



# High-performance ring-opening catalysts based on iridium-containing zeolite Beta in the hydroconversion of decalin



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## ABSTRACT

Decalin was converted in a flow-type reactor under a hydrogen pressure of 5.2 MPa on Ir/H,A-Beta zeolite catalysts, where A stands for an alkali metal cation. In one series of catalysts, the Ir content was 3 wt.%, and the nature of A was varied from lithium to cesium. In a second series, the iridium content in Ir/H,Cs-Beta was varied from 1 to 5 wt.%. On some of these catalysts, open-chain decanes (OCDs) were formed with unprecedented selectivities and yields of up to 47 and 44%, respectively. The term “High-Performance Ring-Opening Catalysts” (HIPEROcs) was defined. Evidence is presented for hydrogenolysis on the metal being the main ring-opening mechanism on HIPEROcs. The main function of the Brønsted-acid sites is a mild isomerization of six-membered into five-membered naphthenic rings which are much easier to open by hydrogenolysis. Valuable mechanistic information can be deduced from the carbon-number distributions and the naphthenes vs. alkanes content of the hydrocracked products (C<sub>9</sub>-).

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## 1. Introduction

There has recently been considerable concern about polynuclear aromatic hydrocarbons (PAHs) in diesel fuel, as they have very poor cetane numbers [1], unfavorable cold-flow properties, excessively high densities, a low hydrogen content leading to high specific CO<sub>2</sub> emissions, and they are considered to be the main precursors of soot in the tail gas. The conversion of PAH-rich refinery streams, such as light cycle oil (LCO) from fluid catalytic crackers or middle distillate fractions from cokers into hydrogen-rich, environmentally benign blending cuts for diesel fuel continues to be among the challenges of heterogeneous catalysis. The ideal products of such a conversion would be alkanes with the same carbon numbers as the PAH reactants. Such a route would comprise two steps, namely the complete hydrogenation of the PAHs to the corresponding multi-ring naphthenes followed by their selective ring opening to alkanes. Since the hydrogenation of aromatics is often considered as state-of-the-art catalysis, various groups were, within the past 10–15 years, looking in detail at the selective catalytic ring opening of multi-ring naphthenes.

The most widely used model hydrocarbons for such studies seem to be decalin and tetralin, and the catalysts can be classified

as monofunctional acidic (e.g., zeolites in a Brønsted-acid form, WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [2–4]), monofunctional metallic (mostly iridium or platinum on non-acidic supports [4–6]), or bifunctional (e.g., platinum or iridium on Brønsted-acid forms of zeolites Y, Beta, or mordenite [3,7–18]).

Literature tells that monofunctional acidic catalysts are inappropriate for ring opening of decalin, because they undergo deactivation due to coking, significant amounts of hydrocarbons with more than 10 carbon atoms are formed at elevated conversions, and the yields of ring-opening products are unacceptably low, generally about 10% at most [2–4]. The chemistry of ring opening on such catalysts proceeds via carbocations, either by classical β-scissions or through direct protolytic cracking at a tertiary carbon atom of decalin [2,4].

On monofunctional metallic catalysts ring opening of naphthenes occurs by hydrogenolysis of endocyclic carbon–carbon bonds. Based on Gault's pioneering work with relatively small monocyclic model hydrocarbons, e.g., methylcyclopentane, and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with various platinum loadings, three distinct ring-opening mechanisms are usually discerned [19]: (a) the non-selective (or multiplet) mechanism proceeding on highly dispersed platinum and featuring an equal probability for cleavage of all five endocyclic bonds, (b) the selective (or dicarbene) mechanism occurring on poorly dispersed platinum and breaking unsubstituted, i.e., secondary carbon–carbon bonds exclusively, and (c) the partially selective (or metallacyclobutane) mechanism competing

