



The Role of the Metal in the Catalytic Reactions of Hydrogenation–Dehydrogenation of Polycyclic Hydrocarbons for Hydrogen Storage

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Abstract: The design of benign and safe hydrogen storage systems is the priority in the development of new energy carriers. The storage of hydrogen in a liquid or compressed state, as well as in metal hydrides and adsorbents, depends on pressure and temperature and under normal conditions does not meet the criteria of the target hydrogen storage capacity, energy consumption for hydrogen storage or safety. The storage of hydrogen in chemical compounds in which it is naturally included in the composition is the only alternative. Aromatic hydrocarbons capable of reversible hydrogenation– dehydrogenation reactions are of the greatest interest among regenerable hydrogen-containing compounds and can be used for hydrogen storage. The role of the metal in the catalytic reactions of the hydrogenation–dehydrogenation of cyclic hydrocarbons for hydrogen storage is discussed in the present review in close relation to the structure and composition of the cyclic substrates.

Keywords: hydrogen storage; liquid organic hydrogen carriers; hydrogenation catalysts; dehydrogenation catalysts

1. Introduction

The rapid growth of global economics led to a significant increase in energy demand [1]. To date, energy is generated mostly from fossil fuels with a negative impact on the environment and climate [2]. In order to mitigate this effect, various types of energy are considered as alternative sources (solar, wind, hydropower, biofuels, etc.) [3]. Hydrogen is of particular interest, because it has the highest energy density (120 MJ/kg), and the processes of its conversion into energy are green and environmentally safe [4–6]. Hydrogen fuel cells have found practical implementation in transport [7]. Thus, economical and safe hydrogen storage systems with a gravimetric content of at least 6.5% by weight H₂ (>2.0 kWh/kg) and a volume density of more than 0.04 kg/L (>1.3 kWh/L) are needed [8] that should be characterized by a high refueling rate and low hydrogen release energy. The storage of hydrogen in a liquid or compressed state, as well as in metal hydrides and adsorbents, depends on pressure and temperature and under normal conditions does not meet the criteria of the target hydrogen storage capacity, energy consumption for hydrogen storage or safety [9–12].

Under these conditions, the storage of hydrogen in chemical compounds in which it is naturally included in the composition and structure is of interest. In this review, a number of hydrogen storage and release systems based on the processes of the heterogeneous catalytic hydrogenation of cyclic and polycyclic aromatic hydrocarbons with a hydrogen capacity above 6.5–7.0% by weight and conjugated dehydrogenation of the corresponding naphthenic compounds are analyzed. The main attention is paid to the identification of differences between the course of reversible processes depending on the structure of



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). substrates. The purpose of this review is to compare the performance of different metals toward both the hydrogenation and dehydrogenation of the substrates with close relation to the nature of the catalytically active metal. Most of the data on the basis of which conclusions are drawn were obtained on platinum and nickel catalysts. The structure of this paper is based on the consideration of organic molecules used as liquid organic hydrogen carriers (LOHCs) and progresses from simple organic molecules (benzene and toluene) to tricyclic compounds.

2. Catalytic Hydrogenation and Dehydrogenation of Cyclic Hydrocarbons on Supported Metals

Due to the incorporation of hydrogen into the composition of liquid organic hydrogen carriers (LOHCs), the content of the hydrogen stored in chemical compounds (over 0.07 kg/L) does not depend on the temperature and pressure, like in the case of cryogenic systems and compressed hydrogen, and is determined solely by the nature of the substance (Figure 1). It is noteworthy that LOHCs exhibit certain advantages over metal hydrides and adsorption systems.



Figure 1. A map of hydrogen storage systems.

This provides an advantage, since hydrogen in the composition of organic compounds can be safely stored and transported over long distances under normal conditions, while other systems require special conditions (T, P) and equipment. Unfortunately, for a variety of chemical compounds with a high content of hydrogen (NH₃, H₂O, CH₄, CH₃OH, HCOOH, etc.), its release requires energy expenses or is irreversible. For the purposes of hydrogen storage and release, aromatic hydrocarbons capable of reversible hydrogen-dehydrogenation reactions are of the greatest interest among regenerable hydrogen-containing compounds. In addition to the high gravimetric (above 7.2 wt. %) and volume content of hydrogen [13], the method is characterized by relatively simple mechanisms of saturation (hydrogenation) and release (dehydrogenation) of hydrogen. The necessary purity of hydrogen for fuel cells is provided by selective catalysts that allow reactions to be carried out without the formation of by-products and CO_x gases [14–18].

According to quantum chemical calculations, arene–naphthene pairs have the greatest potential for the application in hydrogen storage among polycyclic hydrocarbons, in which π -conjugated aromatic compounds have a modulus of negative standard enthalpy change for hydrogenation $|\Delta H^o|$ less than 15 kcal/mol H₂ (or 62.7 kJ/mol H₂) [19]. Analysis of the literature shows that the realization is far behind the theoretically possible values, especially for polycyclic condensed compounds. Thus, in spite of the low value $|\Delta H^o| = 13.8$ kcal/mol

 H_2 , the real amount of hydrogen obtained by perhydrocoronene dehydrogenation to coronene ($C_{24}H_{12}$) is only 1% by weight, whereas the theoretical estimate is 7.4% by weight. Exhaustive hydrogenation of double bonds of fullerene C_{60} without destroying the carbon framework should produce fully hydrogenated fullerene of the composition $C_{60}H_{60}$ with the hydrogen capacity of 7.7% by weight. In reality, the formation of compounds $C_{60}H_{48}$ with a limit of the hydrogen content of 4.5–6.3% H_2 by weight is observed, which is inferior to conventional polycyclic structures [6,19].

