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HETEROGENEOUS-CATALYTIC REACTION OF HYDROGENATION-DEHYDROGENATION OF AROMATIC COMPOUNDS AS THE BASIS OF ACCUMULATION, STORAGE, AND PRODUCTION OF CHEMICALLY PURE HYDROGEN

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Abstract. The quality of hydrogen released from naphthenic substrates (bicyclohexyl, *ortho*-, *meta*-, and *para*-isomers of perhydroterphenyl) as a result of catalytic dehydrogenation over 3% Pt/C (sibunite) is studied as a key criterion for the high degree of regeneration and recyclization of hydrogen storage systems. It is shown that chemically pure hydrogen without impurities of methane and carbon oxides can be obtained by the dehydrogenation of liquid organic hydrogen carriers (LOHC) if the initial aromatic hydrocarbons and the naphthenic substrates obtained from them were previously thoroughly thermally treated before the hydrogenation and dehydrogenation reactions, respectively, in an inert gas.

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Currently, the principal trend of global environmental policy aimed at radically reducing CO_2 emissions is the transition of the current carbon energy to a new economy based on renewable energy sources. In pursuit of this concept, industrialized countries have set themselves the goal of reducing greenhouse gas emissions to almost zero by the second half of this century [1]. In order to achieve such an ambitious goal, it has been planned to replace, in the next few years, a large part of the energy derived from hydrocarbon raw materials with the energy of solar and wind power plants, which should produce 50% of all electricity by 2030 and 80% by 2050 [2]. Additional generation should be provided by hydro- and geothermal energy sources, as well as biomass treatment. At the same time, obviously, it is not sufficient to simply replace fossil fuels in electricity generation to solve the problem of "decarbonization" of the entire energy sector as renewable sources are unstable in terms of energy supply due to seasonal weather fluctuations. This problem is expected to be solved if the electricity produced during off-peak periods is directed to the production of hydrogen, which is then used as an environmentally friendly energy carrier [3–5].

Today, the world's large-scale production of hydrogen and hydrogen-containing products is carried out mainly using fossil fuels such as coal and methane. When fuel interacts with water vapor or air, synthesis gas is formed, viz. mixture of CO and H_2. Another source is wood, petroleum products, industrial combustible gases, as well as agricultural waste, from which biogas is obtained, and then synthesis gas. The hydrogen yield is increased due to the additional "shift reaction" of CO with water at reduced temperatures in the presence of catalysts. The reaction converts carbon monoxide and water to carbon dioxide and hydrogen, which are then separated in an absorber. With the methane conversion method used in single-stage separation, one can achieve a hydrogen concentration of 94.2% [6]. The hydrogen content in steam gasification of coal is also about 94% in single-stage separation of CO_2 and H_2 [7]. Thermal decomposition of methane at 1350°C ($CH_4 = 2H_2 + C$) allows to increase hydrogen content in pyrolysis products up to 98%, the rest is methane (~ 1%) and other gases present in the natural gas [8]. Everywhere, the products of the reaction are carbon dioxide, hydrogen, and carbon monoxide, which, on the one hand, does not comply with the concept of a complete absence of a "carbon footprint". On the other hand, for a number of applications, high requirements are imposed on the hydrogen quality. For instance, automotive fuel cells, according to ISO 14687-2, allow for hydrogen with a purity of 99.97% (vol.). The maximum permissible amount of pollutants should not exceed: < 2 ppm (hydrocarbons C1 and CO_2), < 0.2 ppm (CO), and < 0.004 ppm (S) [9].

Hydrogen with purity of 99.5% without presence of said accompanying gases can be obtained by electrolysis of water, i.e., its decomposition under the influence of the electric current coming from various energy sources [10]. However, this technology is less saving than conversion methods. Thus, the estimated cost of hydrogen produced by water electrolysis (taking into account the full load of the electrolyzer) is ~3 euros/kg H_2 [11] versus ~1.20 euros/kg H_2 for the methane conversion process [1]. In addition, "modern" logistics and hydrogen storage are mainly realized through the use of compressed gas or cryogenic liquid, which is explosive and expensive [12].

A fundamentally different approach to hydrogen storage and transportation is implemented in chemical systems in which hydrogen is naturally included in the structure of substrates in a chemically bound state [13–16]. In chemical compounds, the content and density of stored hydrogen (0.07 kg/l and higher) are determined by the nature (structure) of the substance and do not depend on external factors (P, T). Unfortunately, the recovery of hydrogen from compounds such as ammonia, methanol, organoboron compounds or water, which have a high hydrogen capacity, is practically irreversible. Among the regenerated systems with a hydrogen capacity above 7% wt% [15], LOHC (liquid organic hydrogen carrier) systems, which are a pair of compounds in a liquid or semi-solid state capable of reversible hydrogenation (an aromatic or heterocyclic substrate) and dehydrogenation (a naphthenic compound saturated with hydrogen), are of greatest interest. High cyclicity of hydrogenation-dehydrogenation reactions and purity of released hydrogen should be ensured by highly selective catalysts, which facilitate both reactions without formation of by-products and CO_x gases [13, 14]. The purpose of this work is to study the possibility of producing chemically pure hydrogen by dehydrogenation of bi- and tricyclic naphthenes (bicyclohexyl, *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl) in a flow-type catalytic setup.

