the complete hydrogenation of polynuclear aromatics is well developed [1–3], the selective hydrodecyclization of multi-ring naphthenes without excessive hydrocracking into hydrocarbons with less carbon atoms has recently become a major issue in heterogeneous catalysis.

Three principal families of solid catalysts are usually distinguished for the cleavage of carbon—carbon bonds, viz. (i) monofunctional acidic catalysts, (ii) bifunctional catalysts containing both Brønsted acid and metal sites, and (iii) monofunctional metal catalysts. Since about 2000, a large number of publications has appeared dealing with the hydroconversion of multi-ring, especially bicyclic naphthenes, naphthenoaromatics and aromatics on either bifunctional [4–14] or monofunctional acidic [4,5,9] catalysts. By contrast, the literature on ring opening of multi-ring naphthenes on monofunctional metal catalysts is rather scarce, though there are papers available from two groups who studied the field remarkably thoroughly and comprehensively [15–17].

Much more information is available concerning the metalcatalyzed hydrocracking (often referred to as "hydrogenolysis") of monocyclic naphthenes, in particular cyclopentane, cyclohexane, and their alkyl-substituted derivates. To a large extent, the nomenclature proposed by Maire et al. [18] for the various hydrogenolysis mechanisms applicable to naphthenes has been widely adopted. Basically, three mechanisms are usually discerned that were essentially advanced by Gault and his school for metal-catalyzed ring opening of naphthenes [19]: in the so-called non-selective mechanism the likelihood of all endocyclic carbon—carbon bonds for being cleaved is considered to be equal. By contrast, the salient feature of the selective mechanism is an exclusive cleavage of bonds between

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secondary carbon atoms. Finally, the partially selective mechanism describes the rupture of bonds between carbon atoms which are substituted by at least one methyl group.

For example, when methylcyclopentane is hydroconverted on iridium, the naphthenic ring is opened selectively at the bisecondary positions [15]. Platinum shows a very similar ring opening selectivity, however only, if the metal is poorly dispersed. On highly dispersed platinum, by contrast, the ring is opened non-selectively [18]. Upon introducing an increasing number of alkyl substituents or when a six-membered instead of a five-membered ring is to be opened, higher reaction temperatures have to be applied and more than one ring-opening mechanism occur simultaneously [15,20–22].

Five-membered rings are relatively easy to open on noble-metal catalysts without making hydrocarbons with lower carbon numbers. Six-membered rings can be opened on this type of catalysts as well, but larger amounts of by-products are usually formed. It has been demonstrated in several publications that, on a non-acidic support, iridium is the most active and selective metal for ring opening of naphthenes [15,23].

In their detailed study of hydrogenolytic ring opening of naphthenes on various metals, McVicker et al. [15] used both monocyclic and bicyclic model hydrocarbons. In the hydroconversion of bicyclo[3.3.0]octane on iridium/alumina, for example, both fivemembered rings were readily opened to give octane isomers. When bicyclo[4.3.0]nonane, which contains both a five-membered and a six-membered ring was hydroconverted on the same catalyst, the five-membered rings were again rapidly opened, but open-chain nonanes were formed in low yields only indicating that the sixmembered rings are remarkably recalcitrant to be opened. Decalin (bicyclo[4.4.0]decane), which consists of two six-membered rings, was also hydroconverted on the iridium/alumina catalyst and turned out to react very slowly, with open-chain decanes being formed in traces only.

Recently, we reported on the hydroconversion of decalin on typical bifunctional catalysts, such as Ir/La-X and Pt/La-X zeolites using improved methods for analyzing the very complex product mixtures [24]. In another paper [25] a novel class of highperformance ring-opening catalysts (HIPEROCs) was introduced based on Ir/Na,H-Y and Pt/Na,H-Y zeolites with a low concentration of Brønsted acid sites. On these catalysts, decalin could be hydroconverted to open-chain decanes with unprecedented selectivities and yields up to ca. 40%. Preliminary results obtained in the hydroconversion of decalin on non-acidic Ir/silica catalysts were also published [26]. On these catalysts, a hitherto unknown carbonnumber distribution of the hydrocracked products was observed for which the term "hammock-type curve" was coined. Here, we present the results of a detailed investigation of decalin ring opening on non-acidic Ir/silica and Pt/silica catalysts and interpret the results in terms of hydrocarbon conversion mechanisms on the two noble metals.

2. Experimental

2.1. Preparation and characterization of the catalysts

Four catalysts were prepared, viz. 0.77Ir/silica, 2.59Ir/silica, 0.93Pt/silica, and 2.68Pt/silica, by loading silica (Aerosil 380, Evonik Degussa GmbH, average primary particle size according to the manufacturer 7 nm) with [Ir(NH₃)₅Cl]Cl₂ or [Pt(NH₃)₄]Cl₂ via electrostatic adsorption [27]. The numbers in the catalyst designations indicate the metal content in wt.% on a dry basis. For the preparation of 0.77Ir/silica and 0.93Pt/silica, 8.0 g of silica were suspended in 100 cm³ of demineralized water, this suspension was vigorously stirred for 2 h, and during that time the pH was adjusted to 10 by

dropwise addition of a 1 molar aqueous ammonia solution. Subsequently, 206 mg of the iridium complex or 145 mg of the platinum complex dissolved in 30 cm³ of demineralized water were added dropwise under ongoing stirring. After stirring for another 18 h the solid was filtered off, washed with 100 cm³ of demineralized water and dried at 80 °C. Likewise, 2.59Ir/silica and 2.68Pt/silica were prepared by suspending 4.0 g of silica in 50 cm³ of demineralized water, the pH was again adjusted to 10, and a solution of 300 mg of the iridium complex or 215 mg of the platinum complex in 20 cm³ of demineralized water were added dropwise. Thereafter, the suspension was again stirred for 18 h, and the solid was filtered off, washed with 50 cm³ of demineralized water and dried at 80 °C. The resulting catalyst powder was pressed into tablets without a binder at a pressure of 127 MPa, and the tablets were crushed and sieved. The particle size fraction from 0.20 to 0.32 mm was transferred into the catalytic reactor. There, the adsorbed complex was treated in an air flow at 0.1 MPa and 150 °C for 3 h in order to obtain a high metal dispersion [27]. Finally, the noble metal was reduced in a flow of hydrogen at 0.1 MPa and 400 °C for 2 h.

For elemental analysis of iridium and platinum, an optical emission spectrometer with an inductively coupled plasma (ICP-OES, Varian Vista-MPX CCD) was used. The catalysts were dissolved in a mixture of diluted hydrofluoric acid and aqua regia. Details concerning the measurement of the water content are given in Ref. [24].

The dispersion of the noble metal was determined by measuring the amount of irreversibly adsorbed hydrogen in a Quantachrome Autosorb-1-C instrument. For details of the experimental procedure see Ref. [24]. An adsorption stoichiometry of $n_{\rm H}/n_{\rm metal}$ = 1 was assumed. For the calculation of the metal particle size, a spherical shape and densities of, respectively, 22.42 and 21.45 kg dm⁻³ for iridium and platinum were assumed. The porosity of the catalyst support silica was measured by nitrogen physisorption at T = -196 °C in the same Quantachrome Autosorb-1-C instrument after degassing the samples at T = 350 °C for 16 h. For evaluating the BET specific surface area the range of p/p_0 between 0.1 and 0.3 was used. For the N₂ molecule a cross-sectional area of 1.62 nm² was assumed.