The stability of aromatic compounds during catalytic hydrogenation is due to the thermodynamic stability of the aromatic conjugate system and the high activation energy at the catalytic center. The kinetics of hydrogenation–dehydrogenation processes are determined by the structure, configuration and degree of condensation of aromatic substrates and the corresponding naphthenes. Thus, to ensure the maximum capacity in cyclic hydrogenation–dehydrogenation processes, knowledge of only the enthalpies of the hydrogenation or dehydrogenation of the substrates is not sufficient [20–22], since the structural factor, as well as the correspondence of the morphology of the substrate and the catalyst, make a very significant contribution [13]. This review analyzes the patterns (ways) of the exhaustive catalytic hydrogenation and conjugate dehydrogenation of the most well-known couples of cyclic hydrocarbons (arene–naphthene) with varying degrees of condensation on supported metals, while clarifying the role of the latter (Figure 2):



Figure 2. Hydrogenation-dehydrogenation of cyclic compounds for hydrogen storage.

2.1. Benzene–Cyclohexane

According to the literature data, the hydrogenation of benzene and the dehydrogenation of cyclohexane mainly proceed via a planar mechanism with the sequential addition or removal of hydrogen atoms. In the hydrogenation of benzene, the rate-limiting stage is the addition of the first hydrogen atom, and in the dehydrogenation of cyclohexane, the abstraction from the molecule of the second hydrogen atom is the rate-limiting step [23,24]. The hydrogen abstraction energy corresponds to the activation energy of the entire dehydrogenation process.

The actual sizes of benzene and cyclohexane molecules are large enough and several reacting atoms cannot fit on one metal atom upon contact with the catalyst surface. Therefore, the interaction of the molecule with one metal atom on the surface of the catalyst leads only to adsorption, since the molecule is not activated enough to participate in the reaction. The complete correspondence of the parameters of metal lattices and cyclohexane/benzene molecules is achieved for a limited number of metals crystallizing in systems with cubic (face-centered cubes, A1 lattice) and hexagonal (A3) lattice types (Figure 3, Table 1).

It follows from the literature that the most active and selective in the dehydrogenation reaction of cycloalkanes are Pt catalysts deposited on active carbons. This means that more hydrogenation–dehydrogenation cycles can be carried out on Pt/C systems without the formation of side reaction products such as cracking and hydrogenolysis, which is important for hydrogen storage processes. Fortunately, the target reactions proceed at a higher rate than side reactions at a high dispersion of the metal, which is precisely provided by active carbon carriers with a large surface area. However, the absence of the acid centers that are available in oxide carriers does not result in the breaking of C-C bonds on carbon carriers [13]. According to the XPS data, an ensemble of at least five Pt atoms is needed for the chemisorption of cyclohexane on the surface of platinum Pt(111), and at least eight Pt atoms are additionally needed for the dehydrogenation of adsorbed cyclohexane [25–28].



Figure 3. The scheme of correspondence of the parameters of the FCC lattice of the metal (plane 111) (a) and the cyclohexane molecule ((b)—projection from above) (o—means the location of the metal atoms of the catalyst) (arrows indicate the direction of interaction of hydrogen atoms of cyclohexane with the catalyst atoms) (Figure modified from [25]).

Table 1. Lattice parameters of metals most active in the hydrogenation of benzene and dehydrogenation of cyclohexane (Data from [13]).

Metal	Pt	Pd	Ir	Rh	Cu	Со	Ni
Parameter of the lattice, nm	2.78	2.75	2.71	2.69	2.56	2.51	2.49

Table 2 shows data on the rate of hydrogen release on different heterogeneous catalysts [5]. One of the best examples of the high rate of hydrogen release during the dehydrogenation of cyclohexane given in the literature was obtained for the catalyst 3.8%Pt/C on activated carbon (1800 mmol(H₂)/g_{met}/min) [29,30]. An increase in the platinum content to 10% by weight in the Pt/C catalyst resulted in a decrease in the rate of hydrogen release to 510 mmol(H₂)/g_{met}/min. The combination of platinum with other noble metals did not have a significant effect. When replacing the noble metal with nickel with different parameters of the lattice (Table 1), the rate of hydrogen release decreased even more significantly and at nickel concentrations in Ni/C of 10, 20 and 40% by weight the rates are as low as 7.1, 8.1 and 6.8 mmol(H₂)/g_{met}/min, respectively [5]. The data of Table 2 also indicate a decrease in TOF values with an increase in the size and condensation extent of the molecule to be dehydrogenated.

Table 2. Hydrogen release rates during dehydrogenation of some cycloalkanes.

Substrate	Catalyst	TOF (mmol(H ₂)/g _{Pt} \times min)
Cyclohexane	3.82 wt. % Pt/AC	1800
Methylcyclohexane	3.82 wt. % Pt/AC	1700
Decalin	3.82 wt. % Pt/C	610
Cyclohexane	10 wt. % Ni/AC	7.1
Cyclohexane	20 wt. % Ni/AC	8.5
Cyclohexane	40 wt. % Pt/AC	6.8
Cyclohexane	12 wt. % Pt-Rh/AC	520
Cyclohexane	11 wt. % Pt-Re/AC	550

It was shown [31] that in order to increase the reaction rate and its selectivity, for both the hydrogenation of benzene and dehydrogenation of cyclohexane, certain additives, such as oxygen, can be used, and bimetallic catalysts with a small platinum content also demonstrate good performance. In particular, the addition of 0.5 wt. % Pt in a catalyst 20%Ni/C [5] resulted in an increase in the cyclohexane conversion by almost 50%.

Notably, the yield of the cracking reaction products was significantly diminished. The improvement of reaction kinetics via the modification of the Pt/C catalyst with a second metal presumably occurs due to the promotion of the C-H bond break and/or desorption of aromatic products [13]. A similar effect was observed when platinum was doped with metals such as Mo, W, Re, Rh, Ir, Sn or Pd [5]. The catalytic activity also increased by physically mixing Pd/PCC and Pt/PCC catalysts (PCC stands for petroleum coke carbon), presumably as a result of the synergy of the spillover, migration and recombination of hydrogen over Pt and Pd [28,29].

