

Effective Catalytic Method of Diamantane Isomer Synthesis

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Abstract

General principles of effect of the nature of metal-catalyst, carrier, solvent, method of preparation and temperature of catalyst reduction and other parameters (P_{H_2} , T, etc) on the process of hydrogenolysis of "binor-S" into pentacyclotetradecane have been studied and stated. On the basis of the results obtained a new effective and economical method of diamantane isomer synthesis has been elaborated. The presence of supported platinum catalyst (10-15% Pt/C) allows to proceed the reaction under mild conditions (0.1-10 MPa, 60-80°C and in non-aggressive medium (water) with a quantitative yield of the product.

It was stated with the help of a complex of physico-chemical methods of investigation (RPES, IR-spectroscopy, NMR, ^{13}C , PMR, etc) that the methods of preparation and the temperature range of reduction of supported platinum catalysts contributing to the formation of highly dispersed metal particles (2.5-5.0 nm) and their uniform distribution on the carrier surface increase the activity and selectivity of platinum in the reaction of hydrogenolysis of "binor-S" into pentacyclotetradecane. It was shown that the more is the dispersity of metal and the value of the carrier surface, the higher is the activity and selectivity of supported platinum catalysts due to the peculiarity of electronic structure of small particles as well as the influence of the carrier on stabilization of the metal surface structure, *i.e.* the process of hydrogenolysis of "binor-S" belongs to the type of structure-sensitive reactions.

Introduction

Adamantane hydrocarbons have been widely used lately in the synthesis of new generations of medicinal preparations (symmetrel, remantadine), explosives, artificial diamonds, thermostable polymer compounds etc. [1-5].

Investigations on this work have the aim to develop and improve the method of synthesis of pentacyclotetradecane - diamantane isomer. The process of obtaining diamantane includes two main stages: hydrogenolysis of heptacyclotetradecane ("binor-S") into pentacyclotetradecane and its isomerization into diamantane. Of these stages, the process of hydrogenolysis of "binor-S" is the least studied and developed. The available literature data on this reaction are scanty and reported mainly by American investigators [6-11]. These works deal with a number of problems connected with the search of optimum conditions of the reaction as well as identification of the structure of the initial and obtained interaction products.

According to the literature data, pentacyclotetra-

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decane ($C_{14}H_{16}$), commonly known as "binor-S", is the most suitable initial compound for the preparative synthesis of diamantane [6,10,11]. The process of hydrogenolysis of "binor-S" is carried out in the presence of platinum black in glacial acetic acid with HCl at 200°C and 30.5 MPa, *i.e.*, under quite rigid conditions. The results of these investigations are hardly reproducible (because the method of preparation and reduction of the catalyst, the ratio of HCl and HAc, etc. are not given), the product yield is not high enough and the reaction is carried out in the presence of an aggressive medium. Besides, the use of platinum black as catalyst results in a considerable increase of diamantane preparation cost-price.

The aim of the present work is to find out general regularities of the change of rate and selectivity of the process of hydrogenolysis of "binor-S" into pentacyclotetradecane depending on the nature of metal catalyst, carrier, solvent and other parameters of the process parameters (P_{H_2} , T, etc) as well as to create a more effective and economical catalyst than platinum black for this reaction.

For the aim to be achieved it was necessary to solve the following main tasks:

- To study the effect of metal catalyst, carrier, solvent, the method of preparation and temperature of catalyst reduction and other parameters of procedure on the rate and selectivity of hydrogenolysis "of binor-S" into pentacyclotetradecane;
- To carry out a complex investigation of physico-chemical characteristics of optimal catalysts and to determine the relation of these data with their activity and selectivity in the reaction of hydrogenolysis "of binor-S" into pentacyclotetradecane;
- To find out the mechanism of cyclopropane rings in the definite part of "binor-S" molecules, to determine the structure of products of its hydrogenolysis;
- To create a more selective and economically profitable catalyst than platinum black for the reaction studied.

