

# Hydrogenation/Dehydrogenation Catalysts for Hydrogen Storage Systems Based on Liquid Organic Carriers (A Review)

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**Abstract**—The state of the art in the field of studying catalysts for hydrogenation/dehydrogenation of organic substrates as potential components of modern hydrogen storage systems based on liquid organic hydrogen carriers is analyzed. The ways to reduce the content of noble metals or to replace them partially or fully by cheaper transition metals, prospects for using various supports, and possibilities of enhancing the activity, stability, and selectivity of the catalysts and of regenerating spent catalytic systems are discussed.

**Keywords:** hydrogen storage, hydrogenation, dehydrogenation, catalysts

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The trend of the world economy toward decarbonization and an increase in the stringency of the environmental requirements became prerequisites for the emergence of a new branch, hydrogen power engineering, which is based on the use of hydrogen as a means for accumulation, transportation, and generation of power. Large-tonnage hydrogen production is required for this purpose [1, 2]. This, in turn, will require the development of efficient and safe technologies for storage and transportation of large volumes of hydrogen.

The ways of hydrogen storage differ in the gravimetric and volumetric capacity of the storage medium and in the time of hydrogen accumulation and release. These factors in combination determine the cost of hydrogen transportation and storage [3–6]. The following methods of hydrogen storage are known:

—in the compressed form in steel or composite cylinders (up to 70 MPa, 20–40°C);

—in the liquefied form in cryogenic tanks (0.1 MPa; –252°C);

—in the chemically bound form, liquid ammonia (35–50 MPa; 400–600°C; here and hereinafter, the binding/release conditions are indicated);

—as a constituent of liquid organic compounds acting as hydrogen carriers (0.1–1 MPa; 180–280°C);

—as a constituent of metals and alloys that undergo reversible hydrogenation (metal hydrides, 0.1–0.5 MPa; 100–300°C) [7, 8].

Methods of hydrogen storage in liquid organic hydrogen carriers (LOHCs) are being actively developed. These methods are based on reversible catalytic hydrogenation/dehydrogenation reactions and ensure high gravimetric and volumetric hydrogen storage capacity, moderate technological and investment risks, and low capital investments for the construction of the hydrogen infrastructure [9–11].

The parameters of hydrogen storage using LOHC systems, traditional methods of hydrogen storage and transportation, and methods that are being developed are compared in Table 1.

It follows from Table 1 that the hydrogen storage systems based on LOHCs exhibit high gravimetric capacity and do not require using elevated pressures and low temperatures, which ensures their convenient and simple use, especially in storage and transportation.

Catalysts used in LOHC hydrogen storage systems can significantly influence the service characteristics of these systems, primarily the conditions and rate of hydrogen release.

**Table 1.** Parameters of traditional hydrogen storage methods and methods that are being developed (data of [12])

H <sub>2</sub> storage method	Gravimetric capacity for hydrogen, wt %	Volumetric energy density, MJ L <sup>-1</sup>	Temperature, °C	Pressure, MPa
As compressed gas (in cylinders under pressure)	6.7	4.9	20	70
In liquid form (in cryogenic tanks)	7.5	6.4	-253	0
In partially liquefied form under pressure	5.4	4.0	-233 to -190	30
As a constituent of metal hydrides	7.6	13.2	-13 to -152	2
As a constituent of liquid organic hydrogen carriers (LOHCs)	8.5	7	20	0

This review was aimed at analysis of research and development in the field of catalysts for hydrogenation/dehydrogenation of organic substrates as potential components of hydrogen storage systems based on liquid organic hydrogen carriers.

