



# Dehydrogenation of polycyclic naphthenes on a Pt/C catalyst for hydrogen storage in liquid organic hydrogen carriers



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## ABSTRACT

Exhaustive hydrogenation of polyaromatic compounds with different extents of condensation (benzene, biphenyl, terphenyl) is studied. The reactions of catalytic dehydrogenation of the polycyclic naphthenic hydrocarbons (cyclohexane, bicyclohexyl, perhydroterphenyl) produced by hydrogenation of the aromatic substrates on a 3%Pt/Sibunit catalyst are explored in a flow setup in the temperature range 260–340 °C at the liquid hourly space velocity of 1 h<sup>-1</sup>. The directions of dehydrogenation of each of the studied substrates are studied in detail. Correlation dependences showing the effect of the structure of the molecules under study on their conversion in the dehydrogenation process are revealed. The influence of isomerization of steric and structural isomers on the kinetics of the entire process is established.

## 1. Introduction

The world energy consumption is growing nowadays at an increasing pace. The solution to the energy problem by increasing the production of oil and gas fuels results in an increasing role of heavy oil fractions and solid fossil fuels. Combustion of oil products produced from such a raw material, in addition to the notorious CO<sub>2</sub> emission, brings about a significant footprint and impact in the environment and eventually a harm to human being as a result of increased contents in such heavy oil fractions of aromatic and especially polyaromatic hydrocarbons characterized by carcinogenic and toxic properties [1]. Therefore, the global energy sources based on alternative fuels, including hydrogen and fuel cells, are in strong demand [2]. The further growth of the contribution of alternative energy sources is hardly possible without development of efficient concepts of energy storage, in particular, storage of pure hydrogen as an environmentally friendly fuel.

The use of liquid organic hydrogen carriers (LOHC) for hydrogen storage based on reversible cycles of hydrogenation and dehydrogenation would be a benign and safe solution to the problem [3–5]. The hydrogen storage capacity for LOHC (both on a weight and volume basis) is rather high, unlike the other known methods of hydrogen storage, and hydrogen is present in a chemically bound state. This makes the method based on the use of LOHC safe and compatible with the existing fuel infrastructure and transportation under normal

conditions without the need to use extremely high pressures. Among LOHC capable of reversible hydrogenation-dehydrogenation cycles, benzene-cyclohexane or toluene-methylcyclohexane couples should be mentioned first (6.5/6.1 wt% H<sub>2</sub>) [6]. The general drawback for both systems is the high volatility (low boiling point and high saturated vapor pressure at temperatures below the boiling point). Also, cracking or ring opening may occur at temperatures typical for dehydrogenation. Therefore, these two systems are not considered as perspective candidates, in spite of the significant number of publications related to these systems [7].

It was shown [8–10] that the possibility of the loss of the substrate with releasing hydrogen can be decreased when the LOHC represent  $\pi$ -conjugated aromatic compounds such as polyaromatic compounds (7.2–7.8 wt%) or heterocyclic compounds (5.5–5.7 wt% H<sub>2</sub>). The dehydrogenation of the hydrogenated counterparts of the latter proceeds at relatively low temperatures, while the boiling points of the former are substantially higher than the dehydrogenation temperatures. Usually dehydrogenation is carried out in an intermediate state of a liquid film achieved by simultaneous boiling and flow of a substrate [11,12]. In the course of dehydrogenation, such a thin film becomes overheated, which favors the endothermic reaction (dehydrogenation). Hydrogen diffuses freely through the thin film of the substrate. The use of LOHC based on low-melting substrates (melting points below –30 °C), for instance, a mixture of benzyl- and dibenzyltoluene (6.0–6.2 wt% H<sub>2</sub>) allows one to avoid a complicated and energy-

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consuming thermostating, which is necessary for traditional reactors for endothermic dehydrogenation or exothermic hydrogenation of carbocyclic and nitrogen-containing compounds [13–15].

Side processes (cracking etc.) are minimized by the proper choice of the dehydrogenation catalyst that should exhibit a high activity and a high selectivity toward dehydrogenation. Pt- and Ni-catalysts usually demonstrate a high activity in dehydrogenation of naphthenic molecules [16,17]. Nickel is significantly cheaper than platinum, but its selectivity toward dehydrogenation is lower because of the pronounced cracking activity. The use of Pt-containing catalysts allows one to decrease the activation energy for dehydrogenation [7]. The content of a noble metal in the catalyst should be sufficient for the activation of the dehydrogenation process. Typically activated carbon or other advanced carbon carriers are used as supports [18,19]. The major problem is the occurrence of undesirable side reactions under reversible cycles of hydrogenation-dehydrogenation of complex aromatic compounds, and the structure of the latter, among with the catalyst nature, determines the contribution of such side processes. Understanding of the effect of the structure of LOHC on the hydrogenation-dehydrogenation reactions is crucial for designing an ideal LOHC system.

The objective of this work was the evaluation of the role of the structure of naphthenes (cyclohexane, bicyclohexyl and perhydroterphenyl) on their conversion under dehydrogenation conditions. Since the hydrogenation reaction is thermodynamically linked with dehydrogenation, we departed from the study of exhaustive hydrogenation of the corresponding aromatic compounds (benzene, biphenyl, terphenyl). A series of Pt/C catalysts on different carbon carriers was used in both reactions.