Experimental

To achieve the fulfilment of the set-up tasks of finding out kinetic principles of "binor-S" hydrogenolysis, we have used a special kinetic unit of high pressure "KUVD" that allows to carry out the process at any constant pressure of hydrogen from 0.1 to 15.0 MPa and to measure the reaction rates by absorption of hydrogen per unit of time. The theoretical bases of the method, the scheme and description of the main parts of "KUVD" are considered in work [12].

In the present work the following catalysts were studied: metal blacks of platinum group obtained by methods of Frampton [13], Zelinsky [14] and borhydride method [15], as well as supported platinum catalysts prepared by reduction of platinum ions with titanium trichloride, sodium borhydride by methods of deposition, impregnation and citrate method [16].

Activated coal of different quality (BAU, STK, CFAC, sibunite), Al_2O_3 and SiO_2 (KCM) in the form of powder with particle sizes 0.01-0.02 mm, were used as carriers. The carriers Al_2O_3 and SiO_2 carriers were preliminary calcinated at 500°C for 3 hours, SiO_2 being purified from iron ions with 0.2 M solution of hydrochloric acid and washed out from chlorine ions with distilled water.

The mixtures of acetic acid and hydrochloric acids (in volume ratio HAC:HCl = 1:1, 2:1, 0.5:1, 14:1), pure water, HAC and 1.42 N solution of HCl in water

A new bicycloheptadiene - a crystalline solid ($T_m = 65.0-65.6^\circ\text{C}$) called "binor-S" is endo-cis, endo-heptacyclo [5,3,1,1^{2,6}, 1^{9,11}, 0^{3,5}, 0^{8,10}] tetradecane [17]. The structure was determined by the methods of elemental analysis, IR- and mass-spectroscopy. Synthesis of "binor-S" was carried out in the Laboratory of RAS corresponding member U.M. Djemilev of the Institute of Chemistry BSC (Ufa). PMR spectra were recorded on NMR spectrophotometer by "TESLA" firm (CSSR) of BS-487 C type, at the frequency 80 MHz in reference to internal standard of HMDF (siloxane) CCl_4 , CHCl_3 , CDCl_3 were used as solvents, the concentration of substance being analyzed in the sample was determined by conditions of its extraction from catalysate and was 0.05-10.0 volume %. NMR spectra on ^{13}C nuclei were registered on the Spectrometer by "Bruker" firm of WR-80 type at frequency 20.15 mgh in reference to internal standard of HMDS. CCl_4 , CHCl_3 , CDCl_3 were used as solvents. Spin-to-spin interactions of carbon atoms with substance protons were suppressed when recording spectra. IR spectra of the reaction products were recorded on IR spectrometer "Specord-75 (Karl-Zeiss, Germany) in a capillary cell made of KBr. CCl_4 , CHCl_3 , CDCl_3 were used as solvent. Mass-spectroscopic analysis of substances was carried out by mass-spectra recorded on MNIROI spectrometer with accelerating voltage of 5 kV, ionization voltage was 70 V spectrometer resolution was not less than 1000.

Chromatographic determination of heptacyclotetradecane and products of its hydrogenolysis ($\text{C}_{14}\text{H}_{18}$, $\text{C}_{14}\text{H}_{20}$) was carried out on chromatograph "Chrome-5" with a flame-ionization detector. A stainless column of 6 m length and internal diameter of 3.5 mm filled with 5% SE stationary phase on chromatron N-AW-DMCS with 0.250-0.315 mm particle sizes was used. The temperatures of the thermostat was equal to 180°C and that of the evaporation chamber was 250°C. Argon was used as gas carrier (consumption after heating the column was 1.25 cm^3/s). The volume of substance samples was $1 \times 10^{-3} \text{ cm}^3$. It should be noted that the order of the substance display on the chromatogram was identified by individual substances, and IR spectroscopic, PMR and NMR methods were additionally used to redetermine the structure of a number of pentacyclotetradecane isomers.