With FT-IR spectroscopy and pyridine as a probe molecule, information about the Brønsted acid sites of the silica support and, exemplarily, of one metal-loaded catalyst was collected. A Bruker Vector 22 spectrometer equipped with a high-vacuum sample cell was employed. Self-supporting wafers were made from the powdered samples of silica and of the precursor of 2.68Pt/silica after drying at 80 °C. Subsequently, they were treated in an air flow in the sample holder of the IR cell at 150 °C. After reduction of the noble metal with hydrogen at T = 500 °C, pyridine was adsorbed at T = 100 °C, and desorption took place at T = 200 °C. For experimental details of the IR measurements see Ref. [25].

No evidence was obtained for the existence of Brønsted acid sites on the silica carrier by FT-IR spectroscopy. This result was corroborated by a catalytic test reaction, viz. the hydroconversion of n-octane, which was carried out on the catalysts 0.77Ir/silica and 0.93Pt/silica. If Brønsted acid sites with a sufficient strength and in a sufficient concentration had been present, n-octane would have been converted into the typical products of bifunctional hydrocarbon conversion, namely a mixture of iso-octanes at low and moderate conversions and, at elevated conversions, hydrocracked products with 3–5 carbon atoms, but without C₁, C₂, C₆ and C₇ hydrocarbons [28]. Conversely, in the absence of catalytically active Brønsted acid sites, n-octane would be converted at the respective metal sites and, in particular, hydrogenolysis to light alkanes including C1, C2, C6, and C7 hydrocarbons would occur. For the noctane test, a flow-type apparatus made of glass with a fixed-bed reactor was used. The mass of catalyst, the hydrogen partial pressure, the $\dot{n}_{\rm H_2}/\dot{n}_{\rm n-Oc}$ ratio and the *LHSV* were 0.5 g, 0.1 MPa, 34 and $0.5 h^{-1}$, respectively. The reaction temperature was varied from 217 to 393 °C, and the products were analyzed on-line in a Hewlett-Packard HP 5890 gas chromatograph equipped with a BP1 PONA (50 m \times 0.15 mm \times 0.5 μ m) capillary column and a flame ionization detector (FID).

2.2. Hydroconversion of decalin

The Ir/- and Pt/silica catalysts were tested with cis-decalin (Merck, purity >98%) as reactant in the gas phase. All catalytic experiments were conducted in a high-pressure flow-type apparatus from stainless steel. Its main parts were a saturator filled with an inert solid (Merck, Chromosorb P/AW, particle size 0.25-0.60 mm) and the liquid reactant, in which the hydrogen stream was loaded with vapors of cis-decalin in the desired concentration [29], and a fixed-bed reactor. The mass of dry catalyst, the total pressure, the partial pressure of cis-decalin and the LHSV amounted to 0.17 g, 5.2 MPa, 25 kPa and 0.4 h⁻¹, respectively. The reaction temperature was varied in the range from 250 to 410 °C. The reactor effluent was depressurized in a needle valve, and the product stream was then passed through a heated six-port gas sampling valve which allowed an on-line introduction of full product samples into a gas chromatograph (Agilent 6890N) equipped with a Supelco Petrocol DH 150 ($150 \text{ m} \times 0.25 \text{ mm} \times 1.0 \mu \text{m}$) capillary column and a flame ionization detector. The gas stream leaving the gas sampling valve was routed through a cooling trap held at $-10 \degree C$ where an integral liquid hydrocarbon sample was collected over several hours.

The entire quantitative evaluation of the catalytic experiments was based on the analysis of the full product samples sluiced into the on-line gas chromatograph via the gas sampling valve. The integral liquid product samples were used for qualitative peak assignment via ancillary off-line GC/MS analyses. A second gas chromatograph (Agilent 6890N) which was also equipped with a Supelco Petrocol DH150 capillary column and coupled to a mass spectrometer (Agilent 5876B inert XL MSD) was used for this purpose. Peak assignment was further refined by (i) co-injection of pure hydrocarbons whenever these were commercially available and (ii) co-injection of a mixture of decane isomers of known composition which was generated by catalytic isomerization of n-decane [30]. A more comprehensive description of our methods for peak assignment has been presented elsewhere [24].

For the subsequent discussion, it is convenient to classify the product hydrocarbons from cis-decalin into the following six groups:

- 1. tr-Dec: trans-decalin formed by a rapid stereoisomerization;
- 2. sk-Isos: skeletal isomers of decalin with two remaining naphthenic rings, a molar mass $M = 138 \text{ g mol}^{-1}$, and a molecular formula $C_{10}H_{18}$;
- 3. ROPs: ring-opening products with one remaining naphthenic ring, $M = 140 \text{ g mol}^{-1}$, $C_{10}H_{20}$;
- 4. OCDs: open-chain decanes, $M = 142 \text{ g mol}^{-1}$, $C_{10}H_{22}$;
- 5. DHPs: dehydrogenation products, mainly tetralin and naphthalene;
- 6. C_{9-} : hydrocracked products with less than ten carbon atoms.

As will be shown, by far the fastest reaction of cis-decalin on the noble metal/silica catalysts is its stereoisomerization into transdecalin. We found it convenient not to treat this compound as a product but rather to lump it with cis-decalin to the pseudoreactant decalin (Dec).

For the quantitative discussion of the hydrocracking reactions to C_{9^-} hydrocarbons, the modified hydrocracking selectivities S_j^* will be used. S_i^* is defined as the molar amount of a hydrocarbon or



Fig. 1. Conversion of n-octane on 0.77lr/silica (\bigcirc) and on 0.93Pt/silica (\bullet) and yields of hydrocracked products on 0.77lr/silica (\triangle) and on 0.93Pt/silica (\checkmark) at different temperatures.

a group of hydrocarbons *j* formed divided by the molar amount of decalin converted into C_{9^-} products:

$$S_{j}^{*} \equiv \frac{(\dot{n}_{j})_{\text{formed}}}{(\dot{n}_{\text{decalin}})_{\text{converted to } C_{9}-}} = \frac{(\dot{m}_{j})_{\text{formed}}}{(\dot{m}_{\text{decalin}})_{\text{converted to } C_{9}-}} \cdot \frac{M_{\text{decalin}}}{M_{j}} \quad (1)$$

where \dot{n} , \dot{m} and M are, respectively, the molar flux, the mass flux, and the molar mass. For the evaluation of Eq. (1) and the calculation of the decalin conversion X_{Dec} , the yields of products Y_j , and the selectivities of products S_i see Ref. [24].

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Physicochemical properties

For the silica support, a specific surface area of 391 $m^2 g^{-1}$ and a pore volume of 1.07 $\text{cm}^3 \text{g}^{-1}$ were determined. In Table 1, the results of the physicochemical characterization of the metal components are listed. The amount of noble metal taken up by silica in comparison with the amount of noble metal offered in the solution during electrostatic adsorption was 60%, 69%, 92%, and 90% for 0.77Ir/silica, 2.59Ir/silica, 0.93Pt/silica, and 2.68Pt/silica, respectively. For iridium, metal dispersions above 1 were formally measured by hydrogen chemisorption, in agreement with reports by others [31]. Such a finding is usually attributed to an adsorption stoichiometry $n_{\rm H}/n_{\rm H} > 1$. The platinum particles appear to be larger than the iridium particles with a similar metal loading. For a given metal, the specific surface area referenced to the mass of the overall catalyst, expectedly increases with increasing metal content. Somewhat surprisingly, the catalytic activity of 2.68Pt/silica is not significantly higher than that of 0.93Pt/silica, even though its content of platinum is higher by about a factor of 2.9. This may, in part, be due to the much lower dispersion of 2.68Pt/silica, but further unknown reasons might play a role as well.

