ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 10, pp. 695–701. © Pleiades Publishing, Ltd., 2021.
Russian Text © The Author(s), 2021, published in Koordinatsionnaya Khimiya, 2021, Vol. 47, No. 10, pp. 628–634.

Dedicated to blessed memory of outstanding scientist Il'ya Iosifovich Moiseev

Specific Features of the Catalytic Hydrogenation of the Norbornadiene-Based Carbocyclic Compounds

V. V. Zamalyutin[a], *, E. A. Katsman[a], V. Ya. Danyushevsky[a], V. R. Flid[a], **,
V. V. Podol'skii[a], and A. V. Ryabov[a]

[a] *MIREA—Russian Technological University, Institute of Fine Chemical Technologies, Moscow, Russia*
**e-mail: zamalyutin@mail.ru*
***e-mail: vitaly-flid@yandex.ru*

Received March 22, 2021; revised May 12, 2021; accepted May 13, 2021

Abstract—The gas- and liquid-phase hydrogenation of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) in the presence of the Pd/γ-Al_2O_3 (PK-25) industrial palladium catalyst in an *n*-heptane medium at 75–200°C is studied. The reaction products are identified, the main reaction routes are established, and the material balance is studied. The effect of preferable adsorption of norbornadiene compared to other components of the system on the palladium active site is confirmed. A relationship between possible modes of norbornadiene coordination and the product structure is considered. A parallel-sequential scheme is proposed for the mechanism of the process on the basis of the obtained experimental and theoretical data.

Keywords: norbornadiene, heterogeneous hydrogenation products, parallel-sequential mechanism, palladium catalyst, active site, heterogeneous theories of catalysis

DOI: 10.1134/S1070328421100080

INTRODUCTION

The theory of adsorption advanced by I. Langmuir [1, 2] provided prerequisites for the qualitative understanding and quantitative description of the kinetics of heterogeneous catalytic chemical reactions (HCCR) and many related regularities, including competitive inhibition by substrates or products [3–6]. Since it was necessary to adequately interpret quantitatively kinetic results for some complicated HCCR, the multiple adsorption of reactant molecules in one active site was assumed [7]. This assumption can impart to kinetic models a degree of flexibility higher than they had before using classical concepts about the HCCR mechanisms.

One of the commonly known systems of views upon the HCCR mechanisms is the consideration of their peculiarities based on analogies with homogeneous catalysis. They include resembling features of reaction intermediates, the character of binding of reactants by the active site (e.g., coordination-adsorption), the role of the medium (e.g., solvent or surface), etc. On the one hand, a great contribution to the development of these concepts was made by classical works of I.I. Moiseev and coworkers devoted to homogeneous catalysis on the giant metal clusters close in size and catalytic properties to the metal particles on the carrier surface [4, 8–10].

On the other hand, the adequate examples of multiple adsorption are presented in the studies on the quantum chemical modeling of the interaction of phenylacetylene with the Pd surface (111) [11, 12] and experimental studies of the kinetics and peculiarities of the mechanism of selective phenylacetylene hydrogenation in the presence of Pd/C [13]. This phenomenon is observed for the deoxygenation of fatty acids in the liquid phase on the immobilized palladium and nickel catalysts [14–16].

Selective hydrogenation reactions are widely used in petrochemical industry for the decontamination of ethylene and styrene from acetylene and phenylacetylene impurities in the gas and liquid phases, respectively [17–19].

In spite of a considerable number of publications on HCCR, available data are often insufficient for a deep understanding of the structure and functioning of the active site of the heterogeneous catalyst and purposeful selection of hydrogenation conditions, which is necessary for the construction of adequate kinetic models.

The understanding of the regularities of the heterogeneous hydrogenation of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) can stimulate the development of concepts on the multiple adsorption of substrates on one active site of the heterogeneous catalysts and also can provide prerequisites for the selective synthesis of strained saturated carbocyclic structures with the retention of the carbon skeleton.

The double bonds in NBD are characterized by a higher reactivity due to specific features of the spatial structure and the capability of homocoupling. The compounds based on NBD, including the hydrogenation products, are promising intermediates in organic synthesis, in particular, as components of new perspective polymeric materials or fuels with high specific energy parameters [20].