Results and Discussion

According to literature and our data, destructive

hydrogenation of “binor-S” results in opening of cyclopropane rings and formation of two pentacyclic hydrocarbon isomers (Fig. 1) [1,16,18].

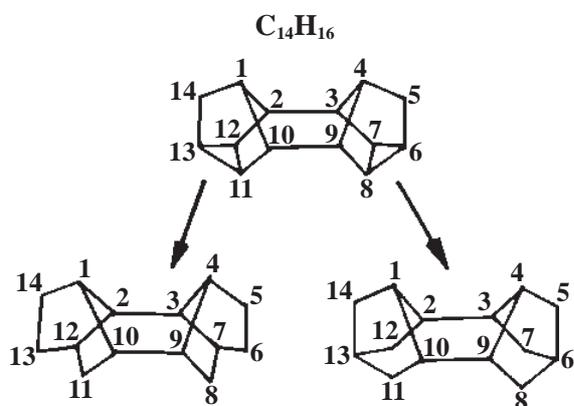


Fig. 1. Diagram of “binor-S” hydrogenolysis

The reaction of destructive hydrogenation of heptacyclic tetradecane (“binor-S”) into the pentacyclic tetradecane was studied under various experimental conditions with the aim to determine general principles of the effect of the nature of metal catalyst, carrier, solvent, methods of preparation and reduction temperature of the catalyst etc., on the kinetic characteristics of the process. It is stated by these investigations that hydrogenolysis of “binor-S” only proceeds on is achieved on platinum black in glacial acetic acid with and without the addition of HCl (optimum solvent; test conditions: 160°C, 0.1 MPa and 0.1 g of catalyst). Hydrogenolysis of “binor-S” was studied under the optimum conditions mentioned above in the presence of Pt, Ru, Rh, Pd black (Table 1).

Table 1

Hydrogenolysis of “binor-S” on blacks of platinum group metals (from oxides by Frampton) in 1.42 N HCl

Metal black	T, °C	P, MPa	Conversion, %	Product yields, %		
				C ₁₄ H ₁₆	C ₁₄ H ₁₈	C ₁₄ H ₂₀
Rh	353	1.0	50	50	3	2 (45*)
Rh	433	1.0	78	22	5	3 (70*)
Ru	353	1.0	50	50	4	4 (42*)
Ru	433	1.0	23	77	2	2 (19*)
Pd	353	1.0	11	89	5	4 (2*)
Pd	433	1.0	24	76	9	8 (7*)
Pt	353	1.0	100	-	3.5	96.5

* The total number of products of hydrogenolysis of five- and six member cycles

Destructive hydrogenation of “binor-S” takes place running on rhodium (Rh) black under the conditions chosen. Conversion increases from 48-50% at 80°C to 78% at 160°C. The degree of “binor-S” conversion on palladium increase from 11 to 24% with temperature increasing to 160°C. The conversion on ruthenium, on the contrary, decreases from 50% to 23% with temperature increasing from 80° to 160°C. Complete conversion of heptacyclic tetradecane occurs on platinum black at 80°C and 1 MPa. Conversion and yield of the product amount to 100 and 96.5% respectively.

The analysis of the reaction mixture -catalysate by chromatographic, PMR and NMR ¹³C methods showed that on rhodium, palladium and ruthenium the oily liquid layer contains several products of hydrogenolysis, *i.e.*, the process is not selective, destruction of C-C- bonds of different cycles followed by hydrogenation takes place. It should be noted that gaseous products are evolved in the process of hydrogenolysis of “binor-S” in case of rhuthenium black. It is only on platinum that “binor-S” undergoes complete conversion with the formation of hydrogenolysis product with formula C₁₄H₂₀ - diamantane isomer (pentacyclic tetradecane).