## HYDROGEN STORAGE SYSTEMS BASED ON LIQUID ORGANIC HYDROGEN CARRIERS AND THEIR ADVANTAGES

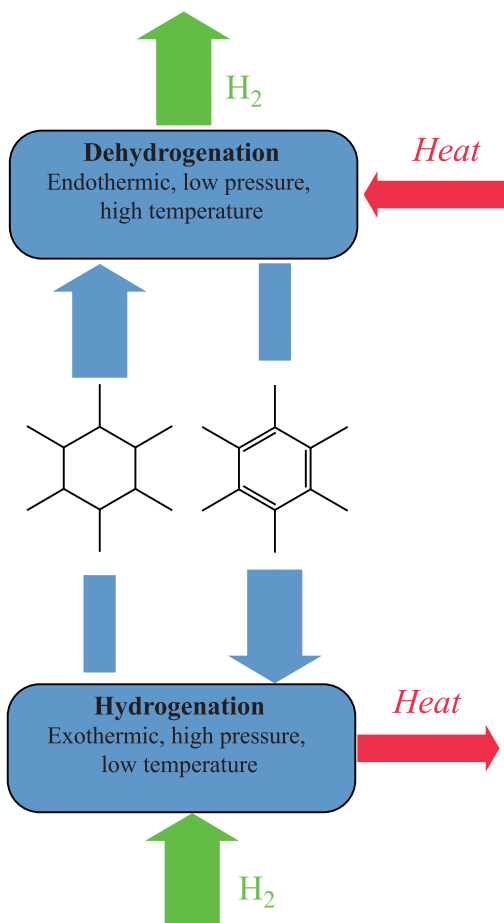
### LOHC Operation Principle

By LOHCs are meant compounds of low molecular mass (which determines their limiting hydrogen content), capable of undergoing reversible catalytic hydrogenation/dehydrogenation reactions [6, 13]. Under normal storage conditions, LOHC systems in the hydrogenated form are liquids. LOHCs contain pairs of hydrogen-rich ( $H_2^+$ ) and hydrogen-deficient ( $H_2^-$ ) molecules; hydrogen in bound by  $H_2^-$  molecules via catalytic hydrogenation (exothermic reaction) and is released from  $H_2^+$  molecules via catalytic dehydrogenation (endothermic reaction) [12]. The advantages of such systems are determined by high levels of the gravimetric and volumetric hydrogen storage capacity [14–17]. The schematic diagram of hydrogen storage in an LOHC system is shown in Fig. 1.

A number of government programs and international projects on hydrogen storage are being implemented in the world. For example, the HySTOC project (Hydrogen Supply and Transportation using Liquid Organic Hydrogen Carriers) of the European Hydrogen Commission (01/01/2018–31/12/2020) is aimed at using a new material of the storage medium (dibenzyltoluene) in LOHC systems, based on the developments of Hydrogenious LOHC Technologies (Germany; the material undergoes trials in a new hydrogen infrastructure created in Finland [18]).

### Compounds Used as LOHCs

Studies concerning the possibility of using liquid organic compounds in systems for hydrogen storage in the chemically bound form, based on reversible hydrogenation/dehydrogenation reactions, were initiated



**Fig. 1.** Schematic diagram of hydrogen storage in a system of liquid organic hydrogen carriers.

in the early 1980s [19]. Various oxygenates, e.g., acetic acid [20, 21], formaldehyde [22, 23], methanol [24, 25], formic acid [26, 27], furfuryl alcohol [28, 29] and many other oxygen-containing compounds were extensively studied as LOHCs.

However, aromatic compounds such as *N*-ethylcarbazole [30], *N*-propylcarbazole [31], 2-methylindole [32], *N*-ethylindole [33], 7-ethylindole [34], etc., exhibiting higher stoichiometric capacity and selectivity in hydrogenation/dehydrogenation, are used as LOHCs most frequently. To reduce the heat consumption for the hydrogen release, efficient LOHC systems based on heterocyclic nitrogen-containing organic compounds, e.g., *N*-heterocycles, have been developed. These compounds exhibit high stoichiometric capacity on the level of 5.3–7.3 wt % and can be activated with various homogeneous and heterogeneous catalysts under relatively mild conditions. The compounds with the gravimetric hydrogen storage capacity exceeding 7 wt % H<sub>2</sub> are considered to be the most promising LOHC systems.

Initially, the system based on the toluene/methylcyclohexane couple was considered to be convenient and promising [35]; then, other couples, e.g., cyclohexane/benzene [36], *N*-heterocycles [37], etc., were studied. On the whole, the choice of organic substrates as H<sub>2</sub> carriers for LOHC systems is usually based on the energy approach. It consists in that, if an unsaturated aromatic form of substrates is characterized by the enthalpy of hydrogenation lower than 15.0 kcal mol<sup>-1</sup> (62.8 kJ mol<sup>-1</sup>), the dehydrogenation temperature of such substrates can be reduced, and this is very important [38]. In such approach to the choice of hydrogen carriers, it is particularly advantageous to use polycyclic and condensed compounds (the values of  $\Delta H$  start to decrease with an increase in the number of aromatic rings in the molecule).

#### *Main Requirements to LOHC-Based Hydrogen Storage Systems*

On the whole, the LOHC systems being developed for commercial use should meet the following requirements [12, 39, 40]:

- they should have low freezing points (<–30°C) and high boiling points (>300°C);
- they should be nontoxic and safe in storage and transportation throughout prolonged service life with the generation of pure hydrogen;

- they should have high volumetric (>56 kg m<sup>-3</sup>) and gravimetric (>6 wt %) hydrogen storage capacities;
- they should be compatible with the existing fuel infrastructure and should be cheap.

#### HYDROGENATION/DEHYDROGENATION CATALYSTS FOR LIQUID ORGANIC HYDROGEN CARRIER TECHNOLOGIES

##### *Active Metals in Catalysts*

One of the main problems in the development of modern commercial LOHC systems is the development of highly active hydrogenation/dehydrogenation catalytic systems combining relatively low cost with high activity, stability, selectivity, and long operation life.