The development of the catalysts and conditions for the liquid-phase hydrogenation of strained polycyclic compounds is practically reasonable, since it is necessary to retain the structure of the carbon carcass, which is urgent for NBD and its derivatives. Therefore, the effect of the catalyst and hydrogenation conditions should be fairly mild. The development of such catalysts and elaboration of their mechanism are carried out on the basis of systematic structural and kinetic studies. The results of preliminary experiments on the gas-phase hydrogenation of NBD at 100–200°C make it possible to advance qualitative analogies observed for some reactions involving acetylenes and dienes on the immobilized heterogeneous palladium catalysts. In spite of comparatively high manufacturability of hydrogenation in the gas phase, these processes are appropriate only for the first representatives of the series: NBD and bicyclo[2.2.1]hept-2-ene (norbornene, NBEN). The heavier norbornene derivatives, such as dicyclopentadiene, 5-vinylnorbornene, penta- and hexacyclic dimers of NBD, and many others can participate only in liquid-phase processes [21].

The purpose of this work is to study specific features of the liquid-phase hydrogenation of NBD in batch and flow reactors and to elaborate prerequisites for the development of a kinetic model that would adequately describe the conversion of NBD to bicyclo[2.2.1]heptane (norbornane, NBAN) in the presence of the core–shell palladium catalyst.

EXPERIMENTAL

Norbornadiene was dried over sodium wire and distilled prior to use. The solvents (*n*-heptane (standard, KHIMMED) and *n*-nonane (for chromatography, reagent grade, REAKHIM)) were used as received. Gaseous hydrogen (trade mark A, purity 99.99%, GOST 3022-80) and nitrogen (special purity grade (sort 1), purity 99.999%) were used without additional purification.

The industrial catalyst PK-25 (TU 38.102178-96) (ZAO Promkataliz) applied for the selective hydrogenation (removal) of impurities of acetylene and diene hydrocarbons in liquid and gaseous pyrolysis products served as the heterogeneous catalyst [22].

Procedure of PK-25 catalyst recovery in an H_2 flow and analysis of NBD hydrogenation products in flow reactor 1 and in batch reactor 2. Reactor 1 (working zone volume 3 cm^3) or 2 (volume 100 cm^3) was purged with hydrogen (25°C, 20 min). A weighed sample of the PK-25 catalyst (0.50–1.50 g) was recovered in a hydrogen flow (4 L/h) for 180 min at an experimental temperature of 100–200°C in reactor 1 or at 75°C in reactor 2. Blackening of the catalyst granules was visualized.

An Agilent 5973N chromatograph/mass spectrometer with an Agilent 6890 accessory (electron impact ionization, Agilent 122-5536 DB-5ms column) was used for the identification of all components of the reaction mixture.

Reaction samples were analyzed on a Kristall 2000 chromatograph (column VS-101 50 m × 0.2 mm, phase 100% dimethylpolysiloxane). The analysis time was 27 min, the temperature of the detector and evaporator was 180°C, the initial temperature of the column was 70°C, the temperature regime of the column was 70°C (10 min)/15°C (1 min)/250°C (3 min), helium served as the carrier gas, the flow rate was 0.8 mL/min, and split ratio was 1 : 125. An analysis by gas-liquid chromatography (GLC) of the initial NBD showed that it contained ~5% NBEN. These data were taken into account when analyzing the samples taken during experiment. The analysis results were processed by the internal standard method with *n*-nonane using the Chromatec Analytic software.

Procedure of kinetic experiments in reactor 1. A quartz flow reactor (reaction volume 3 cm^3) consists of several compartments. The catalyst was loaded into the upper compartment equipped with electrical heating. The second and third compartments were a ball condenser and a condenser-separator. A flask-receiver immersed in an ice bath was placed in the bottom compartment.

A mixture of hydrogen and liquid reactants was permanently fed to the upper compartment using a peristaltic pump. The liquid fraction containing hydrogenation products was collected in the flask-receiver during the experiment. The collected catalyzate was analyzed by GLC at the end of the experiment.