2.2. Toluene–Methylcyclohexane

Due to the low freezing temperatures (T = -95 and -126 °C, respectively), a pair of toluene–methylcyclohexane substrates is the most suitable for storing and releasing hydrogen in winter conditions. Despite the relatively low hydrogen capacity (6.1 wt. %), this circumstance causes a significant number of publications devoted to this system and, especially, the dehydrogenation reaction of methylcyclohexane, as the stage responsible for supplying hydrogen to a fuel cell. The dehydrogenation of methylcyclohexane has been studied by Sinfelt, Klvana, Taube, Usman and many other researchers [32–34]. Despite a significant number of studies, a complete consensus on the mechanisms of toluene hydrogenation and methylcyclohexane dehydrogenation has not yet been achieved. In benzene homologues (such as toluene), the presence of donor substituents with a positive induction effect (+I), such as methyl groups (CH₃-), leads to the deformation of the σ -bonds of the cycle and an increase in the extent of the delocalization of the positive charge of the σ -complex compared to the unsubstituted π -complex of benzene [13] (Figure 4):



Figure 4. Structures of substituted cyclic hydrocarbon and the effect of donor and acceptor substituents. Electron-donating (D) or electron-acceptor (A) groups are shown (the wavy lines mark the shortened lengths of C—C bonds, and the arrows indicate the increased valence angles of C atoms in the benzene cycle).

On the one hand, this results in an increase in the stabilization energy of the toluene molecule (E_{st} ~163 kJ/mol) compared to benzene. On the other hand, the hydrogen substitution reaction in the *meta*- and *para*-positions is accelerated. In most studies, the limiting stage of toluene hydrogenation, as for benzene, is the addition of the first hydrogen atom; after that, toluene loses its aromatic nature. In the dehydrogenation of methylcyclohexane, the limiting stage is considered to be the formation and adsorption of methylcyclohexene [35]. During the reaction, the formation of an intermediate π -allyl compound (C₆H₈-CH₃) was recorded, which is first dehydrogenated to benzyl (C₆H₅-CH₂) with hydrogen cleavage from the methyl group and only then to toluene (C₆H₅-CH₃) [36]. Presumably, the π -allyl cycle is formed due to adsorption of a methylcyclohexane molecule on the catalyst via three carbon atoms. According to NEXAFS, the molecules of methylcyclohexane and toluene have a flat orientation on the surface of Pt(111), while benzyl is oriented almost perpendicular to the surface [37]. The non-competitive Horiuti–Polyani mechanism is well suited for the general description of experimental data, but taking into account the empirical coefficients of pressure and/or temperature affecting the equilibrium constant [35].

It should be noted that the dehydrogenation of methylcyclohexane also achieved a high rate of hydrogen release (from 500 to 1500 mmol(H_2)/g_{met}/min) [28,29]. However, in most studies, high rates were observed only within a few minutes after the start of the reaction, usually for 5–20 min. Longer periods of maintaining a high rate of hydrogen

evolution, for example, several hours, with a conversion and selectivity of 100%, are not described in the literature. Binival et al. [38] confirmed the stability of the catalyst for 200 h, but the conversion of toluene hydrogenation and methylcyclohexane dehydrogenation did not exceed 60% in one cycle of reversible reactions, which is not enough for real hydrogen storage systems. The work of Okada et al., who reported maintaining the conversion of methylcyclohexane dehydrogenation at the level of 95% and toluene selectivity of 99% during 6000 h of the reaction, should be mentioned [39]. At the same time, the rate of hydrogen release exceeded 1000 m³/h, which is significantly higher than the requirements for the supply of hydrogen to a fuel cell and even leaves a reserve for experimenting with the weight and size characteristics of a hydrogen-containing installation. It should be noted that, at present, the use of methylcyclohexane as a liquid organic carrier of hydrogen for the purposes of hydrogen storage and separation has been practically implemented by Chiyoda Corporation (Japan) [40].

The data obtained clearly demonstrate the potential suitability of monocyclic compounds as the basis of high-capacity hydrogen storage systems, but subject to the development of more efficient and stable catalysts. At the same time, in a pair of substrates, benzene–cyclohexane (7.14 wt. % H₂), high saturated vapor pressure ($P_{sat} = 12.7/13.0$ kPa) contributes to the entrainment of substrates together with hydrogen, which, in addition to the loss of capacity for H₂, negates the advantage in the safety of this system. The introduction of substituents into the structure helps to solve the problem of volatility, but leads to a drop in the hydrogen capacity, which in the simplest pair of toluene–methylcyclohexane ($P_{sat} = 3.8/6.2$ kPa) is almost 1% by weight, which as a result leaves practically no reserve with a future increase in the requirements for the capacity of hydrogen storage systems.

2.3. Polycyclic Hydrocarbons

There are fewer studies on polycyclic hydrocarbons compared to monocyclic compounds, especially in the aspect of hydrogen storage systems. Despite the same hydrogen capacity (6.2 wt. %) as for the toluene-melylcyclohexane system, interest in systems based on benzyltoluene and dibenzyltoluene is associated with lower values of hydrogenation enthalpies relative to hydrogen ($\Delta H^{0} = 63.5$ and 65.4 kJ/mol, respectively) than toluene $(\Delta H^{\circ} = 67.4 \text{ kJ/mol})$ and, especially, benzene $(\Delta H^{\circ} = 68.6 \text{ kJ/mol})$ [17,18]. This means that during the dehydrogenation of perhydrobenzyltoluene and perhydrodibenzyltoluene, hydrogen release should take place at lower temperatures than from these monocyclic compounds. However, under reaction conditions already at the hydrogenation stage, the kinetic parameters are inferior to systems based on benzene and toluene. The hydrogenation of benzyl- and dibenzyltoluene (Figure 5) is most effective on Ru catalysts at 180 $^{\circ}$ C and 20–50 atm, but, in the case of dibenzyltoluene, the reaction proceeds at a relatively low rate. In particular, due to the large number of partially hydrogenated intermediate products, as well as steric conformers of perhydrodibenzyltoluene, the formation of which takes place along different routes and at different speeds. The reverse dehydrogenation reaction also takes place more efficiently on Ru catalysts at temperatures of 280–350 °C, but the different reactivity of steric isomers has a negative effect on the volume and rate of hydrogen released.