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with the selective mechanism in cases when at least one carbon atom is substituted by a methyl group. Iridium was found to open the ring of methylcyclopentane [5,20] and pentylcyclopentane [5,21] according to an almost purely selective mechanism, irrespective of the metal dispersion. By converting a variety of monocyclic naphthenes with up to ten carbon atoms, McVicker et al. [5] and Daage et al. [21] disclosed a number of very interesting features of selective ring opening by hydrogenolysis on iridium. Iridium is much more active in the ring opening of naphthenes than platinum, and it opens five-membered naphthenic rings significantly faster than six-membered rings. It is, nevertheless, capable as well to open six-membered rings, e.g., in methylcyclohexane. If the number of alkyl substituents on the naphthenic ring is increased, e.g., by going from methylcyclohexane to 1,2,4-trimethylcyclohexane, both the rate and the selectivity of ring opening on Ir/Al<sub>2</sub>O<sub>3</sub> are markedly reduced [5]. Ring opening of monocyclic naphthenes by hydrogenolysis on various mono- and bimetallic catalysts has also been dealt with in several Exxon patents [22–24] showing a considerable industrial interest in the subject. A concept should also be mentioned that has been advanced in Refs. [5,21], viz. the combination of a metal for hydrogenolytic ring opening with a mildly acidic component for isomerization of naphthenes with a six-membered ring into isomers with a five-membered ring which are much more readily opened by hydrogenolysis.

In two very recent studies, the reaction paths of the hydroconversion of decalin over iridium supported on non-acidic carriers, viz.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [4] and SiO<sub>2</sub> [6], were investigated in much detail. Depending on the iridium content of the catalyst (0.5–2.6 wt.%), decalin conversion starts between 250 and 350 °C. There is virtually no skeletal isomerization, direct opening of one six-membered ring rather occurs leading at low conversions almost exclusively to the “direct ring-opening products” 1-methyl-2-propylcyclohexane, 1,2-diethylcyclohexane and butylcyclohexane in a ratio of about 52:35:13 [4,6]. This result nicely confirms that the selective ring-opening mechanism is clearly (combined selectivity of 87%) predominating, but the partially selective mechanism is operative to a minor extent (13%) as well. Furthermore, the “direct ring-opening products” undergo consecutive hydrogenolysis either of endocyclic carbon–carbon bonds to open-chain decanes (OCDs) or of exocyclic carbon–carbon bonds in the alkyl side chains to methane and C<sub>9</sub> alkylcyclohexanes. The latter show again an endocyclic hydrogenolysis leading to open-chain nonanes (OCNs), and precisely the OCD and OCN isomers predicted by such a pathway were detected in the reaction product [6].

Ref. [4] also contains an evaluation of the possible improvement of the cetane number by catalytic hydroconversion. It is shown there that, in order to achieve a substantial gain in the cetane number, it is mandatory to produce OCDs with an as high as possible yield and an as low as possible degree of branching. OCD yields of up to ca. 20% were achieved on the monofunctional metallic catalysts described in Refs. [4,6].

In spite of the relatively large number of reports on ring opening of decalin on conventional bifunctional catalysts [3,7–18], such as Pt/H-Y, Pt/USY, Pt/H-Beta, Pt/H-mordenite, Pt, Ir/H-Y, or Pt, Ir/H-Beta, remarkably little is known about the maximum attainable yields of open-chain decanes. In the majority of papers, OCDs are even not mentioned as products. This is certainly due to the difficult analysis of the C<sub>10</sub> products which often consist of more than 100, if not 200 individual hydrocarbons. We are aware of just one paper [12], in which the maximum yield of OCDs attained from decalin on a Pt, Ir/H-Y catalyst was reported to be 4%. Our own results obtained in the decalin hydroconversion on Ir/La-X and Pt/La-X zeolites by using gas chromatographic procedures tailored for the analysis of the complex C<sub>10</sub> product mixtures [17] rather suggest that values around 10% are more realistic for the usually employed bifunctional

catalysts with a content of noble metal around 1 wt.% and a relatively high concentration and strength of Brønsted-acid sites.