As noted above, chemical binding of hydrogen in LOHCs in the course of hydrogenation (pressure 5–7 MPa, temperature 100–250°C) is exothermic, whereas the hydrogen release in the course of dehydrogenation (low pressures about 0.1 MPa, high temperatures 270–500°C) is endothermic; i.e., the hydrogenation and dehydrogenation conditions differ [41, 42]. Despite the fact that catalysts active in both these reactions are known in principle, the rates and conditions of these reactions differ because of differences in the thermodynamic characteristics of chemical bonds that should be activated, namely, C–H/O–H/N–H and C=O/C=N/H–H bonds. Therefore, interaction of the full-cycle LOHC systems with the catalysts used, rather than the hydrogenation/dehydrogenation catalysts themselves, is of major interest. It is technologically attractive to perform hydrogenation/dehydrogenation in the same vessel with the same catalyst (or catalyst system). It should also be borne in mind that the catalyst performance is tightly associated with the storage medium (liquid organic hydrogen carriers used); therefore, these catalysts are considered, as a rule, as applied to a specific couple of carriers.

On the whole, the catalytic systems used in LOHCs should favor overcoming of thermodynamic barriers and accelerate the dehydration of liquid organic hydrogen carriers at relatively low temperatures. When assessing the feasibility of using such systems, it is necessary to take into account the technical and economic characteristics of the hydrogenation/dehydrogenation catalysts used and their improvement. In particular, the solution of economic problems is the goal of a new project of the European Commission that is being implemented in accordance with Programme Horizon 2020; its aim is reducing the cost of LOHC systems either by improvement of

known catalysts or by the development of a new design of catalytic systems [43]. According to this program, there can be three possible directions of the development of effective LOHC hydrogenation/dehydrogenation catalysts:

- 1) reducing the content of a noble metal (if present) in the catalyst by enhancing the catalyst activity or partially/fully replacing expensive noble metals in the catalysts;
- 2) enhancing the catalyst selectivity;
- 3) improving the catalyst preparation procedure by performing its synthesis as a one-pot process.

Diverse metal-containing catalysts were studied for efficient hydrogenation/dehydrogenation in LOHC systems. Long-term studies have shown that catalysts based on noble metals exhibit the highest performance in LOHC hydrogenation/dehydrogenation. Numerous homogeneous catalysts capable of activation under relatively mild reaction conditions have been developed using platinum group metals (palladium, platinum, rhodium, ruthenium, iridium) [40, 45, 46]. However, heterogeneous catalytic systems based on noble metals on various supports appeared to be more stable in multiple use in large-scale processes [11, 46]. For example, the activity and selectivity of catalysts based on platinum group metals supported on titanium oxide in dehydrogenation of perhydro-*N*-ethylcarbazole at 190°C were studied; with respect to the catalytic activity in hydrogenation, the metals can be ranked in the following order: Pt > Pd > Rh > Au > Ru [47]. In dehydrogenation of the same substances using noble metal catalysts on another support (aluminum oxide), the catalyst activity decreased in a different order: Pd > Pt > Ru > Rh [48].

In some cases, catalysts based on base metals, e.g., nickel [49], manganese [50], iron [51], and Raney Ni [52], can be used in LOHC systems. The activity of dehydrogenation catalysts can be additionally enhanced by introducing promoters such as Mo, Re, Cu, and Mn [53].

#### *Hydrogenation/Dehydrogenation Catalytic Systems Used in LOHC Technologies*

Monometallic (monofunctional) catalysts based on platinum group metals, exhibiting high activity, selectivity, and stability in dehydrogenation of many liquid organic hydrogen carriers, are being developed for LOHC systems [54]. For example, a study of the catalytic dehydrogenation of octahydroindole has shown that Pt atoms in crystallographic plane (111) on the catalytic

surface are energetically favorable for the adsorption of octahydroindole, indoline, and indole and that the dehydrogenation itself occurs with the release of H<sub>2</sub> along different pathways [55]. Specifically the monometallic Pt catalyst appeared to be the best in methylcyclohexane dehydrogenation in a reactor with a fixed catalyst bed; among a series of different platinum catalysts, it showed the highest levels of catalytic activity, selectivity, and stability [56].

Numerous studies deal with the use of bimetallic (bifunctional) catalysts capable of activating both hydrogenation and dehydrogenation, which can significantly simplify the design of LOHC systems. A Ru–Pd/Al<sub>2</sub>O<sub>3</sub> bifunctional catalyst synthesized by simple impregnation has been reported; it exhibits high catalytic activity, stability, and selectivity both in hydrogenation of *N*-propylcarbazole and in dehydrogenation of the corresponding perhydro-*N*-propylcarbazole [57]. A series of bimetallic catalysts based on Pd–Cu nanoparticles supported on reduced graphene oxide rGO and synthesized by the one-pot method were studied; among them, the Pd<sub>1.2</sub>Cu/rGO catalyst showed the highest performance in dehydrogenation of perhydro-*N*-ethylcarbazole [58].