Procedure of kinetic experiments in reactor 2. When studying the kinetics of liquid-phase NBD hydrogenation, a vibrostand on which a temperature-maintained 100-mL batch reactor was mounted along with a reverse condenser and a sampler in the bottom compartment of the reactor was used to provide vigorous stirring. The reactor was connected to a gasometer filled with hydrogen. The course of experiments was monitored by GLC analysis of reaction samples and by the volumetric method from the hydrogen uptake. The

Table 1. Conditions for gas-phase NBD hydrogenation in the flow reactor

Experimental conditions	Run 1	Run 2	Run 3	Run 4	Run 5
Temperature of reactor, °C	200	155	100	125	100
Time of experiment, min	150	150	120	120	120
Flow rate of H_2 (25°C), L/h	2.4	2.4	2.4	4.86	4.86
Flow rate of initial mixture, mL/h	9.52	9.52	9.52	17.6	24.1

full material balance was calculated from the analysis results for each experiment. Samples were taken without violating the reaction regime. Their number was determined by the conditions of statistical processing of the results in order to obtain an adequate information. The conversion of the reactants in the kinetic experiments reached 100%.

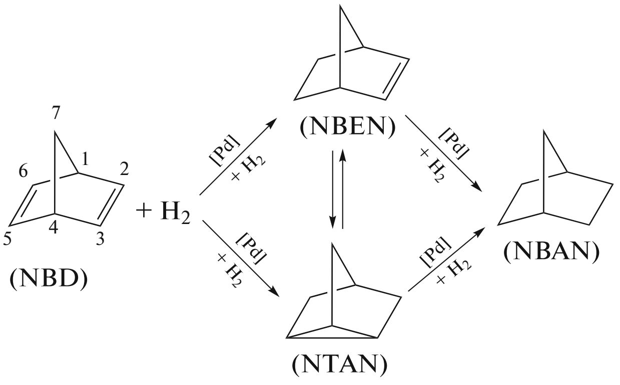
Stirring conditions were selected by special experiments. The process occurs without appreciable diffusional restraints at the shaking intensity higher than 380 min^{-1}. The shape and sizes of the catalyst granules (0.1–0.2 mm) were optimized for the same purpose.

RESULTS AND DISCUSSION

A series of experiments in a hydrogen flow in the temperature range from 100 to 200°C with the variation of the hydrogen and reactant consumptions (Table 1) was carried out to select conditions for the full hydrogenation of NBD in an *n*-heptane medium in a flow reactor and to provide the catalyst stability. The contact time of the reaction mixture was 0.1–0.3 h. The results of an GLC analysis at the outlet of the reactor are presented in Table 2. The major products are NBAN (84–92%) and tricyclo[2.2.1.$0^{2,6}$]heptane (nortricyclane, NTAN) (8–10%), as well as some amount of NBEN (1.5–5%) if any (the latter can be absent completely). No other compounds were found. The catalyst does not lose activity after 20-fold use. Thus, the selected conditions and regimes of hydrogenations make it possible to completely avoid the destruction of the carbon carcass in the norbornane structures and to retain catalyst activity for a prolong time.

The results of gas-phase NBD hydrogenation in the flow reactor show that the full conversion of NBD is accompanied by the high selectivity to NBAN, which increases with decreasing temperature (Table 2, runs 1–3). As the raw materials consumption increases (Table 2, entry 5), the yield of NBEN as an intermediate product of NBD hydrogenation in the final mixture increases and reaches 5%. In all experiments, NTAN is formed (up to 10%), and its yield increases with temperature and is independent of the raw materials flow rate (Tables 1, 2).

Although NTAN is a minor product, the mechanism of its formation is interesting from the viewpoint of variation of the coordination modes of NBD on the catalyst active site. It can theoretically be assumed that NTAN is formed upon the addition of hydrogen atoms to positions 2 and 6 of the NBD molecule and by NBEN isomerization. Possible transformations of NBD during gas-phase hydrogenation are presented in Scheme 1.



Scheme 1.

To check these hypotheses, we performed the quantum chemical analysis of probable transformations of NBD and its hydrogenation products. The Gaussian 09W quantum chemical software (MP2/6-311G(d,p) method) was used for geometry optimization and calculation of the thermodynamic characteristics of all components of the reacting system. The values of $\Delta G°$ in the gas phase were calculated for all reactions (Table 3).