In the present communication, we wish to report on another family of bifunctional catalysts which enable ring opening of decalin with much better yields of OCDs ( $Y_{\text{OCDs}} > 25\%$ ) than those attainable on the above-described conventional classes of catalysts. Salient features of the new catalysts are a high hydrogenolysis activity and a relatively low concentration and strength of Brønsted-acid sites.

## 2. Experimental

### 2.1. Preparation of the catalysts

The parent material for all catalysts used in this study was zeolite Beta synthesized via the dry-gel conversion (DGC) method [25,26]: 9.98 g aluminum sulfate 18 hydrate (Riedel-de Haën, grade chemically pure) were dissolved in 5.0 g demineralized water, heated to 80 °C and stirred for 30 min. Meanwhile, 69.19 g colloidal silica (Aldrich, Ludox HS40, 40 wt.% SiO<sub>2</sub> in H<sub>2</sub>O), 66.84 g tetraethylammonium hydroxide solution (Sigma–Aldrich, 40 wt.%) and 12.98 g NaOH solution (4 mol dm<sup>-3</sup>) were mixed and stirred for 30 min at room temperature. Subsequently, the two solutions were put together and stirred for another 2 h at room temperature. The resulting gel was heated to 80 °C and dried while stirring.

Approximately 1.5 g of the dry gel were placed on a porous plate inside a Teflon-lined autoclave with 2.0 g of demineralized water at the bottom [26]. The conversion was carried out at 175 °C for 48 h. Typically, such a batch resulted in 1.7 g of as-synthesized, template-containing zeolite Beta with an  $n_{\text{Si}}/n_{\text{Al}}$  ratio of 14.0. After each conversion the resulting zeolite was filtered, washed with 1 dm<sup>3</sup> demineralized water and dried for at least 12 h at 80 °C in an oven. The template was removed by first heating in a nitrogen flow of 58 dm<sup>3</sup> h<sup>-1</sup> from room temperature to 450 °C with a heating rate of 1 °C min<sup>-1</sup> and holding at 450 °C for 24 h and then switching the gas to synthetic air with a flow rate of 58 dm<sup>3</sup> h<sup>-1</sup> and holding the temperature for another 24 h. Prior to any further modification step, ca. 3 g of the calcined zeolite Beta were slurried in 100 cm<sup>3</sup> of a 1 molar aqueous solution of sodium nitrate under stirring at 80 °C. After 4 h of stirring at 80 °C, the zeolite was filtered, washed with 1 dm<sup>3</sup> of demineralized water and dried at 80 °C. The so-prepared zeolite will be referred to as Na-Beta.

Subsequently, Li<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, or Cs<sup>+</sup> were introduced into zeolite Na-Beta by ion exchange with the corresponding chlorides. The procedure was similar to the one applied by Rabl et al. [18] for incorporating various alkali cations into zeolite Na-Y with one exception, viz. the ion exchange was conducted only once instead of four times as in Ref. [18]. 3 g Na-Beta (on a dry basis) were suspended in 100 cm<sup>3</sup> of a 1 M aqueous solution of lithium or potassium chloride or a 0.1 M solution of rubidium or cesium chloride. This is, respectively, equivalent to offering a 100- or a 10-fold excess of the ingoing cation compared to the cation-exchange capacity of the zeolite. The suspension was heated to 80 °C and stirred for 4 h. The resulting zeolite was filtered off, washed with 1 dm<sup>3</sup> of demineralized water and dried at 80 °C.

Iridium was introduced into the zeolites by ion exchange as well. The cationic complex [Ir(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> was used. Taking into account the results of preliminary ion-exchange experiments, a 20% excess of the iridium complex was offered to the zeolite. 3 g of the alkali cation-containing zeolite were suspended in 45 cm<sup>3</sup> of demineralized water, and a solution of the calculated (vide supra) amount of [Ir(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> in 50 cm<sup>3</sup> demineralized water was added dropwise by means of a dropping funnel within ca. 20 min under vigorous stirring at room temperature. Next, the suspension was heated to

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