

# Flexibility and Coordination of $M_4$ , $M_9$ , and $M_{19}$ Metal Clusters in Styrene-Divinylbenzene Copolymer in the Absence of Solvent

Alexey V. Bykov\*, Galina N. Demidenko

Tver State Technical University, A. Nikitin str., 22, Tver, 170026, Russia  
 bykovav@yandex.ru

The work is aimed at studying the adsorption of the metal clusters in styrene-divinylbenzene copolymers. The changes in the conformation flexibility of the polymer network in the area of the metal cluster adsorption were studied depending on the temperature in the absence of a solvent. For the first time, the conformational mobility of polymer network in the temperature range of 25-300 °C was calculated for  $M_4$ ,  $M_9$ ,  $M_{19}$  clusters of Pd, Ru, and Ni, based on density functional theory and molecular dynamics methods. The conformational mobility of styrene-divinylbenzene copolymer was found to be strongly limited in the area of cluster adsorption independent of the temperature. The cluster migration in the copolymer network was proved to be impossible in the absence of the solvent in the indicated temperature range.

## 1. Introduction

Styrene-divinylbenzene copolymers and their functionalized analogs are widely used in the modern industry as sorbents, ion-change resins, and materials for hydrogen storage. Another way to use these polymers is the stabilization of heterogeneous metal-containing catalytic systems. For example, Nikoshvili et al. (2022) showed the possibility of the Pd nanoparticles stabilization in aromatic polymers and its application in alkynol hydrogenation. The catalysts on the base of Ru, Pd, and Pt embedded in the pores of hypercrosslinked polystyrenes were effectively used in the hydrogenation (Manaenkov et al., 2023) and oxidation (Manaenkov et al., 2021) of saccharides, in a liquid-phase (Bakhvalova et al., 2021) and supercritical hydrogenation of arenes (Bykov et al., 2020), in the Fischer-Tropsch synthesis (Markova et al., 2023). The similar catalytic systems containing Ni were also studied in the fatty acid conversion into hydrocarbons (Stepacheva et al. 2019). To form such metal-containing catalysts, the reduction of metal from the precursor using hydrogen flow or the precursor pyrolysis in nitrogen flow at temperatures below 300 °C are required. As shown by Bykov et al. (2022), the reduction of metal at temperatures above 300 °C led to the degradation of the network of styrene-divinylbenzene copolymers. Despite the changes in the composition of functional groups and porous structure of the polymers depending on temperature being well studied, the nucleation of metals and the reasons for the formation and stabilizations of small nanoparticles in polymer networks are not fully disclosed. The reduction of metal salts in the rigid polymers allows the fine distributed metal particles with the size of 1-20 nm to be obtained. To understand the metal particle formation, the study of the possibility of metal cluster migration in the styrene-divinylbenzene networks related with the cluster adsorption energy and the conformational mobility of the polymer in the area of cluster adsorption is of great interest. Thus, this work is focused on the study of Pd, Ru, and Ni cluster adsorption in the medium of styrene-divinylbenzene copolymer and the influence of the metal clusters on the conformation mobility of the polymer molecule in the area of its adsorption.

## 2. Computational Methods

All the density functional theory (DFT) calculations were unrestricted and were performed using Orca 5.0.3 (Neese, 2012) package at the BP level of theory. The relativistic effects were taken into account using the zeroth-order regular approximation (ZORA) to the full relativistic Hamiltonian formalism. For C, H, and Ni the

ZORA-def2-TZVP valence triple-zeta basis set was used, including with diffusion and polarized sets. In the case of palladium and ruthenium, an old-ZORA-TZVP basis set was used. During each optimization, the entire structure was allowed to relax. Adsorption energies were calculated as follows (Eq(1)):

$$E_{ads} = E(M_x B_n) - E(M_x) - nE(B) \quad (1)$$

where  $E(M_x B_n)$  - is the energy of the adsorption complex;  $E(M_x)$  - metal cluster energy;  $E(B)$  - is the energy of the benzene molecule.