Bimetallic catalysts allow partial replacement of noble metals by their cheaper analogs. For example, a bimetallic catalyst Pd–Ni/Al<sub>2</sub>O<sub>3</sub> (Pd : Ni = 1 : 1; 5 wt %), which surpasses Pd/Al<sub>2</sub>O<sub>3</sub> in activity in perhydro-*N*-propylcarbazole dehydrogenation (volumetric dehydrogenation rate up to 285 h<sup>–1</sup> against 176 h<sup>–1</sup>) and shows high stability in the process, was prepared by wet impregnation [59]. A series of cheap bimetallic catalysts Pd–Me/SiO<sub>2</sub> (where Me = Cu, Ni) for the *N*-ethylcarbazole/dodecahydro-*N*-ethylcarbazole LOHC system were suggested and studied. The Pd<sub>3</sub>–Ni<sub>1</sub>/SiO<sub>2</sub> catalyst showed the highest activity; in its presence, the conversion was 100%, the selectivity with respect to *N*-ethylcarbazole was 91.1%, and the hydrogen storage capacity was 5.63 wt % (190°C, 101.325 kPa, 8 h); the activity (in TOF units, number of turnovers per catalyst active site in unit time) increased by 42.4% compared to the Pd/SiO<sub>2</sub> monometallic catalyst [60].

In dehydrogenation of perhydro-*N*-ethylcarbazole, the activity of Pd/TiO<sub>2</sub> catalysts can be enhanced under the conditions of microwave activation by introducing a second metal as promoter to obtain bimetallic catalysts Pd–Ru/TiO<sub>2</sub> and Pd–Pt/TiO<sub>2</sub> [61]. A study of the *N*-ethylcarbazole hydrogenation in the LOHC system using bimetallic Ru–Ni catalysts supported on different



modifications of  $\text{TiO}_2$  (rutile, anatase) has shown that the crystal structure of  $\text{TiO}_2$  plays an important role in the hydrogenation. Among titanium supports, P25 commercial support consisting of an approximately 1 : 4 mixture of anatase and rutile phases appeared to be the best [62].

A study of the activity of mono- and bimetallic platinum and palladium catalysts in perhydrodibenzyltoluene dehydrogenation in the LOHC system revealed an increase in the degree of dehydrogenation in the presence of the 1 wt %  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst from 40 to 90% with an increase in the temperature from 290 to 320°C [63]. However, an increase in the temperature led not only to an increase in the hydrogen formation rate, but also to a decrease in the hydrogen purity due to formation of by-products. The degree of dehydrogenation at 320°C in the presence of 2 wt %  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst was 96%, whereas in the presence of catalysts based on Pd, 1 wt % Pt, and Pt–Pd it was 11, 82, and 6%, respectively, which coincided with the results of DFT calculations. It has been concluded that Pd is suitable for perhydrodibenzyltoluene dehydrogenation neither in the monometallic nor in the bimetallic system. The perhydrodibenzyltoluene dehydrogenation kinetics corresponded to a first-order reaction, and the activation energy for the 1 wt %  $\text{Pt}/\text{Al}_2\text{O}_3$ , 1 wt %  $\text{Pd}/\text{Al}_2\text{O}_3$ , and 1 : 1 wt % Pt–Pd/ $\text{Al}_2\text{O}_3$  was 205, 84, and 66  $\text{kJ mol}^{-1}$ , respectively.

An efficient one-pot hydrogen storage system based on the  $\text{H}_2$  release in reversible dehydrogenation/hydrogenation of a methanol–1,2-diamine mixture in the presence of the same bifunctional catalyst, the ruthenium complex  $[\text{Ru}\{\text{HN}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\}\text{H}(\text{CO})\text{Cl}]$ , was studied; the theoretically attainable hydrogen storage capacity in this system is 6.6 wt % [64]. Organic complexes of Fe and Ir can also act as catalysts of reversible hydrogenation of alcohols into carbonyl compounds [65].

As reported in [66], catalysts with pincer-type ligands and iron and manganese atoms as coordination centers are effective in hydrogenation/dehydrogenation, and they can be used in reversible reactions of hydrogen uptake/release, which ensures the development of a rechargeable LOHC system [67]. It has been found that the classical  $\text{LaNi}_5$  alloy can ensure reversible binding and release of hydrogen in systems based on *N*-ethylcarbazole with high efficiency and stability (in particular,  $\text{LaNi}_{5+x}$  particles of approximately 100 nm size were used) [68].

## EFFECT OF CATALYST SUPPORT

Numerous studies aimed at determining how the support influences the activity and selectivity of heterogeneous hydrogenation/dehydrogenation catalysts used in LOHC systems have shown that the surface area and nature of acid sites on the support surface, along with the content and particle size of the catalyst active component, significantly influence the catalytic activity and also influence the dispersity of the metal used, metal–support interaction, and ability to adsorb reagents [69, 70].