By FT-IR measurements with pyridine as a probe no absorption band at $1545 \,\mathrm{cm}^{-1}$ was detected, neither on the silica support without a noble metal, nor on 2.68Pt/silica. Hence, no Brønsted acid sites of sufficient strength for the protonation of pyridine exist on this catalyst. Since the other three noble-metal-containing catalysts were prepared in an analogous manner, it is justified to assume that all four catalysts are lacking Brønsted acid sites.

3.1.2. n-Octane test

In the hydroconversion of n-octane, catalyst 0.77Ir/silica was considerably more active than 0.93Pt/silica, see Fig. 1. Due to catalyst deactivation at the low hydrogen pressure of ca. 0.1 MPa, a more

Table 1

Physicochemical properties of the noble metals on the four catalysts (the specific surface area is referenced to the mass of the overall catalyst).

	Noble metal						
Catalyst	Content/wt.%	Dispersion	Particle size/nm	Specific surface area/m ² g ⁻¹			
0.77Ir/silica	0.77	1.52	0.65	3.16			
2.59Ir/silica	2.59	1.02	0.97	7.12			
0.93Pt/silica	0.93	0.99	1.1	2.28			
2.68Pt/silica	2.68	0.64	1.8	4.25			

detailed interpretation of relative catalyst activities is not possible. Hydrogenolysis was by far the predominating reaction on the iridium catalyst with a selectivity of hydrocracked products beyond 93%, as indicated by the nearly overlapping curves of n-octane conversion and yields of hydrocracked products. Other products were mainly methylheptanes and ortho-xylene, formed by a very minor extent of skeletal isomerization and aromatization, respectively. By contrast, on 0.93Pt/silica, hydrocracking was much less pronounced, with selectivities between 26 and 42%. Several other reactions occurred on platinum, resulting in the diverging values of conversion and yields of hydrocracked products in Fig. 1. These were, in decreasing order of abundance, dehydrocyclization, mainly to propylcyclopentane and 1-ethyl-2-methylcyclopentane, aromatization, mainly to ethylbenzene and ortho-xylene, and skeletal isomerization, mainly to 2-, 3-, and 4-methylheptane. A similar product distribution in the hydroconversion of n-octane on 2.0Pt/alumina was interpreted in terms of pure metal catalysis [32].

In sharp contrast, the n-octane test led to completely different results when bifunctional zeolite catalysts like 0.85Ir/La-X or 1.00Pt/La-X were used [24]: on Ir/La-X, skeletal isomerization via carbocations occurred with selectivities of up to 58%. Likewise, skeletal isomerization and consecutive hydrocracking were the sole reactions on Pt/La-X, while the metal-catalyzed dehydrocyclization and aromatization were virtually absent [24].

Typical carbon number distributions observed in the n-octane test on 0.771r/silica and 0.93Pt/silica are shown in Fig. 2. These curves deviate substantially from those obtained in the hydroconversion of n-octane on bifunctional catalysts [28]. While the latter are bell- (or volcano-) shaped with pronounced maxima at C₄ and smaller but noticeable amounts of C₃ and C₅, significant amounts of C₁, C₂, C₆ and C₇ are additionally formed on 0.771r/silica and 0.93Pt/silica. This is in agreement with the results obtained in noctane hydroconversion on non-acidic 2.0Pt/alumina [32]. The only



Fig. 2. Modified hydrocracking selectivities S_j^* in the hydroconversion of n-octane on 0.77lr/silica (\bigcirc , $T_r = 280 °C$; $X_{n-Oc} = 9\%$; $Y_{C_{j-}} = 8\%$; $\Sigma S_j^* = 263\%$) and 0.93Pt/silica (\bullet , $T_r = 332 °C$; $X_{n-Oc} = 14\%$; $Y_{C_{j-}} = 4\%$; $\Sigma S_j^* = 224\%$).

reasonable interpretation of the distribution curves in Fig. 2 are a hydrogenolytic mechanism of carbon—carbon bond cleavage on the respective metal. It is straightforward to assume that hydrocarbon conversion on the silica-supported catalysts with higher metal loadings occurs on the metal sites as well, without participation of Brønsted acid sites.

3.2. Stereoisomerization of cis-decalin to trans-decalin

On all four catalysts the fastest reaction was stereoisomerization of cis- to trans-decalin. The mole fraction $n_{\text{tr-Dec}}/(n_{\text{c-Dec}} + n_{\text{tr-Dec}})$ assumed values from 0.83 to 0.92 at reaction temperatures from 250 to 410 °C and conversions in the range from 9 to 90%, as found by Moraes et al. who converted a feed mixture of 40 mol% cis- and 60 mol% trans-decalin on Ir/ γ -Al₂O₃ with different iridium loadings [17]. As discussed previously [24], the extent of isomerization corresponds nicely to the values calculated for thermodynamic equilibrium. Since our catalysts lack Brønsted acid sites, the rapid stereoisomerization is very likely to occur on the metal sites via dehydrogenation to 1,9- or 9,10-octalins followed by re-hydrogenation to trans-decalin, as proposed by Weitkamp [33].

3.3. Hydroconversion of decalin on the four metal/silica catalysts

None of the catalysts showed any deactivation up to a time-onstream of 30 h under the conditions used in this study. Moreover, hydrocarbons with more than ten carbon atoms were absent in the product mixtures on all four catalysts.

3.3.1. Conversions and selectivities

The decalin conversions and product selectivities attained on the four catalysts in dependence of the reaction temperature are depicted in Fig. 3a–d. In line with a previous report [15] iridium is found to be considerably more active than platinum in the ring opening reaction. This may have its origin in both the differences in their intrinsic catalytic activity and in the higher dispersion of iridium (Table 1). To arrive at similar decalin conversions much lower temperatures can be applied with Ir/silica than with Pt/silica. Moreover, large differences are observed in the main products made on the iridium and the platinum catalysts: Ring opening is by far the predominating reaction on the two iridium catalysts at low to moderate conversions (Fig. 3a and b). It is furthermore seen that virtually no skeletal isomerization of decalin occurs on iridium, again in agreement with the work of McVicker et al. [15]. On both iridium catalysts, some open-chain decanes are also formed, their selectivities passing through maxima with increasing temperature [26]. These maxima are due to an enhanced formation of OCDs by endocyclic hydrogenolysis of ROPs, as the temperature is increased, and a consecutive hydrocracking of OCDs into C₉- hydrocarbons. The maximum selectivities of OCDs amount to 16% for 0.77Ir/silica and to 28% on 2.59Ir/silica which corresponds to OCDs yields of 11% and 20%, respectively (Table 2). These selectivities and yields are significantly lower than those reported recently for Ir/Na,H-Y zeolite catalysts with a low concentration of Brønsted acid sites (S_{OCDs} up to 36% and Y_{OCDs} up to 31%, [25]). At 290 °C, i.e. under conditions



Fig. 3. Conversion of decalin $X_{\text{Dec}}(\bullet)$ and selectivities of different groups of products $(S_{\text{sk-Isos}}(\bullet); S_{\text{ROPs}}(\bigcirc); S_{\text{OCDs}}(\square); S_{\text{C}_{9^-}}(\triangle); S_{\text{DHPs}}(\blacksquare))$ on the four metal/silica catalysts at different temperatures.

of maximal OCDs selectivity, the following seven isomeric decanes were formed on 2.59lr/silica in the order of their abundance: an unidentified OCD(1), 4-ethyloctane, 3,4-diethylhexane, n-decane, an unidentified OCD(2), 5-methylnonane, and 4,5-dimethyloctane (both diastereomers). Dehydrogenation of decalin to tetralin and naphthalene (DHPs) is negligible on both Ir/silica catalysts with $S_{DHPs} < 1\%$.