In a pair of diphenylmethane (C_6H_5 - CH_2 - C_6H_5)—dicyclohexylmethane (C_6H_{11} - CH_2 - C_6H_{11}), neighboring hydrocarbon cycles are connected via a methylene group, due to which their hydrogen capacity (6.66 wt. %) is higher than that in the toluene–methylcyclohexane system. At the same time, the complete hydrogenation of diphenylmethane on a 5%Ru/C catalyst takes place at a lower temperature (T = 120 °C) than the hydrogenation of benzene. Like methylcyclohexane, the dehydrogenation of dicyclohexylmethane on a Pt(111) catalyst also occurs through the formation of an intermediate π -allyl compound, but with two cycles. The latter are dehydrogenated first with the transformation of one of the π -allyl groups into a phenyl group, and then with the formation of diphenylmethane [41]. In this case, the adsorption of the dicyclohexylmethane molecule on the catalyst occurs by six hydrogen atoms—three on each of the two hydrocarbon cycles. During dehydrogenation,

part of the substrate is desorbed, which slows down the overall kinetics of the reaction. The disadvantages of this system should also include the cleavage of the C-H bond in the methylene group at dehydrogenation temperatures, which leads to the degradation of substrates as hydrogen carriers. When platinum Pt(111) is replaced with palladium Pd(111), the dehydrogenation of dicyclohexylmethane takes place without the formation of an intermediate with one phenyl group. However, the cleavage of the C-H bond begins at lower temperatures, which results in faster degradation of the initial dicyclohexylmethane. The sequence of dicyclohexylmethane (DCHM) conversion on the surface of the Pt(111) catalyst can be represented as follows:



 $C_{6}H_{11}\text{-}CH_{2}\text{-}C_{6}H_{11} \rightarrow [C_{6}H_{8}\text{-}CH_{2}\text{-}C_{6}H_{8}] \rightarrow [C_{6}H_{5}\text{-}CH_{2}\text{-}C_{6}H_{8}] \rightarrow C_{6}H_{5}\text{-}CH_{2}\text{-}C_{6}H_{5}$

Figure 5. General scheme of hydrogenation of dibenzyltoluene (a) and benzyltoluene (b).

According to quantum chemical calculations [19], the replacement of a carbon atom in carbocyclic aromatic hydrocarbons with nitrogen, sulfur or oxygen-containing groups contributes to a decrease in the standard enthalpy of hydrogenation ΔH^{0}_{H2} of the corresponding heterocyclic compound. The enthalpies of dehydrogenation increase in the series [N] << [S]~[O] and for compounds such as tetrahydropyrrol, tetrahydrothiophene and tetrahydrofuran are equal to 40, 50 and 51 kcal/mol H₂, respectively [42]. This indicates a significant advantage of systems based on nitrogen-containing compounds for the purposes of storing and releasing hydrogen. At the same time, for condensed compounds in which benzene rings and a π -conjugated five-membered nitrogen-containing ring alternate, the standard enthalpy of hydrogenation is lower than that of molecules with other combinations of rings. Based on these calculations, Air Products and Chemicals, Inc. (USA) has patented the N-ethylcarbazole/perhydro-N-ethylcarbazole (NEC/H12-NEC) system as a potential hydrogen storage and separation system. However, despite the high theoretical hydrogen capacity of carbazole (7.19% by weight), in real conditions it turned out that reversible hydrogenation-dehydrogenation reactions of systems based on this molecule proceed slowly [43,44]. At the same time, in a carbazole molecule at temperatures below 150 °C, a five-membered ring containing a heteroatom is easily subjected to a hydrogenolysis reaction followed by the breaking of the carbon-heteroatom bond and the removal of the latter [19]. Increasing the resistance to this reaction due to the blocking of the heteroatom with alkyl substituents contributes to a decrease in the capacity of stored hydrogen by 0.4 wt. % H₂ per one methylene chain link, since the substituent is not involved in the absorption and release of hydrogen. With such a significant loss of the capacity, it is impractical to increase the length of the alkyl chain to more than two carbon atoms, despite the fact that even in the N-ethylcarbazole/perhydro-N-ethylcarbazole system (6.79% H_2 by weight) the dehydrogenation reaction is extremely slow due to steric

difficulties in the resulting intermediates [43,44]. For example, at 443 K and 101 kPa, a 100% conversion of perhydro-N-ethylcarbazole on a 5%Pd/SiO₂ catalyst (average Pd particle size of 24 nm) was reached in 17 h of the reaction. In the dehydrogenation reaction of perhydrocarbazole without shielding, the conversion under the same conditions was only 53%. DFT calculations showed that the adsorption energy of perhydrocarbazole on Pd(111) is $E_{ads} = 109.4$ kJ/mol, and in substituted perhydro-N-ethylcarbazole, E_{ads} decreases to 95 kJ/mol. When tetrahydrocarbazole is dehydrogenated at 413 K on a 5%Pd/Al₂O₃ catalyst, an 81% conversion is achieved after 27 h of the reaction [45–47]. Interestingly, after heat treatment of the 4%Pd/SiO₂ catalyst (the average particle size of Pd is 6 nm) in a helium flow, a 100% conversion of perhydro-N-ethylcarbazole at 443 K and 101 kPa was achieved after 1 h 40 min of the reaction.