A special hydrothermal procedure was suggested for preparing a series of  $\gamma\text{-Al}_2\text{O}_3$  supports, which were subsequently impregnated with 1 wt % Pd, for perhydro-*N*-propylcarbazole dehydrogenation. The 100% *N*-propylcarbazole conversion was reached in 360 min at 180°C and 101 kPa, and in this respect the catalyst surpassed the commercial catalyst, 5 wt %  $\text{Pd}/\text{Al}_2\text{O}_3$  [71]. Platinum catalysts on oxide supports ( $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Y}_2\text{O}_3$ ) showed high performance in methylcyclohexane dehydrogenation. Some other supports were also tested, including  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{MnO}_2$ , perovskite, etc.; among them,  $\text{La}_2\text{O}_3$  appeared to be the best [72, 73].

Nanosized  $\text{Pt}/\text{Al}_2\text{O}_3$  и  $\text{Pt}/\text{CeO}_2$  catalysts were synthesized to enhance the catalytic activity in perhydrodibenzyltoluene dehydrogenation in the LOHC system; the  $\text{Pt}/\text{CeO}_2$  catalyst showed considerably higher dehydrogenation rates (80.5% in 2.5 h) compared to the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst (3.5% in 2.5 h), which is due to poor mass transfer in fine pores of the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst [74]. A study of the effect exerted by a support on the dehydrogenation of a eutectic mixture based on biphenyl (35 wt % perhydrobiphenyl, 65 wt % perhydrodiphenylmethane) in the presence of a series of platinum catalysts on  $\text{Al}_2\text{O}_3$  support under various conditions has shown that the pore size distribution and the corresponding surface properties of supports affect the dehydrogenation characteristics [75].

A novel dual-action palladium catalyst on a  $\text{YH}_3$ -promoted  $\text{Al}_2\text{O}_3$  support,  $\text{Pd}/\text{Al}_2\text{O}_3\text{--YH}_3$ , was developed for accelerating the hydrogen adsorption and desorption in LOHC systems based on *N*-ethylcarbazole. It ensures reversible hydrogen storage on the level of 5.5 wt %. The hydrogenation and dehydrogenation are performed at temperatures lower than 200°C within no more than 4 h. Among the existing catalysts of both adsorption and desorption of hydrogen, these parameters are the best [76]. Wang et al. [77] prepared a palladium catalyst on a reduced graphene oxide (rGO) support; it showed

increased activity in dehydrogenation of perhydro-*N*-ethylcarbazole. In the presence of this support, the catalyst activity increased by a factor of 14.4 compared to the commercial dehydrogenation catalyst, Pd/Al<sub>2</sub>O<sub>3</sub>; furthermore, the noble metal content of Pd/rGO was 2 times lower compared to Pd/Al<sub>2</sub>O<sub>3</sub>.

Highly dispersed Pd nanoparticles immobilized in a known organometallic support MIL-101 (Cr) were prepared and tested in catalytic dehydrogenation of perhydro-*N*-propylcarbazole. This support had relatively stable structure, high specific surface area (1500–2000 m<sup>2</sup> g<sup>-1</sup>), large pore volume (1.6 cm<sup>3</sup> g<sup>-1</sup>), and the pore size of 2.9–3.4 nm; however, the mechanical strength of the support was not reported. The catalyst obtained, Pd@MIL-101, surpassed in characteristics the known commercial catalyst, 5 wt % Pd/Al<sub>2</sub>O<sub>3</sub> [70].

A comparative analysis of the catalytic activity of various heterogeneous metal catalysts in dehydrogenation of an LOHC system based on perhydrodibenzyltoluene/dibenzyltoluene couple has shown that the Pt/TiO<sub>2</sub> catalyst is the most promising [78].

The surface of Al<sub>2</sub>O<sub>3</sub> support was modified by traditional plasma treatment to generate hydroxyl groups and oxygen vacancies. The modified support was used for preparing various Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, which were tested in reversible hydrogenation/dehydrogenation of dibenzyltoluene [79]. It has been shown that the hydroxyl groups and oxygen vacancies on the Al<sub>2</sub>O<sub>3</sub> surface can improve the platinum dispersity; furthermore, hydroxyl groups can also participate in the hydrogen transfer, enhancing the hydrogenating and dehydrogenating activity of the catalyst, reducing the contribution of side reaction, and prolonging the catalyst life cycle.