It follows from the experimental data obtained that hydrogenolysis of “binor-S” on platinum is accompanied by C-C bonds splitting with simultaneous hydrogenation resulting in the formation of pentacyclic tetradecane. As it is known, in cyclopropane valence angles are equal to 60°, *i.e.* they greatly differ from a normal tetrahedron hydrogen atom (109.5°). Therefore, three and four member cycles are referred to highly tense systems. This characteristic property is, probably, a driving force for opening cyclopropane rings in the molecule of “binor-S”.

It should be noted that a tense system of a cyclopropane ring is, in a sense, a formal analogue to a tense “two-member cycle” of olefin and, similar to the latter, ia able to add electrophilic agents splitting one of its bonds. Water, hydrochloric and acetic acids may serve as an electrophilic agent. Addition of HCl, HAc into the reaction mixture, probably, increases the effects of tension in a three-member cycle that results in splitting of C-C-bond in the pointed out part of “binor-S” molecule. The addition of an acid, probably, stimulates not only the deformation of a three-member cycle of “binor-S” molecule to form carbon cations but seems also to provide its orientation and adsorption by a cyclopropane ring to

the surface of platinum. This provides high selectivity of the process by pentacyclotetradecane yield.

Catalytic reactions are divided into donor and acceptor ones depending on the direction of electron transfer. Donor reactions are accelerated if in the limiting stage electron drift takes place from the substrate to the catalyst, while acceptor reactions are accelerated on account of electron transfer in the opposite direction. To evaluate approximately the ability of the studied metals for donor or acceptor interactions, it is convenient to use the comparison of values of physico-chemical characteristics of the metals with their activity in "binor-S" hydrogenolysis reaction (Table 2).

It follows from the table data that the highest selectivity of the process is observed for platinum for it has a high value of affinity for electron, adsorption heat and Me-H binding energy. These data may be indicative of the donor nature of the "binor-S"-catalyst interaction.

Proceeding from the data obtained, further investigations of "binor-S" hydrogenolysis were carried out in 1.42 N HCl on platinum black prepared by different methods.

In destructive hydrogenation of heptacyclotetradecane on Pt-black prepared by Frampton, Zelinsky and borhydride methods the forms of kinetic curves are identical, *i.e.*, a gradual decrease of reaction rate with the time is observed (Fig. 2). It follows from the data given that the highest rate of "binor-S" hydrogenolysis is observed in the presence of platinum black prepared by Frampton method, and by the activity of destructive hydrogenation of heptacyclo-

tetradecane into pentacyclotetradecane the studied blacks are aligned as follows: Pt-black (by Frampton) > Pt-black (by Zelinsky) > PtB-black (borhydride method). The values of the process selectivity (by pentacyclotetradecane yield) on all the studied blacks is close to each other and amount to 95.8-96.5 % regardless of the preparation method (Table 3).

The high rate of the "binor-S" hydrogenolysis on platinum black prepared by Frampton method is, probably, accounted for the completeness of platinum reduction and the highest surface value of this

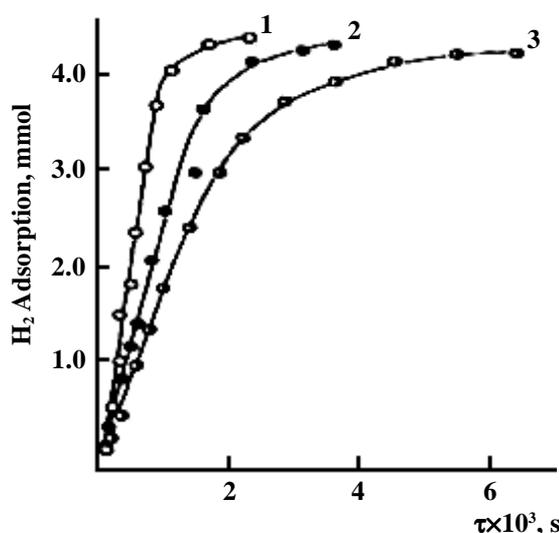


Fig. 2. Kinetic curves of "binor-S" hydrogenolysis (0.822 g) on the Pt spongy blacks (0.1 g) prepared by different methods in 1.42 N HCl solution at 80°C and 1.0 MPa: 1 – Pt spongy black by Frampton method, 2 – Pt spongy black by Zelinsky method, 3 – Pt/B spongy black by borhydric method.