Pt/silica behaves differently from Ir/silica in many respects. Apart from the fact that the platinum catalysts are much less active, an almost threefold increase in the platinum content brings about only a slight increase in the catalytic activity (compare Fig. 3c and d). Perhaps the larger metal particles on 2.68Pt/silica (Table 1) contain only slightly more crystallographic sites that are active in the decalin hydroconversion. Another main difference compared to Ir/silica is the ability of both Pt/silica catalysts to promote the skeletal isomerization of decalin. Mechanistic aspects of decalin isomerization on platinum catalysts without Brønsted acid sites will be discussed below, see Section 3.6. Fig. 3c and d reveals that, at low conversions, the selectivities of skeletal isomerization and ring opening are approximately equal and amount to ca. 40% each. With increasing temperature, both selectivities decrease. Throughout the entire temperature range measured the selectivities of OCDs and C₉- hydrocarbons are very low. Instead, decalin is dehydrogenated to tetralin and naphthalene to a significant extent. Roughly, the amount of dehydrogenated products coincided with the one calculated for equilibrium at a hydrogen partial pressure of 5.2 MPa and temperatures of 350-410 °C. Ancillary experiments with an empty and a silica-filled reactor showed that tetralin and naphthalene were formed with similar yields as in the catalytic experiments, indicating that the reactor walls are capable to promote the dehydrogenation of decalin at these high temperatures.

Another principal difference between the performance of the Ir/silica and Pt/silica catalysts is seen from Table 2, second-last column: Noticeable amounts of open-chain nonanes (OCNs) are formed in the hydroconversion of decalin on the two Ir/silica catalysts, but they do not form at all on Pt/silica. While in our model-compound study with decalin as reactant, these OCNs appear in the group of hydrocracked products (C_{9^-}), such alkanes formed by abstraction of methane from hydrocarbons in a real feedstock

could still represent very valuable components in the products of hydrodecyclization, with a boiling point falling within the range of diesel fuel, a high cetane number and good cold-flow properties. Likely pathways for the formation of OCNs in the ring opening of decalin on Ir/silica will be discussed in Section 3.4.

The degree of branching in the alkanes formed by hydrodecyclization is decisive for both the cetane number and the cold-flow properties of the diesel fuel produced. Whereas the cetane number generally decreases with increasing degree of branching [34], a certain degree of branching is beneficial for the cold-flow properties [30]. Mono- and dibranched iso-alkanes are often considered as a good compromise. In Fig. 4, the distribution of the differently branched decane isomers formed from decalin on the two Ir/silica and one Pt/silica catalysts are shown for the experiments leading to maximal selectivities of OCDs (4-propylheptane was not formed on any of the catalysts). On the two Ir/silica catalysts, very similar isomer distributions with a clear preponderance of multi-branched iso-decanes are found. On 2.68Pt/silica, considerably less multibranched iso-decanes and large amounts of methylnonanes occur. The large amounts of multiply branched iso-decanes on the iridium catalysts accounting for ca. 60% of all OCDs formed are not unexpected. It is reasonable to assume that OCDs are formed from decalin on the iridium catalysts by two successive hydrogenolysis steps of endocyclic carbon-carbon bonds. Since hydrogenolysis on iridium is known to occur preferentially between unsubstituted carbon-carbon bonds [15], the branchings existing in decalin and the intermediate ROPs with one remaining ring are expected to survive the two ring-opening steps, thereby leading to OCDs with at least two branchings.

3.3.2. Formation of hydrocracked products with less than ten carbon atoms

Generally, hydrocracking of decalin, its skeletal isomers, ringopening products, and open-chain decanes into hydrocarbons with less than ten carbon atoms is undesirable, because it is associated with an increased consumption of valuable hydrogen and because such lighter hydrocarbons will, at least in part, be outside the boiling range of diesel fuel. It has been shown, however, that a detailed look at the distribution of these lighter hydrocarbons

Table 2

Maximum yields of open-chain decanes (OCDs) and selectivities of	of open-chain nonanes (OCN	Ns) and hydrocracked products obtain	ed on the four catalysts.
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Catalyst	$T_{\rm r}$ /%	X _{Dec} /%	S _{OCDs} /%	Y _{OCDs,max} ./%	S _{OCNs} /%	S _{C9} - /%
0.77lr/silica	350	71	16	11	7	48
2.59Ir/silica	290	73	28	20	8	35
0.93Pt/silica	410	43	2	1	0	6
2.68Pt/silica	410	53	4	2	0	13



Fig. 4. Breakdown of differently branched open-chain decanes observed on three catalysts in the ring-opening experiments leading to maximal selectivities of OCDs (MBDe: multiply branched decanes).

with 1–9 carbon atoms is worthwhile, since it can furnish valuable information concerning the mechanism of hydrocracking that is operative on the catalyst under investigation [24,26]. For example, hydrogenolysis of decalin on iridium supported on a non-acidic support has been shown to result in carbon number distributions with large amounts of methane and C₉ hydrocarbons, smaller but still appreciable amounts of ethane plus C₈ and propane plus C₇, and very low amounts of C₄–C₆ hydrocarbons [26]. In view of their characteristic shape, these distribution curves were referred to as "hammock-type curves". By contrast, distinctly different M-shaped carbon-number distribution curves were observed when decalin was hydrocracked on bifunctional catalysts comprising metallic and Brønsted acid sites [24].

In Fig. 5 the carbon number distributions of the hydrocracked products measured on the four silica-supported catalysts at comparable decalin conversions are depicted. Typical hammock-shaped distributions are obtained on the two iridium catalysts (Fig. 5a). The curves are slightly unsymmetrical indicating some secondary hydrogenolysis of the largest hydrocarbons, especially C₉, even at the relatively low yields of hydrocracked products. Entirely different distribution curves are found for the two platinum catalysts. Again, methane predominates, but relatively large amounts of C₂, C₃, C₄, and C₆ hydrocarbons are also formed. The large amounts of C1 and C2 rule out a cracking mechanism via carbocations, in line with the lack of Brønsted acid sites of these catalysts. In fact, we believe that the patterns of hydrocracked products shown in Fig. 5b are characteristic for hydrogenolysis of decalin, the skeletal isomers and ring-opening products formed from it around 400 °C on platinum.

More detailed information concerning the compositions of the C_4 , C_6 and C_7 fractions formed on the four catalysts is given in Table 3. Relatively little iso-butane is found in the C_4 fraction on all catalysts, and the molar ratio of methylcyclopentane and isobutane is far from unity. These features are independent evidence for the absence of a carbocationic cracking mechanism via the paring reaction [24]. Relatively large amounts of cyclohexane and methylcyclohexane are found in the C_6 and C_7 fractions, respectively, formed on the two Pt/silica catalysts.