The quantum chemical calculation results confirm that the isomerization of NBEN to NTAN is thermodynamically possible under the studied conditions but is poorly probable. Model experiments were carried out to check this hypothesis. A mixture consisting of 40 wt % NBEN and 60 wt % *n*-heptane was fed to the flow reactor at 200°C in a nitrogen flow in the absence of hydrogen. No NTAN was observed at the outlet of the reactor. Thus, NTAN is formed only due to the one-step hydrogenation of NBD.

A series of six experiments in the batch reactor at the same temperature was carried out to study peculiarities of the kinetics of NBD hydrogenation. Each experiment was duplicated to check reproducibility of the obtained kinetic data. The conditions of selected experiments and the results of liquid-phase NBD hydrogenation are given in Tables 4 and 5, respectively.

Table 2. Results of gas-phase NBD hydrogenation in the flow reactor

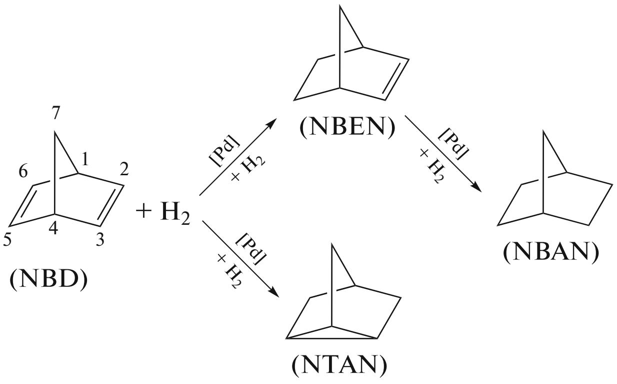
Composition of initial mixture, % (by GLC analysis data)					
Component	Run 1	Run 2	Run 3	Run 4	Run 5
NBD	95.06	95.38	95.37	95.37	95.42
NBEN	4.94	4.62	4.63	4.63	4.58
Composition of final reaction mixture, % (by GLC analysis data)					
NBD	0.69	0	0	0	1.09
NBEN	2.10	0	0	1.52	4.94
NTAN	8.80	10.14	7.68	8.90	9.63
NBAN	88.41	89.86	92.32	89.58	84.34
Quantitative technological parameters					
	Run 1	Run 2	Run 3	Run 4	Run 5
Temperature of reactor, °C	200	155	100	125	100
Conversion, %					
X_{NBD}	99.3	100	100	100	98.8
X_{NBEN}	57.8	100	100	64.9	9.10
Selectivity to NBD, %					
φ_{NBAN}	88.3	89.7	92.2	90.8	85.0
φ_{NBEN}	9.44	0	0	0	9.92
φ_{NTAN}	2.26	10.3	7.80	9.20	5.08

The characteristic kinetic curves for the liquid-phase hydrogenation of NBD (76°C, solvent *n*-heptane) are shown in Figs. 1–3. The material balance was drawn (overall inaccuracy not higher than 5%) for each reaction sample by the internal standard method. Significant amounts of NBEN as an intermediate product were observed in all experiments on NBD hydrogenation. The time of achieving the maximum NBEN concentration depends on the initial NBD concentration (Figs. 2, 3) and nearly coincides with the time of complete consumption of NBEN. Evidently, if the system contains NBD, the involvement of the intermediate product in the second step with the formation of NBAN is low. After the amount of NBD is exhausted, the rate of NBAN formation increases considerably. The kinetic orders with respect to NBD and NBEN are close to zero in a wide time interval. This fact confirms that, similarly to acetylene compounds, NBD is bound to the palladium active site much more strongly than NBEN and other components of the reaction.

An analysis of the kinetic curves allows one to specify the mechanism of the process. The mechanism of NBD hydrogenation (PK-25 catalyst) on the basis of the experimental and theoretical data is shown in Scheme 2. The reaction has a pronounced three-step parallel-sequential character.