Table 2
Physico-chemical characteristics of catalysts

Indexes	Studied metals				
	Pd	Pt	Rh	Ru	Ni
Selectivity by pentacyclotetradecane yield, %	4-8	96-100	2-3	2-4	1-2
Electron outcome work, eV	5.1	5.3	4.8	4.5	5.0
the second ionization potential	19.4	18.5	18.0	16.6	18.1
the member of d-electrons	10.0	9.0	8.0	7.0	8.0
Electronegativity, eV	2.1	2.2	2.1	2.0	2.1
Affinity for electron, eV	1.02	2.56	1.08	1.51	1.28
H ₂ adsorption heat, kcal/mol	14-8	20-4	14-4	10-3	15-3
Q _{K-H} , kcal/mol	58-56	68-54	59-54	57-53	59-53

Table 3
Hydrogenolysis of “binor-S” on Pt-black (0.1 g) prepared by different methods
in 1.42 N aqueous solution of HCl (15 cm³) at 80°C and 1.0 MPa

Catalyst	Specific surface, m ² /g	Sizes, nm		Specific catalytic activity (SCA)		Product yields			Selectivity, %
		of particles	of pores	1 g Pt×10 ⁻²	m ² /g×10 ⁻⁴	C ₁₄ H ₁₆	C ₁₄ H ₁₈	C ₁₄ H ₂₀	
Pt-black (by Frampton)	35	20.0	2.2-3.0	3.0	8.6	-	3.5	96.5	96.5
Pt-black (by Zelinsky)	30	20.0	2.5	2.6	8.6	-	3.8	96.2	96.2
Pt-black (by borhydride method)	25	15.0	3.0	1.7	6.8	Traces	4.2	95.8	95.8

catalyst in comparison with other blacks.

Hence, it may be concluded that the rate of destructive hydrogenation of “binor-S” considerably depends on the methods of preparation of the studied blacks. Therefore, the method of preparation of platinum black provides the completeness of platinum reduction on which hydrogen is well activated, it appears to increase its activity in the reaction of “binor-S” hydrogenolysis, the process selectivity remaining unchanged.

The data obtained indicate the fact that one of decisive factors influencing the activity and selectivity of “binor-S” hydrogenolysis process is the change of the state and size of platinum particles in the catalyst and the increase of its surface value.

To optimize the data obtained we have studied the effect of carriers and temperature of heat treatment of platinum catalysts on the process of hydrogenolysis of the “binor-S” into pentacyclotetradecane.

The platinum catalysts deposited on different carriers are widely used in industry. This is connected with the fact that the deposition of a metal on carriers contributes to the increase of its activity, extends the working life of a catalyst, and in most cases results in changing its action selectivity. It should be noted that all available in literature investigations on heptacyclotetradecane hydrogenolysis were carried out in the presence of platinum black, data on hydrogenolysis of polycycles on supported catalysts are not available [1,5].

Therefore, investigation of “binor-S” hydrogenolysis process in the presence of supported platinum catalysts the activity and selectivity of which were studied in dependence upon the content of the active metal Pt (5-50%), the nature of the carrier (coal of different quality, SiO₂, Al₂O₃), the methods of preparation, the method of reduction by titanium trichloride, sodium borhydride, sodium citrate) was of

practical interest. All in all, 56 samples were studied.