One of the reasons for the slow kinetics of the reaction is the dealkylation of Nethylcarbazole via the C-N bond with the formation of carbazole and hydrocarbon fragments that are adsorbed on the catalyst (Figure 6):



Figure 6. N-Ethylcarbazol as a hydrogen storage material.

Since the carbazole molecule is less reactive compared to alkyl-substituted analogues, its formation during the reaction worsens the kinetic characteristics of the N-ethylcarbazole/dodecahydro-N-ethylcarbazole pair as a hydrogen storage system. When Pt(111) is replaced by Pd(111), the activation energy of the dealkylation reaction decreases, and the reaction itself begins on the Pd catalyst at T = 360 K, which is 30 K lower than that on the Pt catalyst. This leads to a stronger self-poisoning of Pd catalysts during the dehydrogenation of perhydro-N-alkylcarbazoles. An equally important role is played by the presence in the equilibrium state of perhydro-N-alkylcarbazole of at least five steric isomers, whose structural features and different physico-chemical characteristics increase the variability of the dehydrogenation reaction pathways, thereby also affecting the kinetics of the reaction and, accordingly, the volumes and velocity of hydrogen released. As a result, the potential of substituted carbazole homologues as the basis of hydrogen storage and separation systems turns out to be lower than that of the corresponding carbocyclic hydrocarbons [48–50].

Among carbocyclic compounds, most of the studies devoted to the liquid-phase hydrogenation of polyaromatic hydrocarbons are related to the hydrogenation of naphthalene and, to a much lesser extent, anthracene. In the case of the latter, the interest is more based on the need to solve the problem of recycling "heavy" aromatics from petroleum fuels and oils, typical representatives of which are both of these compounds.

It should be noted that the hydrogenation mechanisms on Ni- and Pt-catalysts closely correspond to each other. When naphthalene is hydrogenated onto Ni/ γ -Al₂O₃, both of its unsaturated hydrocarbon cycles are adsorbed as a transition $\pi/6$ complex, which is in equilibrium with the π -planar and 6-vertical (rib) forms [51,52]. The first two forms of

adsorption (π /6- and π -) are associative. Dissociative 6-adsorption leads to the cleavage of the hydrogen atom from the aromatic ring. Based on the studies of Rotanen et al. [51,52], the optimized scheme of the naphthalene hydrogenation reaction on a Ni/Al₂O₃ catalyst looks as follows (Figure 7):



Figure 7. Hydrogenation of naphthalene.

It is believed that the adsorption of naphthalene occurs at one active metal center, and the hydrogenation of naphthalene is a structure-insensitive reaction. The reaction begins with the *cis* addition of two dissociatively adsorbed hydrogen atoms to form tetralin and then hydrogenation to 9,10-octalin occurs, but the rate constant (k_2) of the second stage is almost twice lower. The adsorption of tetralin requires an ensemble of several atoms of the active metal, and its hydrogenation is a structure-sensitive reaction, but a complete consensus on this issue has not been reached. The resulting 9,10-octalin isomerizes to octahydronaphthalene (1,9-octalin), which is hydrogenated to *cis*- and *trans*-decalin at a high rate. The ratio between isomers depends on how the hydrogen atom is oriented at the position 10 ("face" orientation or away from the surface) in the intermediate octahydronaphthalene [53–55]. Under certain conditions, 9,10-octalin can be immediately hydrogenated to *cis*-decalin, but the reaction rate is very low.

Particular interest in the reverse reaction of the dehydrogenation of decalin is due to the fact that, as a component of the diesel fraction, this substrate is an ideal model for studying the possibility of obtaining hydrogen directly on board of a vehicle by dehydrogenating existing hydrocarbon fuel (aviation kerosene, diesel fuel, etc.) [56]. The presence of steric isomers contributes to the separation of the process of the dehydrogenation of decalin into several independent reactions, such as the dehydrogenation of the *cis*- and *trans*-isomers of decalin and mutual cis-trans isomerization, the competitive nature of which has a noticeable effect on the overall kinetics of the reaction [57,58]. At the same time, the nature of the dehydrogenation of decalin has no fundamental differences with the dehydrogenation of cyclohexane and methylcyclohexane. However, bicyclic decalin is inferior to monocyclic cyclohexane and methylcyclohexane in terms of the rate of hydrogen release under the same reaction conditions [39,40]. Comparison of the results of the dehydrogenation of decalin on three Pt catalysts deposited on γ -Al₂O₃, SiO₂ and activated carbon showed that the reaction rate equation in the temperature range 275-345 °C corresponds to the kinetic Hougen-Watson model, which explicitly takes into account the adsorption of various components of the reaction mixture [13].

Conducting a study of the dehydrogenation of decalin as a hydrogen storage system, Kariya and Ichikawa et al. [28,29] and Hodoshima et al. [59,60] found that the reaction rate increases due to the continuous removal of adsorbed hydrogen from the surface of catalysts. The state of the substrate, which is formed due to a sharp temperature gradient at the catalyst/reagent interface due to the different rates of evaporation and condensation of the liquid substrate droplets on the surface of the catalyst, has been called a "liquid film". In a state intermediate between gas and liquid, it was possible to achieve a 90% conversion of decalin at a temperature of 265 °C, despite the fact that the high reaction rate was already observed at a temperature of 240 °C [61]. Distillation of aromatic products helps to slow

down the adsorption and coking of the catalyst, which is often observed in a liquid-phase reaction at high temperatures. At the same time, the authors conducted extensive studies of the effect of additives of the second metal on the activity of Pt-containing catalysts [59,60], as well as tested a wide range of carriers for the catalysts [28,29]. For this purpose, 5%Pt/C, 5%(Pt-Ir)/C catalysts with total metal contents of 5 wt. % were used with a molar ratio of Pt/Ir = 4, as well as 5%(Pt-W)/C (Pt/W = 1) and 5% (Pt-Re)/C (Pt/Re = 2). PCC, CC, Al₂O₃, FSM-16, HZSM-5 zeolites were used as carriers. The authors also investigated the dependence of the reaction rate on the decalin/catalyst ratio and the type of the reactor. It has been shown that the overall reaction rate depends not only on the reaction conditions (temperature, nature of reagents, type and porosity of the carrier, etc.), but also on the size and shape of the catalytic reactor.