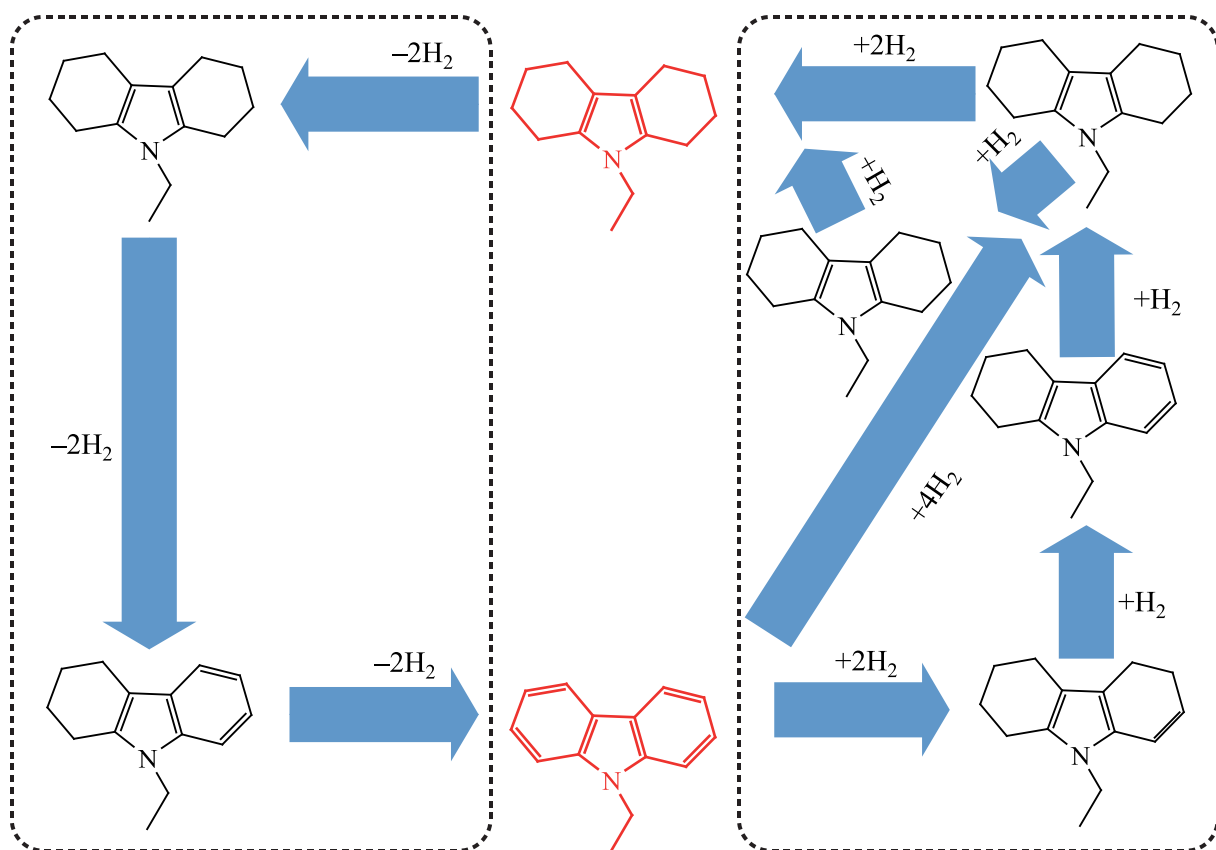
Catalysts based on two noble metals, Pt and Pd, on SiO<sub>2</sub> and modified carbon supports (e.g., on Sibunit porous carbon material prepared from commercial grades of carbon black), owing to easy diffusion of organic molecules into small catalyst particles, can accelerate the terphenyl hydrogenation and perhydroterphenyl dehydrogenation without side reactions of cracking, hydrogenolysis, ring opening, and coking. The Pt/Sibunit-ox catalyst on an oxidized Sibunit support appeared to be the most promising. The use of Sibunit as a catalyst support (catalyst: 3% Pt/Sibunit) in hydrogenation of polyaromatic compounds with various degrees of condensation (benzene, biphenyl, terphenyl), followed by dehydrogenation of the alicyclic products (cyclohexane, bicyclohexyl, perhydroterphenyl), was also reported; the

reactions are performed at 260–340°C and liquid flow velocity of 1 h<sup>-1</sup> [80]. Dehydrogenation of bicyclohexyl on heterogeneous Pt/Sibunit catalysts on neutral and partially oxidized supports at 320°C and space velocities of up to 1.5 h<sup>-1</sup> was studied. Oxidized Sibunit surpassed the neutral support from the viewpoint of possible catalyst reuse, conversion, and selectivity [81]. Such catalysts are less active than those on supports with a highly developed surface but have an important technological advantage, abrasion resistance of the support, which prolongs the catalyst life cycle.

The catalysts supported on titanium and lanthanum oxides exhibit higher activity in dehydrogenation than those on Al<sub>2</sub>O<sub>3</sub> support do. For example, trials of platinum catalysts on a support of TiO<sub>2</sub> of various modifications (rutile–anatase and anatase) in dehydrogenation of perhydrogenated dibenzyltoluene at 290°C have shown that the Pt/TiO<sub>2ra</sub> catalyst on the rutile–anatase support is more active than the Pt/TiO<sub>2ana</sub> catalyst on the anatase support and the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst on the traditional aluminum oxide support and is almost equal in activity to the Pt/C catalyst on activated carbon [82].