Table 3. Calculation results for ΔG° in the gas phase for the conversions involving NBD and its hydrogenation products

Reaction	ΔG°, kJ/mol
$NBD + H_2 \rightarrow NBEN$	−123.57
$NBEN + H_2 \rightarrow NBAN$	−101.44
$NBD + H_2 \rightarrow NTAN$	−138.35
$NBEN \rightarrow NTAN$	−14.78
$NTAN \rightarrow NBEN$	14.78
$NTAN + H_2 \rightarrow NBAN$	−86.67



Scheme 2.

Table 4. Conditions of some experiments of liquid-phase NBD hydrogenation in the batch reactor

Experimental conditions	Run 6	Run 7	Run 8	Run 9
Temperature of reactor, °C	76			
Weight of PK-25 catalyst, g	1.4750	0.5050	0.5049	0.5070
Catalyst shape	Granules 0.1–0.2 mm			
Shaking rate of reactor, min^{-1}	380			

Table 5. Results of the liquid-phase NBD hydrogenation in the batch reactor

Component	Run 6	Run 7	Run 8	Run 9
Composition of initial mixture, % (by GLC analysis data)				
NBD	95.49	95.63	48.06	95.92
NBEN	4.51	4.37	51.94	4.08
Composition of final reaction mixture, % (by GLC analysis data)				
NBD	0.00	0.00	0.00	0.00
NBEN	0.00	0.00	0.00	0.00
NTAN	1.58	1.77	0.70	1.87
NBAN	98.42	98.23	99.30	98.13

The reaction occurs with high conversion of NBD and selectivity to NBAN in both the static and flow systems. A characteristic feature of the process is the formation of NTAN as a minor product (up to 2%), which is generated directly from NBD and is not consumed in the subsequent steps (Fig. 4). Evidently, the yield of NTAN is affected by the temperature only.

The character of the kinetic curves indicates a substantial inhibition of the NBEN hydrogenation step in the presence of NBD. This phenomenon is probably thermodynamic in character because of the strong binding of the catalyst active site by the NBD molecule. An analogous effect is observed for the hydrogenation of acetylenes and dienes [4] and confirmed by the comparative data on the adsorption energies for phenylacetylene and styrene on Pd/C. The difference in ΔG° of adsorption obtained by the quantum chemical methods for various palladium surfaces ranges from 21 to 42 kJ/mol in favor of phenylacetylene [11, 12].

The variation of the coordination (adsorption) modes of NBD (mono-/bidentate, exo/endo) results in the formation of various products, in particular, the chelate coordination mode is confirmed by the formation of insignificant amounts of NTAN. The possible coordination modes for NBD on the palladium catalyst surface are shown in Scheme 3.

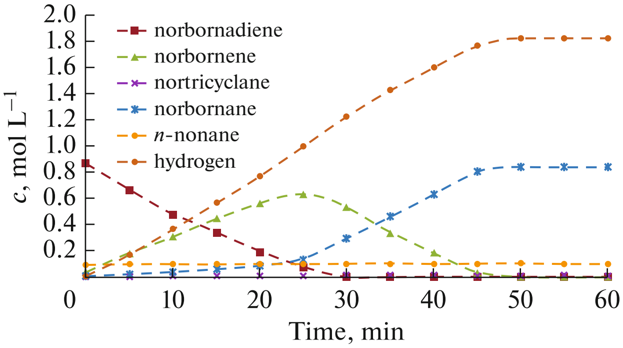


Fig. 1. Characteristic kinetic curves of the adsorbed hydrogen, NBD, and products of its hydrogenation (here and in Figs. 2–4, 76°C, *n*-heptane) (Table 5).