3.4. Direct ring-opening mechanism on the iridium/silica catalysts

As shown in Fig. 3a and b, virtually no skeletal isomerization of decalin takes place on Ir/silica, but the metal is very active in the ring-opening reaction. There are five possible direct ring-opening products (direct ROPs) from decalin, namely butylcyclohexane (B-CHx), cis- and trans-1-methyl-2-propylcyclohexane (1-M-2-P-CHx), and cis- and trans-1,2-diethylcyclohexane (1,2-DE-CHx). Indeed, these direct ROPs are strongly dominating at low conversions, as the relevant section of a pertinent gas chromatogram shows (Fig. 6). It should be noted that these results are fully in-line with the selectivities of decalin ring opening reported very recently by Moraes et al. [17] for Ir/alumina catalysts with metal loadings ranging from 0.6 to 1.8 wt.%. Cyclodecane, another potential direct ROP, which would be formed from decalin, if its bridging carbon-carbon bond were cleaved by hydrogenolysis, was never present in the products obtained on the two iridium catalysts, as ascertained by co-injection of cyclodecane and a liquid product from decalin conversion on 2.59Ir/silica.

The section of the gas chromatogram presented in Fig. 6 furthermore shows that, beside the direct ROPs, a few other important product hydrocarbons appear at low decalin conversion, even though their concentrations are lower than those of the direct ROPs. Two of these peaks were identified as cis- and trans-1-ethyl-2methylcyclohexane (1-E-2-M-CHx) which are predicted to form by a consecutive abstraction of methane from direct ROPs. We refer to these C₉ hydrocarbons as "direct C₉ ROPs". The signal of a third direct C₉ ROP, viz. propylcyclohexane (P-CHx) unfortunately overlaps with the signal of an unidentified open-chain decane designated as OCD(1). By co-injection of propylcyclohexane with a liquid product mixture from decalin it was verified that the signal in question stems mainly from the OCD, so that the relatively small



Fig. 5. Modified hydrocracking selectivities S_j^* in the hydroconversion of decalin (0.77Ir/silica: $T_r = 330 \,^{\circ}\text{C}$; $X_{Dec} = 47\%$; $Y_{C_{9^-}} = 16\%$; $\Sigma S_j^* = 246\%$. 2.59Ir/silica: $T_r = 270 \,^{\circ}\text{C}$; $X_{Dec} = 37\%$; $Y_{C_{9^-}} = 7\%$; $\Sigma S_j^* = 217\%$. 0.93Pt/silica: $T_r = 410 \,^{\circ}\text{C}$; $X_{Dec} = 43\%$; $Y_{C_{9^-}} = 3\%$; $\Sigma S_j^* = 274\%$. 2.68Pt/silica: $T_r = 410 \,^{\circ}\text{C}$; $X_{Dec} = 7\%$; $\Sigma S_j^* = 217\%$. 0.93Pt/silica: $T_r = 410 \,^{\circ}\text{C}$; $X_{Dec} = 43\%$; $Y_{C_{9^-}} = 3\%$; $\Sigma S_j^* = 274\%$. 2.68Pt/silica: $T_r = 410 \,^{\circ}\text{C}$; $X_{Dec} = 7\%$; $\Sigma S_j^* = 294\%$).

Table 3

Details on the C₄, C₆ and C₇ fractions of the products formed in the hydroconversion of decalin (i-Bu: iso-butane; M-CPn: methylcyclopentane; n-Hx: n-hexane; 2-M-Pn: 2-methylpentane; 3-M-Pn: 3-methylpentane; CHx: cyclohexane; M-CHx: methylcyclohexane).

Catalyst	$T_{\rm r}/^{\circ}{\rm C}$	$X_{\rm Dec}/\%$	Y _{C9} - /%	$\frac{n_{i-Bu}}{n_{C_4}}$	$\frac{n_{M-CPn}}{n_{C_6}}$	$\frac{n_{\text{n-Hx}}+n_{2-\text{M-Pn}}+n_{3-\text{M-Pn}}}{n_{C_6}}$	$\frac{n_{M-CPn}}{n_{i-Bu}}$	$\frac{n_{\text{CHx}}}{n_{\text{C}_6}}$	$\frac{n_{M-CHx}}{n_{C7}}$
0.77Ir/silica	330	47	16	0.26	0.03	0.77	0.10	0.16	0.60
2.59Ir/silica	270	37	7	0.12	0.00	0.80	0.00	0.16	0.58
0.93Pt/silica	410	43	3	0.36	0.28	0.23	0.72	0.38	0.75
2.68Pt/silica	410	53	7	0.14	0.05	0.35	0.27	0.53	0.81

amounts of propylcyclohexane could not be reliably determined in a quantitative manner.

The results discussed so far can be accounted for by the reaction scheme in Fig. 7 for decalin hydroconversion on iridium on a support lacking Brønsted acid sites. No skeletal isomerization occurs, because neither the support nor the metal is active for this reaction. Instead, direct opening of one six-membered ring occurs through hydrogenolysis resulting in the five direct ROPs (three are shown of which two form as cis- and trans-isomers). As seen from Fig. 6, the most abundant direct ROPs are 1-methyl-2-propylcyclohexane followed by 1,2-diethylcyclohexane, while significantly less butylcyclohexane is formed. This selectivity is consistent with the known



Fig. 6. Section of the gas chromatogram of the product of decalin hydroconversion on the 2.59Ir/silica catalyst at 250 °C and X_{Dec} = 17%. The direct ring-opening products (direct ROPs) are: butylcyclohexane (B-CHx), cis- and trans-1-methyl-2-propylcyclohexane (1-M-2-P-CHx), and cis- and trans-1,2-diethylcyclohexane (1,2-DE-CHx). The direct C₉ ROPs are cis- and trans-1-ethyl-2-methylcyclohexane (1-E-2-M-CHx) and propylcyclohexane (P-CHx), a and b denote the two stereoisomers.

feature of hydrogenolysis on iridium to preferentially cleave bonds between two secondary carbon atoms over bonds between a secondary and a tertiary carbon atom [15,19]. The direct ROPs undergo consecutive hydrogenolysis on the iridium, either in the remaining six-membered ring or in an alkyl side chain. In the former case, one out of seven decane isomers listed in the bottom-left box of Fig. 7 is predicted to form. We refer to these isomers as "direct open-chain decanes" or "direct OCDs". Side-chain hydrogenolysis of the direct ROPs gives a light alkane, typically methane, and an alkylated cyclohexane with less than ten, typically nine carbon atoms. As shown in the bottom-center box of Fig. 7. methane abstraction from the direct ROPs results in the formation of either 1-ethyl-2-methylcyclohexane or propylcyclohexane. We call these "direct C₉ ROPs". In the group of direct C₉ ROPs, cis- and trans-1-ethyl-2-methylcyclohexane are strongly prevailing, while little propylcyclohexane is formed (see Fig. 6). Endocyclic hydrogenolysis of the direct C₉ ROPs is expected to give one out of seven nonane isomers listed in the bottom-right box of Fig. 7. We call these nonane isomers "direct open-chain nonanes" or "direct OCNs". Of the seven direct OCDs listed in Fig. 7, the five first-mentioned ones were safely identified in the product obtained on 2.59Ir/silica under mild reaction conditions ($T_r = 290 \degree C$, $X_{Dec} = 73\%$). The two remaining ones, denoted as unidentified OCD(1) and OCD(2) in Section 3.3.1, were found to be present in the same product with a high degree of certainty. At more severe conditions and elevated conversions direct OCDs, direct C9 ROPs, and direct OCNs all undergo consecutive hydrogenolysis on iridium to give lighter hydrocarbons, and their quantitative distributions are described by hammock-type curves as shown in Fig. 5a.