Cohesion energy was calculated according to Eq(2):

$$E_{coh} = (E(M_n) - nE(M))/n \quad (2)$$

where  $E(M_n)$  - is metal cluster energy,  $E(M)$  - is the energy of metal atom in the ground state.

For the molecular dynamic study, the styrene-divinylbenzene copolymer macromolecule containing 11 mol. % of divinylbenzene was simulated. The divinylbenzene concentration provides the conformation mobility of the molecule as well as allows the molecule to be sufficiently rigid to prevent the micropore collapse. The molecule simulation was based on the principle of dendrimer construction using the repeating block containing divinylbenzene bonded with four chains consisted of two styrene fragments. The central block and the blocks in the layers of dendrimer-like structure were distributed as follows: 1x4x12x36x108x324. The terminal bonds of the macromolecule were occluded by the methyl radicals. The simulated molecule contains 74082 atoms.

The study of metal cluster stabilization and polymer network dynamics was carried out by the molecular dynamic method using DREADING potential (Mayo et al., 1990) in harmonic approximation at NVT-conditions using LAMMPS software (Plimpton, 1995). To describe the interaction of metal-metal in clusters and metal-element (C.sp<sup>2</sup>, C.sp<sup>3</sup>, H.sp<sup>2</sup>, H.sp<sup>3</sup>) between the metal and polymer based on the data of quantum calculations, the Lenard-Jones potentials characterizing the cluster cohesion energy, benzene molecule adsorption on clusters, metal-metal, and metal-C.sp<sup>2</sup> bond lengths were chosen. The cutoff for Lenard-Jones potentials was chosen to be 15.0 Å for all types of interactions. A velocity-Verlet time integrator with a 0.1 fs time step was applied, and temperature were held constant in the NVT ensemble with a Nosé-Hoover thermostat.

### 3. Results and Discussion

The DFT quantum-chemical calculations in the DFT/ZORA/BP universal approximation were carried out to provide the correctness and fullness of the metal-polymer interaction study and calibration of metal-metal interactions in the clusters. M<sub>4</sub>, M<sub>9</sub>, and M<sub>19</sub> clusters for Pd, Ru, and Ni were investigated. The clusters have the form of tetrahedron, two octahedrons with a shared face, and octahedron respectively. The energies of the ground state and proximate upper states were calculated for the clusters in the equilibrium geometry. The mean metal-metal bond lengths in the clusters were estimated (Table 1). The cohesion energies as an energy of the breaking of all bonds in the cluster normalized to one cluster atom, for all studied cluster ground states were calculated. Apart from the state multiplicity, the cluster geometry was allowed relaxing during the calculations. The cohesion energies for the M<sub>4</sub>, M<sub>9</sub>, and M<sub>19</sub> clusters in a ground state were found to be -235.1, -289.8, -331.3 kJ/(mol-atom) for Pd, -396.6, -500.6, -567.5 kJ/(mol-atom) for Ru, and -194.8, -266.5, -308.7 kJ/(mol-atom) for Ni. The cohesion energy predictably increases when the mean coordination number of atoms in the cluster increases.

The calculations showed the differences in the ground states for the clusters containing similar atom number. The proximate upper state in the equilibrium geometry for the clusters of Ru<sub>4</sub>, Pd<sub>9</sub>, Ru<sub>9</sub>, and Ni<sub>19</sub> was found to be the state with the higher multiplicity. For the clusters of Pd<sub>4</sub>, Ni<sub>4</sub>, Ni<sub>9</sub>, Pd<sub>19</sub>, and Ru<sub>19</sub>, the proximate upper state is in contrast characterized by the lower multiplicity. The mean bond length was calculated to be 4.6-4.8 %, and 11.6-12.2 % lower for Ru, and Ni respectively compared to that for Pd in the clusters with the same atom number. An increase in the atom number in the cluster leads to an increase in the mean metal-metal bond length. This correlates well with the data in the literature.

