



## 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 C<sub>9</sub> naphthenes. The latter can undergo a further endocyclic hydrogenolysis leading to open-chain nonanes. All individual C<sub>10</sub> and C<sub>9</sub> hydrocarbons predicted by this “direct ring-opening mechanism” were identified in the products generated on the iridium/silica catalysts. The carbon-number distributions of the hydrocracked products C<sub>9</sub>– 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, naphthoaromatics 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 metal-catalyzed hydrocracking (often referred to as “hydrogenolysis”) of monocyclic naphthenes, in particular cyclopentane, cyclohexane, and their alkyl-substituted derivatives. 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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