In Fig. 8 the selectivities of direct ROPs, direct OCDs, direct C_9 ROPs, and direct OCNs formed from decalin on the 2.59Ir/silica catalyst are plotted versus the reaction temperature. (Note that the values plotted in Fig. 8 pertain to the *direct* ROPs, the *direct* OCDs, the *direct* C_9 ROPs, and the *direct* OCNs as defined in the four boxes of Fig. 7 and that these values differ from those plotted in Fig. 3b.) As implied by the scheme in Fig. 7, direct ROPs are indeed primary products from which direct OCDs, direct C_9 ROPs, and direct OCNs form in consecutive reactions.



Fig. 7. The direct ring-opening mechanism for hydrogenolytic hydrodecyclization of decalin and consecutive hydrogenolysis reactions over iridium on non-acidic supports (note that decalin, 1-methyl-2-propylcyclohexane, 1,2-diethylcyclohexane, and 1-ethyl-2-methylcyclohexane occur as cis- and trans-isomers).

As column 4 of Table 4 shows, on the two iridium/silica catalysts at low decalin conversion (12 and 17%, respectively), the content of direct ROPs in the total ring-opening products is as high as 96%. Also given in Table 4 are the predicted distributions of individual direct ROPs for the two limiting cases of a purely non-selective ring opening (equal probability of cleavage of all endocyclic bonds) and a selective ring opening (no cleavage of endocyclic bonds between secondary and tertiary carbon atoms; equal rates of cleavage of endocyclic bonds between two secondary carbon atoms). Based on the fact that no cyclodecane was formed on any iridium catalyst, cleavage of the bridging bond between the two tertiary carbon atoms in decalin is viewed to be absent on the two catalysts containing iridium. As the data in Table 4 reveal, the experimental distributions of the direct ROPs observed on the two iridium/silica catalysts can neither be understood in terms of a purely selective nor in terms of a purely non-selective hydrogenolysis mechanism. Rather, the measured distributions of the direct ROPs contain features of both mechanisms, and they may both be operative on the iridium/silica catalysts, in agreement with what has been claimed by McVicker et al. [15] for the hydrogenolytic ring opening of methylcyclohexane and by Moraes et al. [17] for ring opening of decalin on iridium/alumina catalysts. The distributions of the direct ROPs listed in Table 4 for the platinum/silica catalysts will be discussed in Section 3.6.

As already shown in the second last column of Table 2, it is a salient feature of decalin hydroconversion on the iridium/silica catalysts that noticeable amounts of open-chain nonanes (OCNs) are formed. It is worthwhile to throw a closer look at their composition, especially at low decalin conversions. Table 5 reveals that 100% of the nonane isomers found under these conditions belong to the group of direct OCNs, as listed in the bottom-right box of Fig. 7. Particularly abundant isomers are 3-ethyl-4-methylhexane, 3-ethyl-2-methylhexane, 4-methyloctane, 3,4-dimethylheptane, 3-ethylheptane, and n-nonane. The scheme depicted in Fig. 7 implies that the open-chain nonanes are formed by endocyclic hydrogenolysis of the direct C9 ROPs propylcyclohexane and 1-ethyl-2-methylcyclohexane. Of these, propylcyclohexane can probably be neglected as a precursor for the formation of OCNs, since it is present in a much lower concentration than the two stereoisomers of 1-ethyl-2-methylcyclohexane, see Fig. 6.

Table 4

Composition of the direct ring-opening products obtained on the four non-acidic catalysts at low decalin conversions.

Catalyst	$T_{\rm r}/^{\circ}{\rm C}$	$X_{\rm Dec}/\%$	$\frac{S_{\text{direct ROPs}}}{S_{\text{ROPs}}}$ /%	$\frac{S_{\text{B-CHx}}}{S_{\text{direct ROPs}}}$ /%	$\frac{S_{1-M-2-P-CHx}}{S_{direct ROPs}}$ /%	$\frac{S_{1,2-\text{DE-CHx}}}{S_{\text{direct ROPs}}}$ /%
0.77Ir/silica	290	12	96	13	52	35
2.59Ir/silica	250	17	96	13	51	36
0.93Pt/silica	370	15	65	54	34	12
2.68Pt/silica	370	20	79	64	28	8
Predicted for non-selective ring opening of decalin	-	-	100	40	40	20
Predicted for selective ring opening of decalin	-	-	100	0	67	33

Table 5

Detailed composition of the open-chain nonanes (OCNs) formed in the decalin hydroconversion on the iridium/silica catalysts at low conversion.

Catalyst	0.77Ir/silica	2.59Ir/silica	Predicted by ring opening of 1-ethyl-2-methylcyclohexan	
			Non-selective	Selective
T _r /°C	290	250		
X _{Dec} /%	12	17		
S _{direct OCNs} /S _{OCNs} (%)	100	100		
$S_{n-No}/S_{direct OCNs}$ (%)	8	8	16 2/3	0
S _{4-M-Oc} /S _{direct OCNs} (%)	14	12	16 2/3	0
S _{3-E-Hp} /S _{direct OCNs} (%)	11	9	16 2/3	0
S _{4-E-Hp} /S _{direct OCNs} (%)	0	3	0	0
S _{3,4-DM-Hp} /S _{direct OCNs} (%)	9	13	16 2/3	33 1/3
S _{3-E-2-M-Hx} /S _{direct OCNs} (%)	22	20	16 2/3	33 1/3
$S_{3-E-4-M-Hx}/S_{direct OCNs}$ (%)	36	35	16 2/3	33 1/3

It appears hence justified to consider the latter direct C₉ ROPs as the predominant precursors for OCN formation. Also given in Table 5 are the predicted OCN distributions expected for a purely non-selective and a purely selective ring opening of 1-ethyl-2-methylcyclohexane. When comparing the experimentally measured distributions of OCNs with those predicted on the basis of the two ring-opening mechanisms, an explanation for the absence (0.77Ir/silica) or near-absence (2.59Ir/silica) of 4-ethylheptane in the product group of direct OCNs is readily obtained. This nonane isomer cannot form by ring opening of 1ethyl-2-methylcyclohexane, neither via the non-selective nor via the selective mechanism. In quantitative terms, neither the nonselective mechanism alone nor the selective mechanism alone can account for the measured distributions of OCNs. Rather, the real ring-opening mechanism seems to feature elements of both established mechanisms. It should be mentioned that McVicker et al. arrived at similar conclusions for ring opening of 1,2,4trimethylcyclohexane on iridium/alumina [15].