Decalin was dehydrogenated at a temperature of 240 °C in a "liquid film" state on Pt/C catalysts deposited on carbon nanotubes [62]. The highest rate of hydrogen release (732 mol H₂/mol Pt) was achieved on a catalyst 5%Pt/C (D_{Pt} = 57%, d_{Pt} = 1.8 nm), despite the fact that the conversion of decalin was only 46%. This rate was maintained for 2 h of the reaction. When the Pt content decreased to 1 wt. % (D_{Pt} = 85% and d_{Pt} = 1.2 nm, respectively), the conversion decreased to 7%, and the rate of hydrogen release decreased to 335 mol H₂/mol Pt. The authors attributed the decrease in velocity with a general increase in the dispersion of Pt particles to the inefficient operation of a part of platinum due to its blocking in the micropores of the carrier. Platinum blocking is also facilitated by the adsorption of naphthalene formed in the pores [63]. At the same time, an increase in temperature accelerates the removal of hydrogen, which helps to unblock the active centers of the catalyst. The efficiency of the reaction depends on the design of the catalytic reactor used for the reaction.

It should be noted that the naphthalene–decalin pair is a typical example of substrates in which the modulus of the negative standard enthalpy change in the hydrogenation reaction $|\Delta H^{\circ}|$ is different for *cis*-decalin (-15.1 kcal/mol H₂) and *trans*-decalin (-15.8 kcal/mol H₂) [19]. The difference correlates with the different kinetics of the dehydrogenation of the two decalin conformers. Thus, when dehydrogenation is carried out on a 3%Pt/C catalyst, the conversion of *cis*-decalin to naphthalene at a temperature of 320 °C is 97%, whereas the conversion of *trans*-decalin is only 66%. This example clearly demonstrates the expediency of using *cis* isomers that are predominantly more active in dehydrogenation, which can be obtained by selective hydrogenation of the initial arenes.

Regarding the hydrogenation of anthracene ($|\Delta H^{0}| = -15.8 \text{ kcal/mol H}_{2}$), it should be noted that, in the literature, most authors declare that polyaromatic hydrocarbons are hydrogenated faster than monoaromatic, and tricyclic aromatics are hydrogenated faster than bicyclic. This is due to a decrease in the stabilization energies of the anthracene molecule relative to naphthalene as a result of the redistribution of the electron density due to the influence of two unsaturated hydrocarbon cycles on the central cycle. Indeed, it was shown [64] that a high conversion of anthracene to 9,10-dihydroanthracene on a Cu catalyst is achieved at 120–150 °C, which is significantly lower than when naphthalene is hydrogenated on a Pt catalyst. In the case of a modified $Cu-Cr_2O_3$ catalyst, a high yield of 9,10-dihydroanthracene was achieved under even milder conditions (T = 100 °C, P = 95 atm). However, in order to reach complete hydrogenation, which is important for hydrogen storage systems, higher temperatures and pressures are needed for the sequential formation of other reaction products. In particular, for further hydrogenation into 1,2,3,4tetrahydroanthracene, a temperature of 240–260 °C is already required. All intermediate compounds, as well as the final perhydroanthracene, were obtained via hydrogenation on a Ni/kieselguhr catalyst at 180-220 °C and 98 atm [8], but, during a long experiment, the catalyst lost activity and was replaced with a fresh one. The formation of perhydroanthracene with a selectivity above 25% was observed during the hydrogenation of anthracene on a Pd/C catalyst at a temperature of 300 $^{\circ}$ C and a pressure of 30 atm [65]. The formation of perhydroanthracene with a selectivity above 99% was achieved by hydrogenation of anthracene on a 3%Pt/C catalyst at a temperature of 280 °C and a pressure of 90 atm [66,67]. However, it took about 40 h for the complete transformation of anthracene into perhydroanthracene. The substitution of Pt and Pd for Rh, Ru and Ir [68–73], as well as the improvement of the methods of preparation of catalysts and the use of supercritical media, affects the rate of transformation of anthracene intermediates, but not the production of the final perhydroanthracene. Achieving a 100% selectivity of perhydroanthracene is still a difficult task. Moreover, the final perhydroanthracene is a mixture of at least five structural conformers, the quantitative ratio between which depends on the path along which the anthracene hydrogenation reaction takes place, and which, in turn, depends on the reaction conditions used [67,68] (Figure 8):





The main product preceding the formation of perhydroanthracene is the octahydroanthracene isomer with a central unsaturated ring [67,68]. Moreover, the formation of the latter is due to structural differences between 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene. In turn, when 9,10-dihydroanthracene is dehydrogenated on 3%Pt/C, the main products at temperatures of 300–360 °C are anthracene and two steric isomers of octahydroanthracene (1,2,3,4,4aa,9,10,10 a- and 1,2,3,4,4aa,9,9aa,10-). Interestingly, the OGA *sim* isomer was not found among them, which indicates a formal discrepancy between the routes of direct and reverse reactions. In general, the dehydrogenation of the perhydroanthracene conformers is characterized by a relatively rapid conversion of less stable isomers into the target reaction products, as well as into the most stable *trans-syntrans* isomer. Dehydrogenation of the latter occurs at high temperatures (>400 °C), which leads to the formation of cracking and hydrogenolysis products and is unacceptable for hydrogen storage systems.