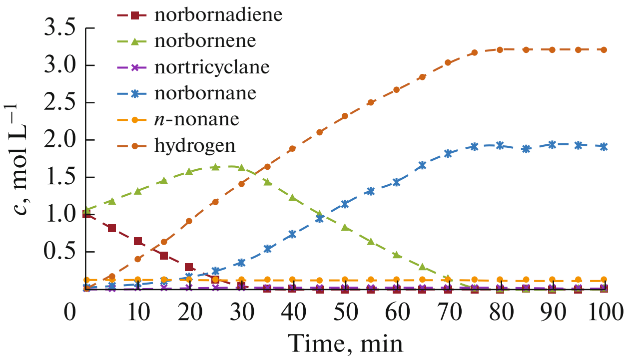
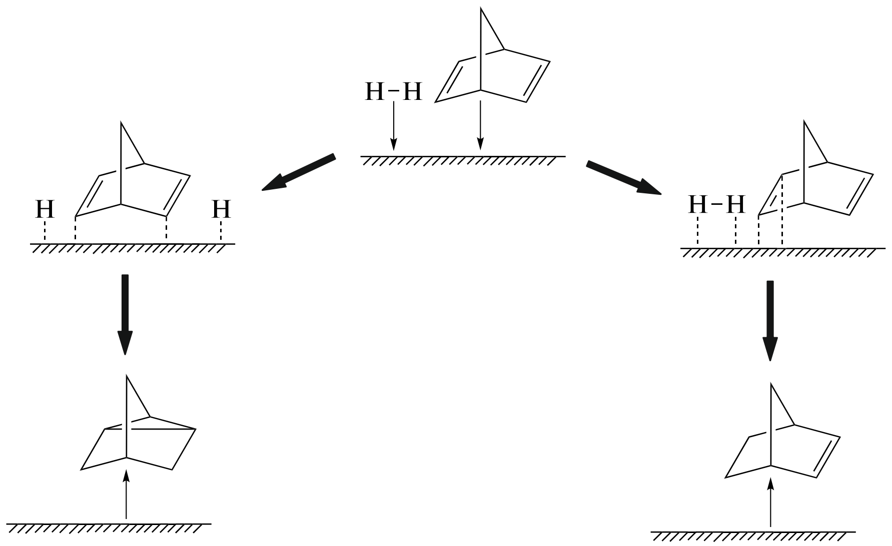


Fig. 2. Kinetic curves of adsorbed hydrogen, NBD, and its hydrogenation products at the equal initial concentrations of NBD and NBEN in entry 8 (Table 5).



Scheme 3.

Additional systematic studies are needed for more substantiated conclusions about the character of NBD coordination on the palladium active sites and steric peculiarities of the hydrogenation of the norbornene derivatives. Since the range of structural features, including those associated with the steric shielding of double bonds, is large for compounds of this class, a specific approach to the development of the catalyst structure and conditions of the process is necessary for each object.

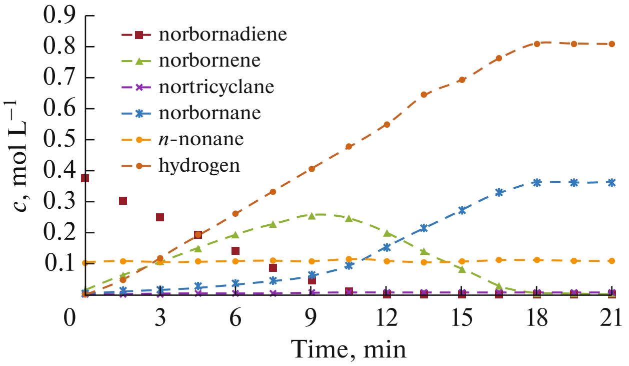


Fig. 3. Kinetic curves of adsorbed hydrogen, NBD, and its hydrogenation products at the NBD concentration decreased by a factor of 2 over that in entries 6 and 7 (Table 5, entry 9).

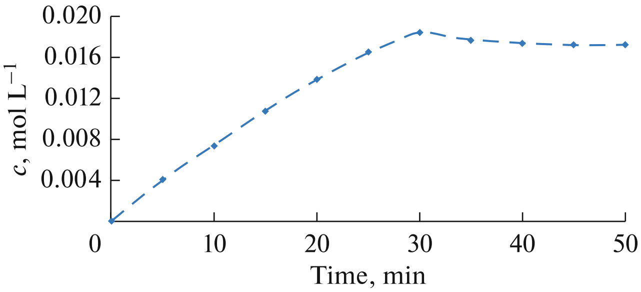


Fig. 4. Regularities of NTAN formation (Table 5).

Further we assume to draw more detailed conclusions about the mechanism of the studied reaction using a structural kinetic model constructed on the basis of a specially planned experiment.