The DFT calibration of the interactions between the metal atom in the clusters and polymer atoms was carried out using the calculated adsorption energies for the benzene rings on the M<sub>4</sub>, M<sub>9</sub>, and M<sub>19</sub> clusters. The adsorption energies and metal-C.sp<sup>2</sup> bond lengths are presented in Table 2. The adsorption of three or more benzene molecules on the small clusters leads to the appearance of benzene rings slope-coordinated with two metal atoms in addition to the plane-coordinated molecules. The metal-C.sp<sup>2</sup> bond length increases by 5-6 % in this case. The data obtained were used for the calibration of Lenard-Jones potentials while describing the metal-C.sp<sup>2</sup> interactions.

To describe the interactions between metal and C.sp<sup>3</sup> atoms, the equality of such interaction for all systems studied was taken into account. The interaction energy for the M<sub>19</sub> cluster was chosen to be the same as for the Pd(111), a.i. 44.5 kJ/mol (Weaver et al., 2010). The potentials obtained above were used to study the

interactions between the styrene-divinylbenzene macromolecule containing 74082 atoms and M<sub>4</sub>, M<sub>9</sub>, and M<sub>19</sub> clusters.

Table 1: Cluster state energies in kJ/mol (multiplicity) and mean metal-metal bond length in Å

Cluster	Pd	Pd <M-M>	Ru	Ru <M-M>	Ni	Ni <M-M>
M <sub>4</sub>	43. (1)		0.0 (1)	2.47	27.8 (1)	
	0.0 (3)	2.59	44.6 (3)		21.1 (3)	
	104.4 (5)		21.6 (5)		0.0 (5)	2.29
			29.8 (7)		45.2 (7)	
M <sub>9</sub>	20.7 (1)		0.0 (1)	2.54	68.8 (1)	
	0.0 (3)	2.66	5.5 (3)		53.9 (3)	
	4.7 (5)		15.4 (5)		49.9 (5)	
			17.5 (7)		32.8 (7)	
M <sub>19</sub>					0.0 (9)	2.34
					36.8 (11)	
	27.1 (3)		7.0 (9)		69.0 (3)	
	16.8 (5)		0.7 (11)		74.2 (5)	
	6.0 (7)		0.0 (13)	2.58	68.4 (7)	
	0.0 (9)	2.71	20.3 (15)		47.9 (9)	
	20.8 (11)				34.1 (11)	
					0.0 (13)	2.38
					0.4 (15)	

Table 2: Benzene molecule adsorption energies on the metal cluster (kJ/mol) and mean M-C.sp<sup>2</sup> bond lengths (Å)

Cluster	n Benzene	M <sub>4</sub>	M <sub>9</sub>	M <sub>19</sub>
Pd	1	-145.9 (2.25)	-116.2 (2.24)	-110.3 (2.24)
	2	-200.4 (2.23)	-326.7 (2.21)	-218.5 (2.25)
	3	-256.6 (2.23, 2.35)	-437.1 (2.21, 2.32)	-330.0 (2.26)
	4	-286.1 (2.23, 2.35)	-515.3 (2.23, 2.32)	-360.3 (2.29)
Ru	1	-234.7 (2.18)	-188.3 (2.22)	-121.6 (2.23)
	2	-330.0 (2.24)	-303.6 (2.20)	-233.5 (2.23)
	3	-449.5 (2.27)	-618.9 (2.24)	-383.7 (2.24)
	4	-495.9 (2.16, 2.21)	-704.3 (2.24)	-489.9 (2.25)
Ni	1	-116.6 (2.05)	-131.9 (2.08)	-135.1 (2.05)
	2	-207.2 (2.19)	-241.0 (2.09)	-276.1 (2.06)
	3	-229.8 (2.08, 2.10)	-329.5 (2.09)	-353.9 (2.07)
	4	-282.4 (2.08, 2.15)	-394.8 (2.10)	-491.6 (2.08)