Unlike condensed hydrocarbons, in linearly linked compounds, neighboring hydrocarbon cycles are connected via a C-C bond, so that each of them has relative autonomy. However, in the case of aromatic hydrocarbons, the tendency to occupy an energetically more advantageous position leads to the fact that, in the most stable conformation, neighboring hydrocarbon cycles turn out to be rotated relative to each other. This leads to steric hindrances with planar adsorption on the metal sites of the catalyst during hydrogenation, not only in comparison with benzene, but also in comparison with the condensed analogue. The simplest analogues of naphthalene- and anthracene-based systems are biphenylbicyclohexyl pairs (7.23 wt. % H₂) and terphenyl–perhydroterphenyl (7.26 wt. % H₂).

The hydrogenation of biphenyl is quite simply carried out on Pt-, Pd- or mixed (Pt-Pd) catalysts. As in the case of naphthalene, the reaction proceeds with the formation of one intermediate product—cyclohexylbenzene (Figure 9):



Figure 9. Biphenyl as liquid organic hydrogen carrier.

It was found [74] that biphenyl is adsorbed on the surface of the catalyst five times stronger than cyclohexylbenzene. Since the effect of biphenyl adsorption is incomparable with the rate of dissociative hydrogen adsorption, the authors used a pseudo-first-order kinetic equation to describe the hydrogenation reaction of biphenyl. In our work [75], we used the first-order equation to compare substrates with different condensation extent to describe the hydrogenation reaction of biphenyl on a 3%Pt/C catalyst (oxidized Sibunite). The calculation showed that the initial hydrogenation rate of biphenyl is lower than that of naphthalene; however, the hydrogenation of intermediate cyclohexylbenzene into bicyclohexyl occurs faster than hydrogenation of tetralin into decalin [58,75]. The difference is apparently due to the low accessibility of nodal carbon atoms of tetralin, which generally reduces the overall hydrogenation rate of naphthalene, compared with the hydrogenation of biphenyl.

Dehydrogenation of bicyclohexyl also takes place most effectively on Pt- and Pdcatalysts and takes place at temperatures above 250 °C [76–78]. In the case of a 3%Pt/C catalyst, the conversion of bicyclohexyl to biphenyl with a selectivity of 97.6% at a temperature of 320 °C reaches 99.9%, which is higher than for decalin under the same conditions. Interestingly, such parameters are achieved despite a less favorable ratio of reaction enthalpies. Thus, the modulus of the negative standard enthalpy change $|\Delta H^0|$ for the biphenyl hydrogenation reaction is -16 kcal/mol H₂ versus -15.1 and 15.6 kcal/mol H₂ when naphthalene is converted into *cis-* and *trans-*decalin, respectively [19]. The probable cause is steric difficulties in the adsorption of decalin isomers on the same metal active centers, compared with bicyclohexyl.

Unlike the bicyclic biphenyl–bicyclohexyl system, both substrates in the tricyclic terphenyl–perhydroterphenyl system have three isomers (*ortho-, meta-* and *para-*), each of which has a different reactivity in both hydrogenation and dehydrogenation reactions. The hydrogenation of *ortho-, meta-* and *para-*isomers of terphenyl proceeds mainly along terminal rings with the formation of partially hydrogenated compounds with one cyclohexane ring ($C_{18}H_{20}$)—diphenyl–cyclohexane (E) and cyclohexyl–biphenyl (C) and with two cyclohexane rings ($C_{18}H_{26}$)—bicyclohexyl–benzene (H) and dicyclohexane–phenylene (D) (Figure 10):



Figure 10. Possible ways of terphenyl hydrogenation.

The initial hydrogenation rate of three terphenyl isomers by 3%Pt/C is inferior to that of anthracene, which is partly due to steric difficulties with planar adsorption on the metal sites of the catalyst. However, a more significant role is played by the deformation of the π -system of the anthracene molecule due to the influence of two terminal unsaturated

hydrocarbon cycles on the central one, which is not present in terphenyl with relatively independent benzene rings [79,80]. It was shown [76,78] that, for benzene, naphthalene, biphenyl and anthracene, there is a correlation between the standard enthalpies of formation and the initial hydrogenation rates with the formation of intermediate reaction products mainly with one saturated ring. For tricyclic isomers of terphenyl, such a correlation is not observed, which is explained by the stronger influence of steric hindrances on the hydrogenation process. At the same time, in the series of *ortho-*, *meta-* and *para-*isomers, the influence of intramolecular interaction on the thermodynamic stability of these compounds and, accordingly, on the initial hydrogenation rate, increases. In the process of saturation with hydrogen, the hydrogenation rates of these aromatic hydrocarbons with the formation of products with two and three saturated hydrocarbon cycles are significantly reduced. However, the greater accessibility of nodal carbon atoms results in a higher overall rate of hydrogenation of terphenyl isomers, compared with the hydrogenation of condensed anthracene.

The reverse reaction of the dehydrogenation of the corresponding isomers of perhydroterphenyl is carried out in the range T = 250–350 °C. The dehydrogenation of ortho-, metaand *para*-isomers of perhydroterphenyls, as well as the hydrogenation of the corresponding terphenyl isomers, mainly proceeds along terminal rings, which may be associated with the formation of π -allyl cycles, as in the dehydrogenation of methylcyclohexane. More routes of the dehydrogenation of perhydroterphenyl isomers lead to an increase in the number of intermediates, which slows down the reaction compared to bicyclohexyl [75–80]. At the same time, during the reaction, all three isomers of perhydroterphenyl are capable of mutual transformations of *cis* conformations into a *trans* form, and the *ortho*-isomers of terphenyl and perhydroterphenyl also have a tendency to mutual isomerization into derivatives of *meta-* and *para-*isomers. During the dehydrogenation of the latter, reactions of intermolecular cyclization of perhydro-ortho-terphenyl into cyclic triphenylene were also observed. However, in general, the behavior of the *cis*- and *trans*-forms of the *ortho-, meta*and *para*-isomers of perhydroterphenyl during dehydrogenation in the temperature range 260–340 °C has more similarities than their condensed analogues of perhydroanthracene or decalin. As a result, isomerization reactions do not have such an effect on the rate of hydrogen release as during the dehydrogenation of condensed compounds.