Martynenko et al. [83] synthesized platinum catalysts with different platinum particle size, supported both on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> and on mesostructured silicates SBA-15 and MCM-48 with a regular honeycomb framework and specific surface area of 800–850 and 1100 m<sup>2</sup> g<sup>-1</sup>, respectively. The kind of the supports used significantly influences the formation of active phases on the catalyst surface; for example, the catalyst activity in decalin dehydrogenation decreased in the order Pt/MCM-48 > Pt/SBA-15 > Pt/SiO<sub>2</sub> > Pt/Al<sub>2</sub>O<sub>3</sub>. The amount of hydrogen released from decalin in the presence of the Pt/MCM-48 platinum catalyst on the silicate support was 5.7 wt %; thus, this catalyst shows promise for use in LOHC technologies.

Recent studies of perhydro-*N*-ethylcarbazole dehydrogenation in the presence of Pt/TiO<sub>2</sub> catalysts demonstrate the occurrence of strong electronic interaction between Pt and TiO<sub>2</sub> support, favoring the formation of active sites owing to agglomeration of Pt nanoparticles deposited on the TiO<sub>2</sub> surface heterogeneously. For example, Pt/TiO<sub>2</sub> catalysts with the platinum content varying from 0.5 to 5 wt % were prepared in the course of studying hydrogen storage in an *N*-ethylcarbazole/perhydro-*N*-ethylcarbazole LOHC system. The Pt/TiO<sub>2</sub> catalyst containing 1.0 wt % Pt showed the highest catalytic activity in perhydro-*N*-ethylcarbazole dehydrogenation;



**Fig. 2.** Scheme of hydrogenation (to the right) and dehydrogenation (to the left) reactions in the *N*-ethylcarbazole/perhydro-*N*-ethylcarbazole LOHC system, according to [84].

in its presence, 5.75 wt % hydrogen was released at 190°C [84]. A mechanism in which the dehydrogenation is a structure-sensitive reaction occurring owing to strong interactions between Pt and  $\text{TiO}_2$  support, which accelerate the limiting step and the dehydrogenation process as a whole, was suggested. The hydrogenation (to the right) and dehydrogenation (to the left) reactions in the *N*-ethylcarbazole/perhydro-*N*-ethylcarbazole LOHC system are schematically shown in Fig. 2.

When studying the *N*-ethylcarbazole hydrogenation in the presence of heterogeneous catalysts based on Pd and Ru on mesoporous  $\text{MoO}_3$  support, Fei et al. also noted their higher activity compared to the catalysts on the traditional  $\text{Al}_2\text{O}_3$  support [85]. As they found, the hydrogenation mechanism as a whole in the presence of catalysts on such support essentially differs from that in the presence of traditional hydrogenation catalysts based on noble metals on other oxide supports. Even

a small amount of Pd in the  $\text{MoO}_3$ -supported catalysts considerably accelerates the cleavage of H–H bonds, accelerating the hydrogen atom generation rate and increasing the hydrogen amount in  $\text{H}_x\text{MoO}_3$ , which improves the performance of such catalysts. An increase in temperature also favors an increase in the hydrogen concentration in  $\text{H}_x\text{MoO}_3$ .

Feng et al. [86] studied the catalytic dehydrogenation of perhydro-*N*-ethylcarbazole in the presence of heterogeneous catalysts based on Pd nanoparticles on various supports: Pd/C, Pd/ $\text{Al}_2\text{O}_3$ , Pd/ $\text{TiO}_2$ , and Pd/ $\text{SiO}_2$ . The catalyst activity as a function of the Pd particle size passes through a maximum, and the catalytic activity increases with an increase in the specific surface area. Among the catalysts studied, the Pd/C catalyst showed the highest performance in perhydro-*N*-ethylcarbazole dehydrogenation; it ensured 99.9% conversion and release of 5.69 wt % hydrogen at 180°C.

MODIFICATION OF THE EXISTING CATALYSTS  
FOR LOHC TECHNOLOGIES

Attempts to modify the existing hydrogenation/dehydrogenation catalysts are also being made. For example, a procedure for preparing Pt/Al<sub>2</sub>O<sub>3</sub> catalysts using a sulfur-containing compound was improved. It consists in sulfur adsorption on active sites of the platinum catalyst that are responsible for the occurrence of side reactions. Blocking of these sites enhanced the catalyst activity and selectivity [87]. The efficiency of LOHC systems is always a compromise between the hydrogen storage capacity and operation stability in repeated charging/discharging cycles. For example, Modisha and Bessarabov [88] studied deep (up to 98%) hydrogenation of dibenzyltoluene in the presence of a commercial nickel catalyst with the Ni content on the level of 50 wt % at a relatively low pressure, 1.5 MPa (instead of frequently used 3–5 MPa); the perhydrodibenzyltoluene dehydrogenation was performed in the presence of the 1 wt % Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The study was aimed at determining the number of cycles in which the LOHC molecule remains tolerant to the amount of by-products formed in each hydrogenation/dehydrogenation cycle. Trials under stress conditions were performed to determine the decomposition time of LOHC molecules. In particular, the methane formation in the gas phase increased in the order benzene < C21 < xylene < C13–C15 < toluene < dibenzyltoluene. These experiments demonstrated the stability of LOHC systems based on dibenzyltoluene (the amount of by-products formed under stress conditions was as low as 7 mol %).