The obtained kinetic data on hydrogenolysis process on supported catalysts showed that the maximal activity and selectivity of the process was observed in the presence of platinum catalysts deposited on carbon carriers-sibunites 619-P and GECE (commercial French activated coal, CFAC) prepared by citrate methods.

It should be noted that the degree of conversion and selectivity of the process are mainly determined by the method of preparation of a catalyst. For example, catalysts: 10% Pt/sibunitite, GECE, prepared by citrate method provide 100% conversion and selectivity of the process, when using other methods conversion does not exceed 7%.

Deposition of different amounts of platinum on activated coal practically does not influence the forms of kinetic curves, and hydrogenolysis of “binor-S” proceeds with the rate gradually decreasing with time (Fig. 3). The order of the reaction is the first one by hydrogen, and by substrate it is close to zero.

The increase of platinum contents in the catalyst from 3% to 5% does not provide a complete conversion of the “binor-S” (curves 4 and 3 under comparable conditions, Fig. 3), and the product yield on these catalysts is 34.0% and 82.0%, respectively. (Table 4).

The amount of intermediate compound on these catalysts is 38.0% (3% Pt/C) and 18.0% (5% Pt/C). Under the conditions chosen (Table 4) a complete conversion of “binor-S” and almost quantitative yield of the product (C₁₄H₂₀) are observed in the presence of 10% and 15% Pt/C catalysts.

From the data mentioned it also follows that the rate of hydrogenolysis and completeness “binor-S” conversion increase with the increase of the amount of 5% Pt/c catalyst from 0.2 to 0.4 g. It should be

Table 4Hydrogenolysis of "binor-S" on Pt/C (sibunite 619-P; $q_{kt} = 0.2$ g) in 1.42 N HCl solution (15 cm^3) at 80°C and 1.0 MPa

Catalyst	Specific catalytic activity (SCA)		Product yields			Selectivity, %
	1 g Pt $\times 10^{-2}$	$\text{m}^2/\text{g}\times 10^{-5}$	$\text{C}_{14}\text{H}_{16}$	$\text{C}_{14}\text{H}_{18}$	$\text{C}_{14}\text{H}_{20}$	
3% Pt/C	0.25	0.5	28.0	38.0	34.0	47.2
3% Pt/C (0.4 g)	-	-	21.0	41.0	38.0	48.0
5% Pt/C	0.9	1.7	Traces	18.0	82.0	82.0
5%Pt/C(0.4 g)	-	-	Traces	8.0	92.0	92.0
8% Pt/C	3.1	5.9	-	3.0	97.0	97.0
10% Pt/C	16.7	32.1	-	Traces	≈ 100.0	≈ 100.0
15% Pt/C	16.7	32.1	-	Traces	≈ 100.0	≈ 100.0

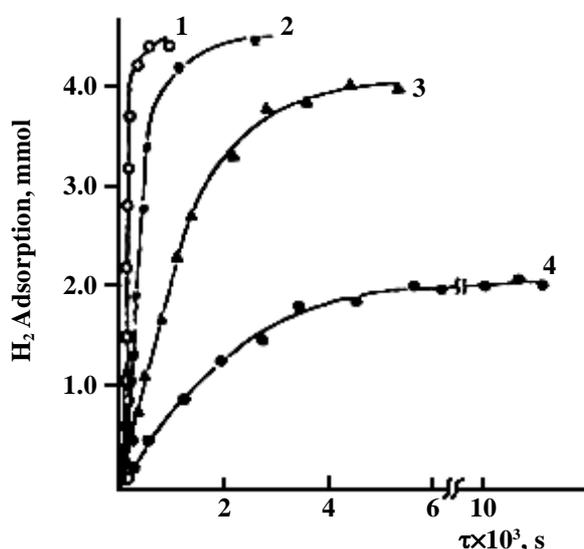


Fig. 3. Kinetic curves of "binor-S" hydrogenolysis (0.822 g) on the Pt/C catalyst (0.2 g) in 1.42 N HCl solution at 80°C and 1.0 MPa: 1 – 15% Pt/C, 2 – 10% Pt/C, 3 – 5% Pt/C.