In the absence of objectively developed criteria for comparing substrates with different condensation [78], a first-order equation was used to describe the dehydrogenation reaction of perhydroterphenyl isomers on a 3%Pt/C catalyst. This is consistent with the literature data: the first order for hydrocarbon substrates was found in the case of cyclohexane and methylcyclohexane dehydrogenation [81–83]. The calculation showed that in the cyclohexane–bicyclohexyl–perhydro-*para*-terphenyl series, there is a linear relationship between the apparent activation energies (E_a) and the pre-exponential factors (A). The parameters for *cis*-decalin, for which the dehydrogenation process proceeds no less efficiently, are also close to the presented correlation dependence. This apparently indicates a similar dehydrogenation mechanism for these compounds. The *meta-* and *ortho*-isomers of perhydroterphenyl deviate from the linear dependence, presumably due to competing processes that affect the process of dehydrogenation of these compounds.

3. Conclusions and Outlooks

In this review, based on the information available in the literature, a number of hydrogen storage and release systems based on the processes of the heterogeneous catalytic hydrogenation of cyclic and polycyclic aromatic hydrocarbons with a hydrogen capacity above 6.5–7.0% by weight and conjugated dehydrogenation of the corresponding naphthenic compounds are analyzed. The main attention is paid for the first time to the identification of differences between the course of reversible processes depending on the structure of substrates. Summarizing the above data from the point of view of the saturation of aromatic hydrocarbons with hydrogen, several qualitative patterns can be distinguished. For condensed systems, an increase in activity in hydrogenation reactions from benzene to anthracene is correlated with a decrease in stabilization energies. In this connection, most authors believe that polyaromatic hydrocarbons are hydrogenated faster than monoaromatic ones, and tricyclic aromatics are hydrogenated faster than bicyclic ones. The benzene ring conversion into a fully saturated six-membered cycle is quite difficult; naphthalene is hydrogenated more easily than benzene, but into tetralin only. Anthracene is easily hydrogenated by bonds 9,10, but then the process is much more difficult. For polycyclic hydrocarbons with 3-4 and a larger number of benzene rings, thermodynamic and steric limitations must be taken into account during high-temperature hydrogenation. At the same time, the key factor for the operation of storage systems based on polycyclic compounds is the development of effective catalysts that facilitate the hydrogenationdehydrogenation processes without the formation of reaction by-products. The addition of a second metal (W, Mo, Re, Rh, Ir, Pd and Sn) to the Pt catalyst in some cases leads to a synergistic effect in the dehydrogenation of a number of cycloalkanes, such as cyclohexane, methylcyclohexane, decalin and tetralin [84]. The increase in conversion and selectivity in the case of two-component Pt-M catalysts (M is the second metal) is due to an increase in the overall activity during the cleavage of the C-H bond, the hydrogen spillover occurring on metal sites via hydrogen dissociation, as well as the hydrogen-recombination abilities of Pt, which together facilitate the removal of hydrogen from the reaction medium and shift the chemical equilibrium of the reaction in favor of the formation of target products.

For linearly linked polycyclic aromatic hydrocarbons, the dependence of activity and stabilization energies is not as explicit as for condensed systems, and the occurrence of reactions and the overall reaction pattern largely depend on steric factors. During the dehydrogenation of polycyclic naphthenes, there is no correlation at all like the correlation with the stabilization energy in the corresponding arenes, whereas the role of the structural factor increases many times. The mechanism of the dehydrogenation of such hydrocarbons is usually described through the adsorption of cycloalkane on metal sites of a catalyst (in particular, Pt) with simultaneous or subsequent rapid dissociation of hydrogen atoms through the formation of a π bond [39], but in each case such a mechanism requires experimental confirmation. Analysis of the literature data shows that this area of research in the aspect of creating hydrogen storage and separation systems based on the reversible hydrogenation–dehydrogenation reactions of organic compounds is practically not considered, which opens up a wide field for research.

This promising area of research will further develop along the way of developing methodological approaches to the creation of a "substrate-catalyst" system that can ensure the implementation of a high-capacity H₂ arene–naphthene pair in multiple saturationrelease cycles. The works aimed at understanding the effect of the substrate structure on the effectiveness of the substrate-catalyst systems are necessary for further tailor-wise tuning of these systems by changing the substrate structure. The development of an effective catalyst for hydrogen saturation-release processes will develop along the alley of increasing the activity and selectivity of heterogeneous catalysts, primarily by reducing the content of noble metals by combination with less critical metals, including base metals. Progress in this direction is impossible without determining the role of electronic and geometric factors and their mutual ability to modify under the influence of the metal-carrier interaction, which can largely determine the catalytic properties of the nanoparticles located on the surface of the carrier, including the creation of hierarchical structures. The challenge in the future research is related to the design of catalysts with extremely high selectivity in both processes of hydrogenation and dehydrogenation with an ultra-low content of noble metals. Obviously, at this stage, it is not possible to replace completely platinum and other expensive metals for nickel and other cheap counterparts, but the inventive approaches to the synthesis of bimetallic nanoparticles will make it possible to reduce the noble metal content below 0.1 wt. %. Another intriguing question is whether or not we could increase the limit of the hydrogen storage capacity exceeding 7.5 wt. %. Also important is the question of the operation with the physical state of the LOHC substance, which ideally should be liquid at temperatures as low as -40 °C for use in Arctic conditions and as

high as +320–340 °C in order to avoid evaporation and losses during the dehydrogenation process. Here, the use of eutectic compositions seems to be promising.

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