The macromolecule geometry was smoothed at 300 °C in NVT-conditions for 1000 ps before the studies on the cluster adsorption. In each experiment, 15 M<sub>4</sub> clusters, 10 M<sub>9</sub> clusters, and 5 M<sub>19</sub> clusters of Pd were randomly distributed on the surface and in the internal cavities of the polymer macromolecule. The system was set in equilibrium at 300 °C for 200 ps to provide the cluster capture with polymer and cluster adaptation to the chemical environment. The dynamic of clusters and polymer was recorded for 100 ps at 300 °C. Then the system was cooled down to 25 °C at the rate of 1 °C/ps. The dynamic of clusters and polymer was recorded at 25 °C for 100 ps. The experiment was rerun 10 times. The initial geometry of the Pd clusters was reduplicated for Ni and Ru to provide equal experiment conditions. The estimation of the number of phenyl coordinated with metal clusters (Table 3) allowed the energy of cluster adsorption and the polymer flexibility to be calculated (Figure 1).

Table 3 shows the appearance of both plane- and slope-coordinated phenyl radicals adsorbed on metal clusters for all studied systems at all temperatures investigated. The plane-coordinated adsorption prevails in this case. An increase in temperature from 25 up to 300 °C does not lead to changes in the number of phenyl radicals adsorbed on M<sub>4</sub> clusters which is 2-2.6 depending on the metal nature. This does not correlate with the benzene

adsorption energy but depends on the mean metal-metal bond length. Obviously, the geometric effect of the chemical environment plays the main role for all  $M_4$  clusters at the compared adsorption energies. For  $M_9$  and  $M_{19}$  clusters, the average number of the adsorbed phenyl radicals decreases by 0.1 and 0.2-0.4 for Pd, Ni, and Ru respectively when the system temperature increases from 25 up to 300 °C. The number of the adsorbed phenyl radicals also correlates with metal-metal bond length, but not with benzene adsorption energy. Table 3 shows that the heating of the system leads to both partial desorption of phenyl rings and their re-orientation from plane- to slope-coordinated. This effect is more obvious for Pd with a higher cluster size in contrast to Ni.

The adsorption energy of the metal clusters on the polymer network can be calculated as the multiplication of benzene molecule adsorption energy and the average number of phenyl radicals adsorbed on the metal cluster. The comparison of the data obtained showed that the adsorption energy of  $M_{19}$  clusters on the polymer amounts to 490-550 kJ/mol at 25 °C and decreases by 20-50 kJ/mol when the temperature increases up to 300 °C. Thus, the metal clusters are strongly held by the polymer in the absence of the solvent, and the metal particle migration is frustrated even at 300 °C. The effectiveness of metal precursor distribution in polymer mesopores is critical to provide the synthesis of small metal nanoparticles stabilized in the polymer during the gas-phase reduction or pyrolysis of the precursor.

Table 3: Average number of benzene rings coordinated with metal clusters

Cluster	300 °C	300 °C	300 °C	25 °C	25 °C	25 °C
	Total	Plane	Tilted	Total	Plane	Tilted
Pd <sub>19</sub>	4.8	4.4	0.4	5.0	4.6	0.4
Pd <sub>9</sub>	3.6	2.9	0.7	3.7	3.1	0.6
Pd <sub>4</sub>	2.6	2.0	0.6	2.6	2.1	0.5
Ru <sub>19</sub>	3.6	3.2	0.4	4.0	3.8	0.2
Ru <sub>9</sub>	3.2	2.8	0.4	3.3	2.9	0.4
Ru <sub>4</sub>	2.2	2.1	0.1	2.1	2.0	0.1
Ni <sub>19</sub>	3.6	3.4	0.2	3.8	3.6	0.2
Ni <sub>9</sub>	2.3	2.2	0.1	2.4	2.3	0.1
Ni <sub>4</sub>	2.0	1.7	0.3	2.0	1.9	0.1

The study of the flexibility of polymer network in and out of the area of cluster adsorption was carried out at 25 and 300 °C. For this purpose, the maximum distance of each C.sp<sup>2</sup> atom from the chosen central atom was estimated for each registered system geometry at a chosen temperature of 100 ps. The Deviation parameter was estimated as a difference between the maximum distance and the average spacing from the chosen C.sp<sup>2</sup> atom to the central atom. The Deviation calculation was carried out for all metals studied. The central atom was chosen to be the central atom of the  $M_{19}$  cluster. The calculation of Deviation was also performed for the random C.sp<sup>2</sup> atom of the internal part of the polymer network.