noted that even at full conversion of "binor-S" (5% Pt/c = 0.4 g, the amount of platinum corresponds to 10% Pt/c = 0.2 g), the catalyst still contains 8% of intermediate compound ($\text{C}_{14}\text{H}_{18}$). This means that a simple increase of platinum content in the catalysats does not result in quantitative yield of pentacyclotetradecane ($\text{C}_{14}\text{H}_{20}$). Therefore, only deposition of platinum on coal in the amount of 10 and 15% gives the desired effect, and the yield of pentacyclotetradecane is equal to 100%.

By specific catalytic activity (per 1 g Pt) in the reaction of hydrogenolysis of "binor-S" into pentacyclotetradecane the studied platinum catalysts are aligned as follows: 10 and 15% Pt/c > Pt black (by

Frampton) > Pt black (by Zelinsky) > PtB black (by borhydride method) and by selectivity of the process they have the following sequence: 10 and 15% Pt/c > Pt black (by Frampton, Zelinsky and borhydride methods). It should be noted that selectivity of 10 and 15% Pt/C-catalysts in the reaction of hydrogenolysis of "binor-S" into pentacyclotetradecane is 4-5% higher than that of platinum blacks (95-96%).

The RPES (X-ray phase electron spectroscopy) data on investigation of platinum state in catalysts in the form of blacks and supported platinum catalysts are given in Table 5.

The analysis of the table data allows to suppose

Table 5

The state of platinum in blacks and supported catalysts (RPES data)

Catalyst	Ess $4f_{7/2}$	Valent state of Pt	Quantitative contents of Pt^{+2} and Pt^0 , %
10% Pt/sibunite	70.6	Pt^0	15
	73.4	Pt^{+2}	85
Pt black (by Zelinsky)	70.6	Pt^0	85
	73.4	Pt^{+2}	15
Pt black (by Frampton)	70.6	Pt^0	100
10% Pt/BAU	70.6	Pt^0	90
	73.4	Pt^{+2}	10
10% Pt/STK	70.4	Pt^0	80
	73.4	Pt^{+2}	20

that optimum state of platinum for "binor-S" hydrogenolysis. may be the presence of a definite ratio of Pt^{+2} and Pt^0 . Processes of destruction and hydrogenation generally proceed in the presence of active centers of a catalyst different by their nature. It should be taken into account here that in the reaction of hydrogenolysis structural parameters of catalyst particles may appear to be prevailing.

The supported platinum catalysts (10% Pt) deposited on carbon carriers -sibunite 619-P, GEGE and BAU are studied on electron microscope EM-125K. It was stated by the investigations that supported catalyst 10% Pt/sibunite-619-P prepared at 60°C is represented by dense metal particles with the sizes of 3.5-5.0 nm (mainly) which are uniformly distributed on the carrier surface. For a supported catalyst 10% Pt/GEGE (60°C), metal particles are mainly of sizes: 2.0-2.5 nm and 5.0 nm. In case of 10% Pt/BAU (60°C) the sizes of the platinum particle are 12.0 -15.0 nm and distribution of particles on the carrier surface is not uniform. The surface of catalyst determined by adsorption of nitrogen is 495 m²/g (10% Pt/GEGE), 520 m²/g (10% Pt/sibunite 619-P) and 136 m²/g (10% Pt/BAU).

The data mentioned show that the difference in activity and selectivity of supported platinum catalysts (10% Pt) deposited on carbon carriers-sibunite-619P, GEGE and BAU in the reaction of "binor-S" hydrogenolysis, depending on the nature of carrier is mainly due to the change of platinum dispersivity and catalyst surface values,

The results of hydrogenolysis of "binor-S" on 10% Pt/sibunite-619P and GEGE, depending on the temperature of thermal treatment of catalysts showed that with the increase of temperature of thermal treatment of catalysts (10% Pt/sibunite-619P, GEGE) from 60-80°C to 100-120°C their activity sharply decreases, and at temperatures above 150°C the reaction practically does not proceed.