Ouma et al. [89] studied the structural modification of the catalytic surface of platinum and palladium to minimize the energy of the first step of perhydrodibenzyltoluene dehydrogenation in the LOHC system. The energies of adsorption of perhydrodibenzyltoluene on Pt and Pd atoms in crystallographic plane (110) on the catalytic surface were calculated for the cases with the removal of H atoms on the Pt (110) and Pd (110) surfaces and without it. In both cases, the perhydrodibenzyltoluene adsorption with the removal of H atoms and without it is energetically feasible. The calculated activation energies show that the catalytic activity in the dehydrogenation is higher when Pt, and not Pd, forms the upper layer of the catalytic surface, and the surfaces with the Pt–Pd–Pd and Pt–Pd–Pt configurations show the same catalytic activity as the unmodified Pt surface does.

## REGENERATION OF DEACTIVATED CATALYSTS

## OF LOHC SYSTEMS

One of the most serious problems in implementation of LOHC technologies, especially on the large scale, is the loss of the activity of the dehydrogenation catalysts used in the course of prolonged operation. Therefore, numerous studies deal with the deactivation of catalysts and with the regeneration procedures. Heterogeneous catalysts often rapidly lose the activity because of coke formation and deposition on their surface. A three-step process is commonly used in this case for restoring the catalytic activity: coke burn-out → oxychlorination → sulfurization; as a result, coke deposits are gradually removed from the active sites of the catalyst [90]. One of the methods suggested for restoring the catalytic activity of heterogeneous dehydrogenation catalysts is low-temperature catalyst regeneration by treatment with ozone in supercritical carbon dioxide [91].

The catalyst deactivation can be caused not only by the coke formation and deposition, but also by poisoning with undesirable compounds adsorbed on catalyst active sites, by sintering of catalyst active particles, and by washout of the active metal from the support. For example, a special microstructured membrane reactor was suggested for inhibiting the deactivation of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst intended for methylcyclohexane dehydrogenation in an LOHC system [92]. As has been shown, the coke formation and the dehydrogenation catalyst deactivation can be considerably decelerated by additionally feeding hydrogen and by making high pressure in the reactor. The deactivated catalyst can be regenerated by oxidation in air at high temperatures (approximately 400°C); nevertheless, the catalyst activity decreases considerably faster with an increase in the number of regeneration cycles.

Regeneration of spent LOHC catalysts (model and real platinum catalysts) was also studied, and a microscopic mechanism of the removal of decomposition products from the active surface of catalysts of various compositions was suggested [93]. The Pt/Al<sub>2</sub>O<sub>3</sub> catalysts can be regenerated by oxidation under mild conditions (about 600 K) in the dehydrogenation vessel itself (the degree and temperature conditions of the regeneration depend on the catalyst morphology).

It should also be noted that hydrogenation/dehydrogenation catalysts for LOHC systems can be used for performing the processes in standard reactors. However,



in some cases, to reach higher levels of the activity and stability, especially in large-scale processes, it is necessary to develop novel designs of reaction vessels in which the catalysts will operate more efficiently.

### CONCLUSIONS

The hydrogen storage in the medium of liquid organic hydrogen carriers (LOHCs), based on reversible catalytic hydrogenation/dehydrogenation reactions, can ensure high gravimetric and volumetric hydrogen storage density, low technological and investment risks, and low capital investments. Nevertheless, such concept of hydrogen storage has not yet been commercially implemented (especially on a large scale) because of a number of technical limitations, including those associated with insufficient stability of dehydrogenation catalysts [13, 94].

For successful commercialization of hydrogen storage technologies using LOHCs, it is necessary to develop active, selective, and stable high-performance hydrogenation/dehydrogenation catalysts with long life cycle, decreasing the thermodynamic and ensuring high dehydrogenation rates at relatively low temperatures. Recent studies demonstrated the possibility of complete or partial replacement of expensive catalysts based on noble metals by cheaper analogs. Other approaches to improvement of such catalytic systems were also developed. Various types of supports for hydrogenation/dehydrogenation catalysts, including novel supports with a highly developed surface (e.g., based on organometallic frameworks), were studied. At the same time, studies aimed at the development of catalysts based on traditional supports are also being continued. Such catalysts exhibit lower activity than catalysts on supports with highly developed surface do, but have an important technological advantage: abrasion resistance of the support, which increases the catalyst operation life.

### AUTHOR INFORMATION

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### CONFLICT OF INTEREST

I.V. Sedov is the Deputy Editor-in-Chief of *Neftekhimiya/Petroleum Chemistry Journal*. I.A. Makaryan declares no conflict of interest requiring disclosure in this article.

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