3.5. Simulation of the hammock-type distribution curves for the hydrocracked products formed on the iridium/silica catalysts

As a characteristic feature of decalin ring opening over iridium on a non-acidic support, hammock-type curves result for the



Fig. 8. Selectivities of direct ROPs (\triangledown), direct OCDs (\square), direct C₉ ROPs (\bigcirc), and direct OCNs (\triangle) in the hydroconversion of decalin on 2.59Ir/silica.

carbon-number distribution of the hydrocracked products (see Fig. 5a). The predominance of methane and C_9 fragments plus ethane and C_8 fragments can only be rationalized by invoking a hydrogenolytic mechanism for carbon—carbon bond cleavage (rather than by a bifunctional hydrocracking via carbocations). One such mechanism which accounts, in a qualitative manner, for the products observed at low decalin conversion, has been presented in Fig. 7. It implies that no skeletal isomerization of hydrocarbons happens in this catalytic system, neither on metallic iridium nor on the non-acidic support. To gain more quantitative insight into the catalytic chemistry on iridium/silica, an attempt was made to simulate the hydrogenolytic pathways and to compare the carbon number distributions thereby predicted with those measured experimentally on 2.59Ir/silica.

The underlying reaction network for the simulation is depicted in Fig. 9 which is a simplified version of Fig. 7. The relevant information from Fig. 9 is that hydrocracked products (C_{9-}) are formed from decalin on iridium/silica via two principal pathways: Both start with the hydrogenolytic opening of one six-membered ring to the five direct ROPs. The latter are key intermediates on the way to hydrocarbons with nine or less carbon atoms: in path 1, C_{9-} products are readily made from direct ROPs by hydrogenolysis in an alkyl side chain. Alternatively, in path 2 direct OCDs are first formed by endocyclic hydrogenolysis of direct ROPs, and the direct OCDs undergo a consecutive hydrogenolysis to C_{9-} hydrocarbons.

For translating the network in Fig. 9 into quantitative carbonnumber distributions of the C_{9^-} products, assumptions have to be introduced as to the relative probabilities of cleavage of the various carbon—carbon bonds in the respective precursor hydrocarbons. In the simplest version of the simulation, it is assumed that all carbon—carbon bonds in decalin (except the bridging bond, vide infra), all exocyclic carbon—carbon bonds in the direct ROPs, all endocyclic carbon—carbon bonds in the direct ROPs, and all carbon—carbon bonds in the direct OCDs undergo hydrogenolysis at equal probabilities. The bridging carbon—carbon bond in decalin is assumed not to be cleaved at all, as no cyclodecane was formed (cf. Section 3.4.). Furthermore, the assumptions are made that the rates of formation of C_{9^-} hydrocarbons via routes 1 and 2 in Fig. 9 approximately equal each other and that no further hydrogenolysis of C_{9^-} to smaller moieties happens.

The curve in Fig. 10 with the open circles shows the result of this simulation. A comparison with the experimental distribution curves in Fig. 5a reveals that the principal feature of the hammock-type distribution curves, i.e. a strongly decreasing contribution of hydrogenolysis leading to $(C_1+C_9)>(C_2+C_8)>(C_3+C_7)>(C_4+C_6)>(C_5+C_5)$ is already correctly predicted in qualitative terms, but in the experiment, the preponderance of hydrocracking reactions leading to C_1+C_9 is even more pronounced than in the simulation. In an attempt to obtain a better match between the result of the simulation and the experimental curves, the simulation was repeated starting from the



Fig. 9. Underlying network for the simulation of hydrocracking decalin to hydrocarbons with less than ten carbon atoms via hydrogenolysis on non-acidic iridium catalysts.

distribution of the individual direct ROPs measured on 2.59Ir/silica at $T_r = 250 \circ C$ and low conversion of $X_{Dec} = 17\%$ (see Table 4), instead of from decalin. This simulation led to a slightly improved fit with the experiment (Fig. 10, full circles), but the quantitative agreement continued to be poor.

A more rigorous simulation takes into consideration the well established fact that, in the hydrogenolysis of hydrocarbons on iridium, cleavage of carbon—carbon bonds between two unsubstituted (secondary or primary) carbon atoms is faster than cleavage of carbon—carbon bonds between carbon atoms of which at least one is substituted (tertiary or quaternary). To account for this regiose-lectivity in a quantitative manner, the factors $\alpha_{unsubst.}$ or $\alpha_{subst.}$ are, respectively, defined:

$$\alpha_{\text{unsubst.}} \equiv \frac{\text{number of hydrogenolyzed C-C bonds between unsubstituted C-atoms}}{\text{total number of C-C bonds hydrogenolyzed}}$$
(2)

$$\alpha_{\text{subst.}} \equiv \frac{\text{number of Hydrogenolyzed C = bonds involving substituted C = atoms}{\text{total number of C=C bonds hydrogenolyzed}}$$
(3)

and

$$\alpha_{\text{unsubst.}} = 1 - \alpha_{\text{subst.}} \tag{4}$$

From the distribution of the direct ROPs formed from decalin on 2.59Ir/silica at low conversion ($X_{Dec} = 17\%$) at $T_r = 250 \text{ °C}$ (Table 4), $\alpha_{subst.} = S_{B-CHx}/S_{direct ROPs} = 0.13$, and $\alpha_{unsubst.} = 0.87$ are obtained. Starting from the measured distribution of the individual direct ROPs and applying the applicable value of α for the exocyclic hydrogenolysis of direct ROPs (route 1 in Fig. 9), the endocyclic hydrogenolysis of direct ROPs (route 2 in Fig. 9), and the



Fig. 10. Predicted carbon-number distributions of the hydrocracked products in the hydroconversion of decalin on iridium/silica using the assumption of equal probabilities of carbon—carbon bond cleavage in the precursors of C_{9^-} .

hydrogenolysis of direct OCDs (route 2 in Fig. 9) allows one to calculate a simulated carbon number distribution of the hydrocracked products. It is depicted in Fig. 11 along with the experimentally determined distribution for decalin hydrogenolysis on 2.59Ir/silica at $T_r = 250 \degree C$ and $X_{Dec} = 17\%$. Obviously, this simulation results in a carbon-number distribution that matches the experimentally determined one significantly better. The grey and black bars at each carbon number in Fig. 11 indicate to what extent the hydrocarbons were, respectively, formed by exocyclic hydrogenolysis of direct ROPs (route 1 in Fig. 9) or via direct OCDs (route 2 in Fig. 9). The results of the simulation based on the underlying assumptions suggest that slightly more than 50% (black bars) of the hydrocracked products are formed via route 2, i.e. via direct OCDs. The relatively good agreement between the experimental and the simulated distribution of the hydrocracked products are also considered to be strong support for the mechanistic pathways suggested in Fig. 7 for decalin hydroconversion on non-acidic iridium/silica catalysts.

In the course of this simulation, a predicted distribution of the formed direct OCDs was also obtained (Fig. 12). Although the mechanistic input for the simulation was taken from the catalytic experiment at $T_r = 250$ °C, whereas the measured OCD distribution on 2.59Ir/silica shown in Fig. 4 holds for $T_r = 290$ °C, both graphs are qualitatively similar. Furthermore, in the experiment 95% of all OCDs were direct OCDs at $T_r = 290$ °C. Even though 76% of all OCDs are predicted to be multi-branched by the simulation, whereas a lower value of 63% was obtained in the experiment, we believe that the qualitative similarity of both distributions can be looked upon as supporting the underlying mechanistic assumptions.



Fig. 11. Predicted carbon-number distribution of the hydrocracked products in the hydroconversion of decalin on iridium/silica using the assumptions of a preferred cleavage of unsubstituted carbon—carbon bonds (filled circles). The experimentally determined curve for decalin hydroconversion on 2.59Ir/silica at $T_r = 250$ °C and $X_{Dec} = 17\%$ is also shown (empty circles). For the significance of black and grey bars see text.