The results presented in this work include a study of the quality (purity) of hydrogen released during dehydrogenation of bi- and tricyclic naphthenic compounds (bicyclohexyl, *ortho*-, *meta*-, and *para*-isomers of perihydroterphenyl) obtained by hydrogenation of conjugated aromatic compounds (biphenyl, *ortho*-, *meta*- and *para*-isomers of terphenyl) as a determining criterion for high cyclic work of hydrogen storage systems based on hydrogenation-dehydrogenation reactions. The data obtained prove the promise of using LOHC (liquid organic hydrogen carriers) as accumulation, storage, and release systems for chemically pure hydrogen designed to create "carbon-free" energy.

EXPERIMENTAL PART

Biphenyl, 99% (Acros Organics), as well as a mixture of Santowax-R terphenyl isomers (11.03 wt% o-$C_{18}H_{14}$, 59.22 wt% m-$C_{18}H_{14}$, and 29.75 wt% p-$C_{18}H_{14}$) were used for dehydrogenation. Hydrogenation was carried out in a PARR-5500 (USA) high pressure autoclave with an internal volume of 600 ml at 180°C and 70 atm with the reaction mass stirred at 600 rpm. The completeness of the reaction was determined by chromatography. As the hydrogenation and dehydrogenation catalyst, a prepared catalyst of 3 wt% Pt/C (sibunite, Omsk, Russia, $\rho = 0.62$ g/cm^3) was used. Platinum was dispersed on the surface of the carbon support by impregnating the support with an aqueous solution of $[H_2PtCl_6]$ ($\omega_{Pt} = 36.3\%$) according to the procedure in [17]. The substrate/catalyst volume ratio was 10/1 (V_{sub}/V_{cat}, cm^3).

The dehydrogenation reaction of the resulting naphthenic substrates was carried out in the original flow catalytic unit. The temperature was monitored by external (master) and internal (control) thermocouples. A 6 cm^3 batch of catalysts was taken for the reaction, placed at the center of a steel reactor, and the HPP 5001 high pressure pump fed substrates at a linear feed rate of 6 ml/h. Hydrogen and reaction products were separated by a system of cooling elements and membranes [18]. Prior to the reaction, fresh catalyst was reduced in the reactor at 320°C in a stream of hydrogen (30 ml/min) for 2 hours.

The products obtained after 4 hours of reaction were analyzed on a Kristaluks-4000M chromatograph (Russia) using a ZB-5 capillary column (Zebron, USA) and on a flame ionization detector of a FOCUS DSQ II chromatographic mass spectrometer (Thermo Fisher Scientific, USA) with capillary column TR-5ms. The analysis was carried out in a programmable 70–220°C temperature mode at a heating rate of 6°C/min. The purity of the released hydrogen was determined by gas chromatography with thermal conductivity detection on a Porapak Q bulk column.

DISCUSSION OF RESULTS

Obviously, the hydrogen storage stage of materials or hydrogen storage devices is important for the mass application of renewable energy. At the same time, in the concept of using LOHC as hydrogen accumulation, storage, transport, and recovery method, the key goal for the aromatic hydrogenation reaction is purity and rate of release of hydrogen released from the

Table 1. Parameters of dehydrogenation of naphthenic compounds on the catalyst 3% Pt/C (T = 320°C, P = 1 atm, V_L = 1 h^{-1})

Naphthenic substrate	X, %	S, %	k_d, h^{-1} [20]
Bicyclohexyl	99.9	99	4.605
Perhydro-*ortho*-terphenyl			
Cis-isomer	84	41	1.172
Trans-isomer	81	41	1.666
Perhydro-*meta*-terphenyl			
Cis-isomer	97	97	3.507
Trans-isomer	96	97	3.219
Perhydro-*para*-terphenyl			
Cis-isomer	95	92	2.733
Trans-isomer	94	90	3.000

Designations. X is the conversion, S is the selectivity, and k_d is the rate constant.