The dependence of the Deviation parameter on the average distance of the C.sp<sup>2</sup> atom from the central atom in the sphere with a radius of 20 Å for all metals and temperatures studied is shown in Figure 1. Figure 1 shows that the thermal vibrations of the polymer network decrease due to the adsorption of phenyl radicals of polymer on the metal clusters independently of the metal nature. An increase in temperature from 25 to 300 °C leads to an increase in the amplitude of thermal vibrations of the polymer matrix in the area of metal cluster adsorption. However, the flexibility observed was found to be lower than that for the polymer matrix free of metal clusters. The quantitative estimation of the Deviation was carried out by the approximation of the data with the logistic function presented in Eq(3). The function chosen allows the data to fit well with the prediction. The values of the approximating function in the sphere with a radius of 20 Å from the central atom are presented in Table 4.

$$y = \frac{a}{1 + \left(\frac{x}{x_0}\right)^b} \quad (3)$$

Obviously, the Deviation value ratio for the polymer free of metal cluster and the polymer containing adsorbed metal cluster remains constant and does not depend on the metal nature for the same temperature. This can be explained by the proximity of the total values of phenyl radical adsorption energies on the metal clusters. Summarizing the absolute values of the Deviation, the divisive tendencies can be observed at low and high temperatures. At 25 °C, the Deviation parameter value decreases in the row of Pd, Ru, and Ni for the areas both free of metal clusters and containing adsorbed clusters. At 300 °C, in contrast, the Deviation parameter value increases in the same row.