## 2. Materials and methods

### 2.1. Procedure of dehydrogenation

Substrates prepared by exhaustive hydrogenation of the commercial aromatic hydrocarbons were used for the dehydrogenation tests: benzene, 99.5% (Acros Organics), biphenyl, 99% (Acros Organics), individual isomers of *ortho*-terphenyl, 99% (Aldrich) and *meta*-terphenyl, 99% (Aldrich), as well as a mixture of terphenyl isomers Santowax-R (11.03 wt% *o*-C<sub>18</sub>H<sub>14</sub>, 59.22 wt% *m*-C<sub>18</sub>H<sub>14</sub> and 29.75 wt% *p*-C<sub>18</sub>H<sub>14</sub>). Hydrogenation was carried out in a high-pressure autoclave PARR-5500 (USA) with the internal volume of 600 mL at 180°C and 70 atm using a 3 wt% Pt/C catalyst (Aldrich, Lot no. HI06523BT). The reaction was run until complete saturation of each of the studied aromatic hydrocarbons. The reaction completeness was checked by gas chromatography. Schemes of the hydrogenation and selected physicochemical characteristics of the starting hydrocarbons are presented in Table 1.

The reaction mixture obtained after hydrogenation was separated from the catalyst and analyzed. The completely hydrogenated products were used for dehydrogenation performed in a flow catalytic reactor. The pipelines of the setup were kept at 90–120 °C. The saturated substrates in a liquid state were supplied to the reactor using a high-pressure pump HPP 5001. Hydrogen and liquid products were

separated at the reactor outlet. Samples for analysis were collected every hour after the start of the test. In order to produce pure hydrogen with no traces of other gases at the exit of the setup, a system of condensers and filters, including membranes were used [20].

For dehydrogenation, a 3 wt% Pt/C (Sibunit, Omsk) catalyst was prepared and used. Platinum was supported on the surface of the carrier by incipient wetness impregnation with an aqueous solution of [H<sub>2</sub>PtCl<sub>6</sub>] (ω<sub>Pt</sub> = 36.3%) according to the procedure described elsewhere [21]. The catalyst before the reaction was activated in the reactor at 320 °C in a hydrogen flow (30 mL/min) for 2 h. The average particle size of 1.92 nm was determined from TEM images of the catalyst. The platinum dispersion of 49% was calculated from CO adsorption using ASAP-2020 Micromeritics instrument.

### 2.2. Chromatographic analyses

The products of hydrogenation and dehydrogenation reactions were analyzed using a Krystal-Luks-4000M gas chromatograph with a flame-ionization detector and capillary columns ZB-5 (ZEBRON, USA) and TR-FFAP (“Thermo Scientific”, USA). Analyses were carried out in a temperature-programmed regime in the range of 70–220 °C at the heating rate 6 °C/min. For a detailed analysis of the semi-hydrogenated products and side products of the reactions, some samples of the reaction mixtures were analyzed using a GC-MS instrument FOCUS DSQ II (“Thermo Fisher Scientific”, USA) with a capillary column TR-5MS (“Thermo”, USA). The purity of evolving hydrogen was determined by gas chromatography using a thermal conductivity detector and a packed column Porapak Q.

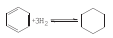
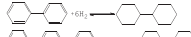
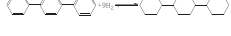
The conversions in hydrogenation and dehydrogenation (*X*) were calculated by the formula:  $X = (c^0 - c) / c^0 \times 100\%$ , where *c*<sup>0</sup> and *c* are the initial and final concentrations of the substrate.

The selectivity (*S*) was calculated by the formula:  $S(i) = \Sigma c(i) / \Sigma c(k) \times 100\%$ , where  $\Sigma c(i)$  and  $\Sigma c(k)$  are the sums of the concentrations of a group of products and all products, respectively.

## 3. Results and discussion

The reversible reactions of hydrogenation of polycyclic aromatic substrates with a different extent of condensation and the reactions of dehydrogenation of the corresponding polycyclic naphthenic molecules represent multi-stage processes with a general scheme:  $A-H_{2n} \leftrightarrow A + H_{2n}$ . The study was started with a classical pair benzene/cyclohexane, and the results of their hydrogenation/dehydrogenation were used as an objective criterion for comparison with other studied pairs of the substrates. The ability of the completely hydrogenated compounds to undergo dehydrogenation with the maximum possible conversion and the highest possible selectivity to the main product without any losses of the substrates as a result of side processes (cracking, hydrogenolysis etc.) was considered as the main criterion for comparison. Benzene hydrogenation was carried out at 180 °C and 70 atm. The complete benzene conversion with a selectivity to cyclohexane over 99.9% was achieved under the chosen conditions after 20 min since the

**Table 1**  
Physicochemical characteristics of the hydrocarbons to be hydrogenated.

Substrate	Scheme of the reaction	T (°C)		Enthalpy of 95% hydrogenation, ΔH° (300 K) (kkal/mol) [9]	H <sub>2</sub> storage capacity (wt%)
		b.p.	m.p.		
Benzene		80	5–6	– 15.6	7.69
Biphenyl		255	69–72	– 16.0	7.79
Terphenyl:					
<i>o</i> -Terphenyl		337	58–59	– 15.8	7.83
<i>m</i> -Terphenyl		379	86–87	– 15.7	7.83
<i>p</i> -Terphenyl		389	212–213	– 15.7	7.83

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