ACKNOWLEDGMENTS

This work was carried out using equipment of the Center for Collective Use of the Russian Technological University MIREA supported by the Ministry of Education and Science of the Russian Federation.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Langmuir, I., *J. Am. Chem. Soc.*, 1918, vol. 40, p. 1361.
2. Masel, R., *Principles of Adsorption and Reaction on Solid Surfaces*, New York: Wiley, 1996.
3. Nishimura, S., *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, New York: Wiley, 2001.
4. Berenblyum, A.S., Danyushevsky, V.Ya., and Katsman, E.A., *Kinet. Catal.*, 2019, vol. 60, no. 4, p. 381.
5. Berenblyum, A.S., Al-Wadhaf, H.A., Katsman, E.A., and Flid, V.R., *Kinet. Catal.*, 2011, vol. 52, no. 2, p. 296.

6. Tagandurdyyeva, N., Maltseva, N.V., Vishnevskaya, T.A., et al., *Fine Chem. Technol.*, 2020, vol. 15, p. 7.
7. Katsman, E.A., Danyushevskii, V.Ya., Shamsiev, R.S., and Flid, V.R., *Teoriya i praktika geterogennykh katalizatorov i adsorbentov* (Theory and Practice of Heterogeneous Catalysts and Adsorbents), Koifman, O.I., Ed., Moscow: URSS, 2020.
8. Moiseev, I.I. and Vargaftik, M.N., Catalysis with giant palladium clusters, in *Perspectives in Catalysis*, Thomas, J.M. and Zamaraev, K.I., Eds., Oxford: Blackwell, 1991, p. 91
9. Moiseev, I.I. and Vargaftik, M.N., *Catalysis by Di- and Polynuclear Metal Complexes*, New York: Wiley, 1998, no. 4, p. 395.
10. Moiseev, I.I., Gekhman, A.E., Tsodikov, M.V., et al., in *Multimetallic Catalyst in Organic Synthesis*, Shibasaki, M., and Yamamoto, Y, Eds., Weinheim: Wiley-VHS, 2004, p. 249.
11. Shamsiev, R.S., Danilov, F.O., and Morozova, T.A., *Russ. Chem. Bull.*, 2017, vol. 66, no. 3, p. 401.
12. Shamsiev, R.S., Danilov, F.O., Flid, V.R., and Shmidt, E.Yu., *Russ. Chem. Bull.*, 2017, vol. 66, no. 12, p. 2234.
13. Berenblyum, A.S., Al'-Vadkhav, Kh.A., and Katsman, E.A., *Neftekhimiya*, 2015, vol. 55, no. 2, p. 125.
14. Berenblyum, A.S., Podoplelova, T.A., Katsman, E.A., et al., *Kinet. Catal.*, 2012, vol. 53, no. 5, p. 595.
15. Katsman, E.A., Danyushevsky, V.Ya., Kuznetsov, P.S., et al., *Kinet. Catal.*, 2017, vol. 58, no. 2, p. 147.
16. Katsman, E.A., Danyushevsky, V.Ya., and Kuznetsov, P.S., *Petroleum Chemistry*, 2017, vol. 57, no. 12, p. 1190.
17. Basimova, R.A., Pavlov, M.L., and Myachin, S.I., *Neftekhimiya*, 2009, vol. 5, no. 5, p. 360.
18. Nazarov, M.V., Laskin, A.I., Il'yasov, I.R., et al., *Kataliz v Promyshlennosti*, 2013, no. 2, p. 39.
19. Stytsenko, V.D. and Mel'nikov, D.P., *Russ. J. Phys. Chem.*, 2016, vol. 90, no. 5, p. 932.
20. Flid, V.R., Gringolts, M.L., Shamsiev, R.S., and Finkelshtein, E.Sh., *Russ. Chem. Rev.*, 2018, vol. 87, p. 1169.
21. Shorunov, S.V., Zarezin, D.P., Samoilov, V.O., et al., *Fuel*, 2021, vol. 283, p. 118935.
22. Catalogue. Redkino Catalyst Company. http://www.recatalys.ru/katalog/.

Translated by E. Yablonskaya