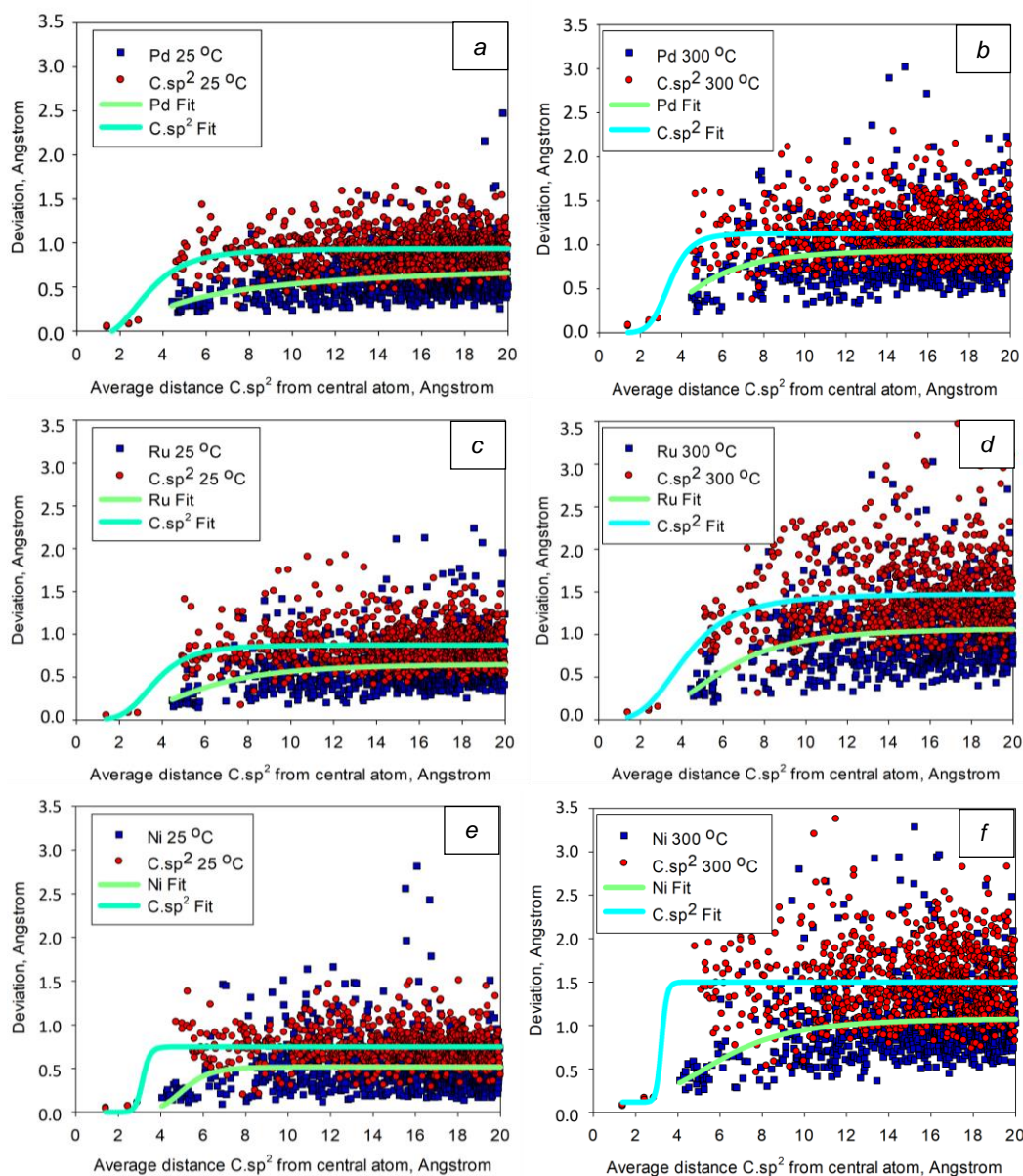


Figure 1: Absolute Deviation values of C.sp<sup>2</sup> atom depending on the average distance from the central atom. Blue dots – central atom is the atom of M<sub>19</sub> cluster, red dots – central atom is C.sp<sup>2</sup> atom of polymer, lines – correlation according to Eq(3)

Table 4: Values of the approximating function in the sphere with a radius of 20 Å from the central atom and its ratio

Central atom:	Metal	Metal	C.sp <sup>2</sup>	C.sp <sup>2</sup>	Metal/Metal	C.sp <sup>2</sup> /C.sp <sup>2</sup>	C.sp <sup>2</sup> /Metal	C.sp <sup>2</sup> /Metal
M <sub>19</sub>	25 °C	300 °C	25 °C	300 °C	300 °C /25 °C	300 °C /25 °C	25 °C /25 °C	300 °C /300 °C
Pd	0.66	0.94	0.94	1.13	1.4	1.2	1.4	1.2
Ru	0.65	1.06	0.88	1.47	1.6	1.7	1.4	1.4
Ni	0.52	1.07	0.75	1.50	2.1	2.0	1.4	1.4

#### 4. Conclusions

In the current work, the coordination of M<sub>4</sub>, M<sub>9</sub>, and M<sub>19</sub> metal clusters of Pd, Ru, and Ni with the network of the styrene-divinylbenzene copolymer in the absence of the solvent was studied using the quantum mechanics and molecular dynamic methods. The adsorption energies of the benzene ring on the metal clusters were shown to

be close for each cluster type. The average number of phenyl radicals adsorbed on the clusters correlated with the metal-metal bond length and metal atom number in the cluster. An increase in temperature from 25 up to 300 °C did not lead to the desorption of metal clusters from the polymer macromolecule. The clusters were found to maintain their chemical environment decreasing slightly the coordination with the polymer phenyl radicals. The coordination of Ni clusters with the phenyl radicals was found to be slightly lower than that for Ru and Pd in the temperature range of 25-300 °C. A decrease in the conformation flexibility of the polymer network caused by the thermal vibrations in the area of metal cluster adsorption was shown. This effect strongly depends on the metal nature but changes simabatically for the polymer in and out of the cluster adsorption area. While using the styrene-divinylbenzene copolymers for the stabilization of metal nanoparticles, the effectiveness of the distribution of metal precursor in the polymer mesopores is critical to obtain small nanoparticles. The significant adsorption of the metal cluster on the polymer network even at high temperatures prevents the cluster migration during the gas-phase reduction or pyrolysis leading to particle aggregation. The data obtained allow to determine the reasons of the metal cluster and nanoparticle stabilization in the medium of aromatic polymers during the gas phase reduction as well as the local tension of the polymer matrix in the cluster adsorption area. The further interest should be focused on the study of the migration of metal clusters in the polymer in liquid medium.