Fig. 12. Breakdown of the simulated selectivities of OCDs.

3.6. Details of the reactions on the platinum/silica catalysts

On both platinum/silica catalysts, the most abundant product hydrocarbons at all conversions were butylcyclohexane and spiro[4.5]decane (beside tetralin at elevated temperatures). For example, on 2.68Pt/silica at the lowest conversion of 9% (Fig. 13), ca. 50% of all ROPs formed consisted of butylcyclohexane, and spiro[4.5]decane accounted for 62% of all sk-Isos. In fact, Fig. 14 strongly suggests that butylcyclohexane and spiro[4.5]decane are primary products in decalin conversion on the two non-acidic platinum/silica catalysts.

The formation of butylcyclohexane from decalin is readily understood in terms of a hydrogenolytic rupture of the endocyclic secondary-tertiary carbon—carbon bond, in much the same manner as n-heptane has previously been reported to be the prevailing product in the hydrogenolysis of methylcyclohexane on Pt/alumina [15]. Cleavage of the bonds between two secondary carbon atoms leading to the ROPs cis- and trans-1-methyl-2-propylcyclohexane and cis- and trans-1,2-diethylcyclohexane occurs to a considerably lesser extent on the platinum/silica catalysts than on iridium/silica (see Table 4). It is remarkable that for the iridium catalysts the distribution of direct ROPs is practically independent of the metal



Fig. 13. Section of the gas chromatogram of the product of decalin hydroconversion on the 2.68Pt/silica catalyst at 350 °C and X_{Dec} = 9%. a and b denote the two stereoisomers.



Fig. 14. Selectivities of butylcyclohexane on 0.93Pt/silica (\blacksquare) and 2.68Pt/silica (\Box) and of spiro[4.5]decane on 0.93Pt/silica (\blacktriangle) and 2.68Pt/silica (\triangle) in dependence of the decalin conversion.

content, whereas for the platinum catalysts the selectivities depend on the metal content as reported by others [18,19]. Interestingly, even the bridging C–C bond in decalin, i.e. the bond between the two tertiary carbon atoms, is broken to a small extent on the two platinum/silica catalysts, at variance to hydrogenolysis on iridium. On 2.68Pt/silica, for example, cyclodecane was formed from decalin with a maximal selectivity of 0.5% at a reaction temperature of 410 °C.

As demonstrated very recently [24], spiro[4.5]decane is readily formed from decalin on bifunctional catalysts, such as Pt/La-X zeolite, probably at the level of carbocations at the Brønsted acid sites via a rapid type A rearrangement [35]. However, the platinum catalysts used in this study are lacking Brønsted acid sites, and no spiro[4.5]decane at all was formed on the iridium/silica catalysts. We hence prefer to invoke a purely platinum-catalyzed mechanism for isomerizing decalin into spiro[4.5]decane. In fact, the capability of platinum metal to induce skeletal isomerization of hydrocarbons is well established in the catalytic chemistry of light alkanes and referred to as the bond-shift mechanism [36,37]. It is generally believed to proceed via cyclopropanoid species and was observed to be the predominant type of metal-catalyzed isomerization of n-octane when the hydrogen pressure was increased from 0.5 to 2.0 MPa [32]. As shown in Scheme 1, applying the bond-shift mechanism to decalin leads one to predict spiro[4.5] decane as a primary product.

It should be mentioned that a rigorous application of the bond-shift mechanism to decalin results in the prediction of ten additional isomers, viz. the cis- and trans-isomers of bicyclo[5.3.0]decane, 1-, 2- and 3a-methylbicyclo[4.3.0]nonane and of bicyclo[4.3.1]decane, beside spiro[4.5]decane. A pattern of ten prominent peaks with a size comparable to that of spiro[4.5]decane was not observed. The two stereoisomers of bicyclo[5.3.0]decane were formed with a maximal total selectivity of only 2%. As an alternative pathway, one could consider the formation of spiro[4.5]decane by a platinum-catalyzed 1,5-dehydrocyclization [19,38,39] of butylcyclohexane formed by ring opening of decalin (Scheme 2).

The problem with such a mechanism is that spiro[4.5]decane would be expected to be a secondary product formed from the primary product butylcyclohexane, whereas Fig. 14 seems to suggest that spiro[4.5]decane is rather a primary product.



Scheme 2. Hypothetical platinum-catalyzed formation of spirol4.5 ldecane from decalin via ring opening to butylcyclohexane followed by 1.5-dehydrocyclization.

4. Conclusions

Two iridium/silica and two platinum/silica catalysts with different metal contents were prepared and tested in the hydrodecyclization of cis-decalin. Two characterization techniques, viz. FT-IR with pyridine as probe and measuring the selectivities of n-octane hydroconversion, indicated that catalytically active Brønsted acid sites were lacking on the metal/silica catalysts. This enabled a detailed study of cis-decalin conversion on the respective metal without overly complex product distributions or an interference of bifunctional catalysis via carbocationic intermediates.

Stereoisomerization of cis- to trans-decalin was by far the fastest reaction: the cis/trans-equilibrium corresponding to a mole fraction $n_{tr-Dec}/(n_{c-Dec} + n_{tr-Dec}) \approx 0.8-0.9$ was attained at all reaction temperatures from 250 to 410 °C over the whole range of decalin conversions. This rapid stereoisomerization must be concluded to occur on the respective metal via 1,9- or 9,10-octalins, as proposed in the literature [33]. It is likely that this result has a considerable bearing on decalin hydroconversion over metal catalysts which do possess acid sites [24,25].

On the non-acidic catalysts used in this investigation, ring opening of decalin occurs by hydrogenolysis on the metal. There are pronounced differences in hydrodecyclization on the two metals used: Iridium is much more active than platinum in the ring opening reaction, but iridium supported on non-acidic silica has practically no activity for skeletal isomerization of hydrocarbons, at variance to platinum. As a consequence, decalin hydroconversion on Ir/silica starts with the direct opening of one six-membered ring resulting in a small number of direct ring-opening products (direct ROPs). These alkylated cyclohexanes undergo consecutive hydrogenolysis reactions, either of an endocyclic carbon-carbon bond to give one out of seven open-chain decanes (direct OCDs) or of an exocyclic carbon-carbon bond to give a small alkane, typically methane, and one out of two C₉ naphthenes (direct C₉ ROPs). The latter can undergo another endocyclic hydrogenolysis leading to one of seven open-chain nonanes (direct OCNs). All individual C₁₀ and C₉ hydrocarbons thereby predicted could be identified in the products generated on iridium/silica at low conversions. The direct ring-opening mechanism could be simulated in a quantitative manner whereby the peculiar carbon-number distributions of the C₉₋ hydrocarbons referred to as hammock-type curves could be readily predicted.

Platinum/silica catalysts require high reaction temperatures in the vicinity of 400 °C. This brings about the formation of relatively large amounts of tetralin and naphthalene. The dominating primary products found on Pt/silica at low conversions are spiro[4.5]decane and butylcyclohexane. The latter is readily accounted for by a hydrogenolytic rupture of a secondary-tertiary carbon—carbon bond in decalin. Platinum on non-acidic silica appears to catalyze skeletal isomerization beside hydrogenolysis, and the so-called bond-shift mechanism [37] via cyclopropanoid species could be responsible for the direct formation of spiro[4.5]decane.

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