naphthenic hydrocarbons produced at the first stage. Table 1 shows the conversion and selectivity data obtained by dehydrogenating the tested naphthenic substrates on a 3% Pt/C catalyst. Experiments were carried out in the temperature range 260 to 340°C at atmospheric pressure and a substrate space velocity of 1 h^{-1}. However, for comparison, we took data obtained at a temperature of 320°C at which close to maximum conversion was achieved without formation of reaction by-products. After reaching this temperature, cracking or hydrogenolysis products were observed for some substrates, which contaminate the released hydrogen and reduce the potential number of hydrogenation-dehydrogenation cycles. Naphthenic substrates for the dehydrogenation reaction were prepared by prehydrogenating the respective commercial aromatic compounds in an autoclave-type reactor. For comparative studies, we took samples with a base product content of at least 99.5% for the dehydrogenation reaction. At the same time, in order to avoid the presence of even trace amounts of oxygen-containing organic compounds in the target products of the hydrogenation reaction, which produce undesirable gases CH_4, CO_2 and, especially, CO poisoning the catalysts on noble metals, special attention was paid to the preparation of initial aromatic compounds, as well as the catalyst.

One knows that in addition to the contact of hot LOHC with air, other potential sources of oxygen contributing to the formation of oxygen-containing organic compounds may be (a) water in the original aromatic hydrocarbons, (b) water present in pores of the catalyst support, and (c) oxygen of the catalyst support. To eliminate water, the substrate and catalyst were carefully prepared and calcined in a stream of nitrogen until the decomposition products such as nitrogen oxides, carbon dioxide, carbon monoxide, and water vapors were completely removed. The system is filled with nitrogen, and a certain heating mode is applied, which eliminates drastic heating such that water boils and washes platinum from the surface of the support. Upon reaching T = 150°C, heating to the operating temperature was carried out in a hydrogen flow at a rate of 40–50 ml/min. The temperature is then fixed, and the catalyst is activated for 2 hours in a hydrogen flow. Then, the hydrogen supply is stopped, and the substrate prepared in a similar manner (without activation) is supplied.

As a direct consequence of the effectiveness of the measures taken, all hydrogenated substrates were free of even trace amounts of oxygen-containing organic compounds in the samples of all hydrogenated substrates. A relatively neutral carbon support sibunite was taken as a carrier, which showed both high efficiency in the studied hydrogenation-dehydrogenation reactions and avoided the formation of cracking products [15]. For all substrates, only minor amounts of unreacted starting substrates, as well as their partially hydrogenated forms, were found as impurities in the main product of the hydrogenation reaction. Note that due to structural differences in molecules, the conversion index of 99.5% for each of the hydrogenated compounds is achieved at different rates [19, 20]. Thus, while less than 1 hour was required for the bicyclic biphenyl molecule to achieve this conversion on the 3% Pt/C catalyst, it took from 5 hours for the *para*-isomer, up to 6 hours for the *meta*-isomer, and 8 hours for the *ortho*-isomer in the case of terphenyl isomers. However, taking into account the purpose of the studies, the total hydrodynamic residence time of aromatic hydrocarbons in the autoclave was not taken into account in this study.

A distinctive feature of biphenyl hydrogenation is the absence of steric isomers in the target product, viz. bicyclohexyl, while *ortho*-, *meta*-, and *para*-perhydroterphenyl — the final products of *ortho*-, *meta*-, and *para*-terphenyl hydrogenation — have *cis* and *trans* isomers. The dehydrogenation kinetics of bicyclohexyl and *cis*- and *trans*-forms of perihydro-*para*-terphenyl was found to be sufficiently well described by a simple rate expression assuming the first order with respect to the concentration of the starting substrates: $k_d = (1/t) \times \ln(C_o/C)$, where k_d is the rate constant, C_o is the substrate concentration at $t = 0$, and C is the current substrate concentration [20]. For other substrates, the probability of describing the reaction according to the second order equation ($k_d = (1/t) \times [(C_o–C)/(C_o–C)]$)