### Nomenclature

C.sp <sup>2</sup> – carbon atom of the benzene ring	H.sp <sup>3</sup> – hydrogen atom of the alkyl chain part
C.sp <sup>3</sup> – carbon atom of the alkane chain	M – metal atom
H.sp <sup>2</sup> – hydrogen atom of the benzene ring	

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### References

- Bakhvalova E.S., Pinyukova A.O., Mikheev A.V., Demidenko G.N., Sulman M.G., Bykov A.V., Nikoshvili L.Z., Kiwi-Minsker L., 2021, Noble Metal Nanoparticles Stabilized by Hyper-Cross-Linked Polystyrene as Effective Catalysts in Hydrogenation of Arenes, *Molecules*, 26(15), 4687.
- Bykov A.V., Nikoshvili L.Z., Demidenko G.N., 2022, Impregnating Noble Metals into the Polymer Matrix of Super Cross-Linked Polystyrene, *Catalysis in Industry*, 14 (2), 157-170.
- Bykov A.V., Alekseeva D.V., Demidenko G.N., Vasiliev A.L., Nikoshvili L.Z., Kiwi-Minsker L., 2022, New Approach to Synthesis of Tetralin via Naphthalene Hydrogenation in Supercritical Conditions Using Polymer-Stabilized Pt Nanoparticles, *Catalysts*, 10, 1362.
- Manaenkov O.V., Kislitsa O.V., Ratkevich E.A., Kosivtsov Y.Y., 2021, Polymeric Catalysts for Oxidation of Cellobiose into Gluconic Acid in Aqueous Medium, *Chemical Engineering Transactions*, 88, 289-294.
- Manaenkov O.V., Nikoshvili L.Z., Bykov A.V., Kislitsa O.V., Grigoriev M.E., Sulman M.G., Matveeva V.G., Kiwi-Minsker L., 2023, An Overview of Heterogeneous Catalysts Based on Hypercrosslinked Polystyrene for the Synthesis and Transformation of Platform Chemicals Derived from Biomass, *Molecules*, 28, 8126.
- Markova M.E., Stepacheva A.A., Matveeva V.G., Sulman M.G., 2023, Structure of Polymer-Stabilized Co-Containing Particles Synthesized in Subcritical Water, *Russian Journal of Physical Chemistry B*, 17(7), 1442–1446.
- Mayo S.L., Olafson B.D., Goddard III W.A., 1990, DREIDING: A Generic Force Field for Molecular Simulations, *Journal of Physical Chemistry*, 94, 8897-8909.
- Neese F., 2012, The ORCA program system, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2(1), 73-78.
- Nikoshvili L.Z., Popov A.Y., Bykov A.V., Sidorov A.I., Kiwi-Minsker L., 2022, Pd-Nanoparticles within Polymeric Network in Selective Hydrogenation of Alkynols: Influence of Support Porosity, *Molecules*, 27, 3842.
- Plimpton S.J., 1995, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *Journal of Computational Physics*, 117, 1-19.
- Stepacheva A.A., Markova M.E., Matveeva V.G., Sulman M.G., Sulman E.M., 2019, Novel Catalyst Synthesized by Hydrothermal Method for Fatty Acid Conversion into Hydrocarbons, *Chemical Engineering Transactions*, 74, 223.
- Weaver J.F., Hakanoglu C., Hawkins J.M., Asthagiri A., 2010, Molecular adsorption of small alkanes on a PdO(101) thin film: Evidence of  $\sigma$ -complex formation, *Journal of Chemical Physics*, 132, 024709.