This effect is due to the enlarging of sizes of catalyst particles with the temperature of its treatment. Electron-microscopic pictures showed that 10% Pt/sibunite-619P sample (60°C) is presented by dense metal particles with the sizes of 3.5-5.0 nm which are uniformly distributed on the carrier surface. After thermal treatment completed (120°C) metal particles are considerably enlarged (up to 10.0-30.0 nm) and the distribution of particles on the carrier surface is not uniform. 10% Pt/GEGE is presented by metal particles with the sizes of 2.5-5.0 nm. With the increase of temperature of thermal treat-

ment from 60°C to 120°C platinum particles are enlarged to 15.0-30.0 nm. In case of 10% Pt/BAU at already 60°C the sizes of platinum particles are 12.0-13.0 nm, and the distribution of metal particles on the carrier is not uniform.

Consequently, we may state that the process of "binor-S" hydrogenolysis belongs to the type of structure-sensitive reactions, and optimum thermal treatment of the catalysts mentioned is observed at 60-80°C.

On the basis of these results it may be concluded that the greater is metal dispersivity and value of the carrier surface, the higher is the activity and selectivity of supported platinum catalysts in the reaction of hydrogenolysis of "binor-S" into pentacyclotetradecane due to the peculiarity of the electron structure of small particles, as well as the effect of the carrier on stabilization of the metal surface structure.

Conclusions

On the basis of the investigations carried out the following conclusions have been made:

1. It was shown that in the series of the studied metals (Pt, Pd, Rh, Ru, Co, Mo, Cu, and Ni) only platinum (in the form of black or deposited on activated coal-sibunite 619-P or GEGE) in water (added with HCl or without HCl additions) and HAc (with or without additions of HCl) is able to carry out hydrogenolysis of the "binor-S" into pentacyclotetradecane (with 100% conversion of the original compound).
2. It was stated that by SCA (per 1 g Pt) in the course of hydrogenolysis of "binor-S" into pentacyclotetradecane the studied platinum catalysts are aligned as follows: 10% Pt/c > Pt black (by Frampton) > Pt black (by Zelinsky) > PtB black (by borhydride method). The yield of the aimed product on these catalysts is 95-96%.
3. It was found that under conditions chosen, in "binor-S" hydrogenolysis on supported platinum catalysts maximum yield (H•100%) of pentacyclotetradecane is achieved when the content of the active metal is equal to or more than 10% (weight), and at a lower amount of platinum the yield of the aimed product decreases and is 82-92%.
4. Using a complex of physico-chemical methods of investigation (RPES, IR spectroscopy, NMR, I3C PMR etc.) it was stated that methods of preparation and temperature range of reduction of supported platinum catalysts, contributing to obtain-

ing highly dispersed metal particles (2.5-5.0 nm) and their uniform distribution on the carrier surface, increase the activity and selectivity of platinum in the reaction of hydrogenolysis of "binor-S" into pentacyclotetradecane.

5. It was stated by NMR, PMR and GLC that the aimed product (pentacyclotetradecane) consists of two isomers of the composition $C_{14}H_{20}$, *i.e.*, there occurs a splitting of carbon-carbon bond of the three-member cycle in positions 6.8 and 11.13 (89-90%), 7.8 and 12.11 (10-11%).
6. A new effective method was developed for preparation of diamantane isomer (pentacyclotetradecane) by destructive hydration of "binor-S" in the presence of supported platinum catalyst (10-15% Pt/C) that allows to carry out the process under mild conditions (0.1-1.0 MPa, 60-80°C) and non-aggressive medium (water) with a quantitative yield of the aimed product. These developments are protected by patents of the Republic of Kazakhstan and Russia.

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