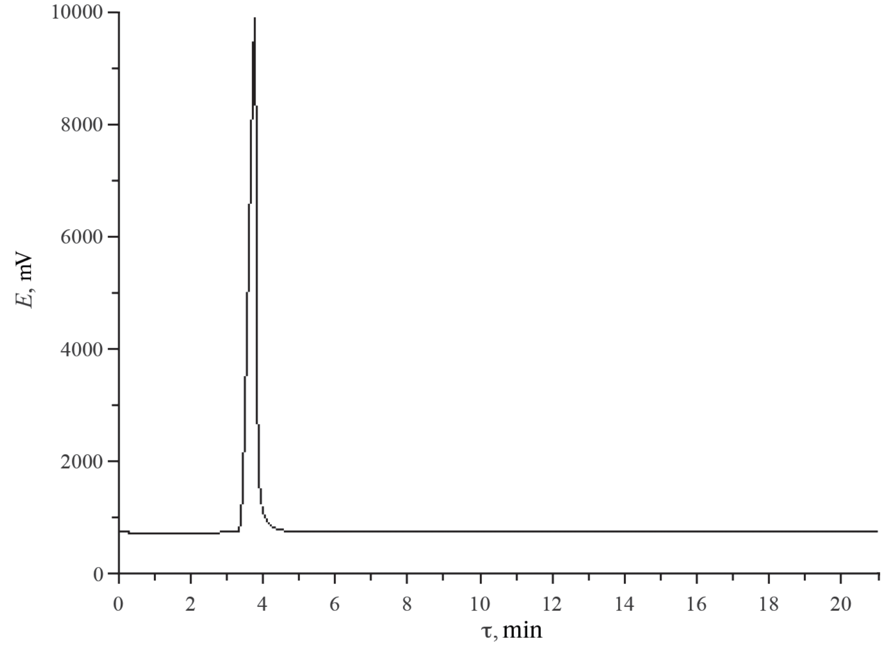

Fig. 1. Chromatogram of gaseous products of the dehydrogenation reaction.

is markedly increased, which may indicate an increasing role of the influence of competitive factors on the dehydrogenation reaction, especially for *cis* and *trans* isomers of perhydro-*ortho*-terphenyl. In particular, reactions of mutual isomerization of *ortho*-isomer to *meta*- and *para*-isomers and cyclization of perhydro-*ortho*-terphenyl to cyclic triphenylene were observed [21].

At the same time, analysis of gas samples of dehydrogenation reaction products of all studied substrates showed the presence of only pure hydrogen in the sample without impurities of light hydrocarbons and carbon oxides (Fig. 1). It is possible to confidently separate hydrogen and air components using packed columns filled with molecular sieves using Ar as the carrier gas. In this work, CaA molecular sieves were used. Table 2 summarizes the release times of the gaseous components that can be determined using this column.

However, note that carbon monoxide is not necessarily the final product because it can react with hydrogen released during dehydrogenation to form methane. On the other hand, the carbon carrier sibunite is also not neutral to the action of hydrogen and exhibits its ability to undergo the hydrogenation reaction ($C + 2H_2 = CH_4$), which is due to dissociative activation of hydrogen [22]. According to the data of the method of thermo-programmable reduction in the hydrogen [23], the maximum on the TPR profile corresponding to the sibunite methanation process corresponds to a temperature of 680°C. When platinum is applied to sibunite, the maximum peak on the TPR of the catalyst 3% Pt/C is strongly shifted towards low temperatures ($T = 510°C$). This is apparently caused by the catalytic effect of metal [24], which on X-ray photoelectron spectra is expressed in forming a large number of highly dispersed electron-deficient particles of metal platinum $Pt^{\delta+}$ stabilized by strong interaction with the functionalized surface of sibunite [25]. The process of electron transfer from platinum particles to the support's carbon seems to block the sibunite methanation reaction, which explains the absence of methane in the gas samples we studied.

Thus, the results obtained in this work confirm the high prospect of using LOHC for accumulation, storage, transportation, and release of chemically pure hydrogen. The obtained data provide useful information on the quality of hydrogen released from the naphthenic substrates involved by catalytic dehydrogenation. The starting substrates do not contain sulfur, but the possible presence of impurities of water and oxygen-containing organic compounds may act as precursors for the formation of CH_4, CO_2, and especially CO, a deactivating agent for noble metal catalysts. To eliminate these undesirable processes, the starting compounds and catalyst were thoroughly prepared prior to hydrogenation and dehydrogenation experiments. This yielded a high quality of chemically pure hydrogen released from naphthenic substrates without catalytic poisons, which is a decisive condition for maintaining a high cyclicity of heterogeneous catalytic hydrogenation-dehydrogenation reactions of aromatic compounds

Table 2. Values of retention time of analyzed gases on CaA

Analysis conditions	T_r, min					
	He	H_2	O_2	N_2	CH_4	CO
60°C	3.1	3.7	6.5	9.0	17.2	20.2

without loss of hydrogen capacity. At the same time, one can say that if the system may have impurities of undesirable gases, it is due to insufficient purity of the technical hydrogen supplied for hydrogenation, as well as the purity of the substrates used as LOHC. The conducted study is an important contribution to the trend of using renewable energy sources without CO_x gas emissions.

In this work, we proposed a heterogeneous catalytic hydrogenation-dehydrogenation reaction of aromatic compounds as a promising method of accumulating, storing, transporting, and producing chemically bound hydrogen. We studied the quality of hydrogen released from naphthenic substrates (bicyclohexyl, *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl) as a result of catalytic dehydrogenation as a key factor in the high regenerability and recycling of hydrogen storage and recovery systems. We showed that chemically pure hydrogen without methane and carbon oxides impurities can be obtained by dehydrogenation of organic hydrogen carriers (LOHC) if a thorough thermal treatment in an inert gas atmosphere was previously carried out on the starting aromatic hydrocarbons and naphthenic substrates obtained out of them before the hydrogenation and dehydrogenation reactions, respectively.

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