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Polymerization and Catalytic Properties of Cluster-Containing Monomers and Polymers

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Summary: Cluster-containing monomers were obtained and characterized. Mono- and disubstituted products were obtained under mild conditions via the interaction of $Rh_6(CO)_{16}$ with 4-vinylpyridine (4-VPy). Substitution of labile acetonitrile ligand in $Rh_6(CO)_{15}NCMe$ by allyldiphenylphosphine ($AlPPh_2$) yields $Rh_6(CO)_{14}(\mu,\eta^2$-$PPh_2CH_2CH{=}CH_2)$ with formation of π-complex. The copolymerization of cluster-containing monomers synthesized with traditional monomers has been studied. It was found that Rh_6- containing monomers change neither the ligand surroundings nor the structure of cluster monomer framework during polymerization reaction. Polymer-immobilized clusters were found to be active in hydrogenation reactions of cyclohexene.

Keywords: 4-vinylpyridine; allyldiphenylphosphine; hydrogenation; radical polymerization; Rhodium carbonyl custers

Introduction

The metal cluster complexes with ligands capable to polymerization are of interest because of the peculiarities of their structure determined by the presence of double bonds. Also, on the base of such clusters the potential polymer-immobilized catalysts of numerous reactions for basic organic synthesis can be constructed.[1,2] There are two main approaches to synthesis of the cluster-containing monomers: i) via increasing the nuclearity of traditional metal-containing monomers; and ii) by introducing a polymerizable fragment into common type of clusters with well-defined structure.[3] The latter procedure was used, for example, in the synthesis of cluster-containing monomers based on Co and Fe carbonyls and methyl ether of n- vinyldithiobenzoic acid or N-cyclohexyl-4-vinylthiobenzamide.[4] Recently we have elaborated the method to introduce the unsaturated allyldiphenylphosphine ligand ($P(CH_2CH{=}CH_2)Ph_2$) into the osmium cluster [μ-H)Os_3(μ-$OCNMe_2$)$(CO)_9$L] (R′=H, Alk; R″;=Alk, Ar; L=CO, amine, phosphine and other 2-e ligand).[1]

In particular, introducing of a polymerizable group is more important in the case of Rh_4 and Rh_6 rhodium clusters types. The $Rh_6(CO)_{16}$ (**I**) cluster is known to be one the most tolerant carbonyl clusters with respect to the substitution with various organic ligands. The rhodium clusters are the effective immobilized catalysts (especially, phosphorous-containing ones[5]) for hydrogenation, hydroformylation, and other reactions.[6] The aim of this work was the study of radical copolymertization carbonyl rhodium clusters with 4-vinylpyridine **(4-VPy)** or allyldiphenylphosphine (**AllPPh$_2$**) with styrene and catalytic properties of the polymer-immobilized rhodium clusters in the catalytic hydrogenation of a model substrate – cyclohexene. The ligands were choozen because 4-VPy is characterized by pronounced basicity and high polymerization ability, therefore copolymers with a high rhodium content can be obtained. The $AllPPh_2$ ligand is less reactive in

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copolymerization reactions from the degradation chain transfer that allows one to produce the copolymers with a small content of rhodium, so called low percent rhodium catalysts.

Results and Discussion

Preparation and Structure of $Rh_6(CO)_{15}$(4-VPy) (II) and $Rh_6(CO)_{14}(4\text{-}VPy)_2$ (III)

The reaction of $Rh_6(CO)_{16}$ with 4-VPy in the presence of N-trimethylaminoxide proceeded under mild conditions and resulted in the oxidation of coordinated CO to CO_2:

$$Rh_6(CO)_{16} + 4 - VPy$$

$$\xrightarrow[-CO_2]{Me_3NO} \begin{cases} Rh_6(CO)_{15}(4{-}VPy) \\ \quad\quad\quad \mathbf{II} \\ Rh_6(CO)_{14}(4{-}VPy)_2 \\ \quad\quad\quad \mathbf{III} \end{cases}$$

The main product of this reaction was the monosubstituted derivative $Rh_6(CO)_{15}$(4-VPy) (**II**). The disubstituted compound $Rh_6(CO)_{14}(4\text{-}VPy)_2$ (**III**) was also produced in a small quantity. Compounds **II** and **III** can be easily separated chromatografically and isolated as individual species.

The molecular structure of compound **II** was studied in our previous work.[7]

The structure of **II** is an octahedral cluster of Rh atoms with eleven terminal and four μ_3-bridging CO ligands. The 4-VPy substituent is linked to the Rh(3) atom and occupies the coordination site of the twelfth CO terminal ligand. The Rh–Rh bond lengths are within 2.736–2.787 Å (the mean value is 2.762 Å). The geometric parameters of the μ_3-bridging CO ligands reveal a distinct asymmetry in the distribution of the Rh–Rh bond lengths caused by the non-equivalence of Rh atoms in the cluster due to the substitution of a 4-VPy ligand for a terminal CO ligand at the Rh(3) atom.

Though an alkene group can, in principle, replace a terminal CO group in the parent $Rh_6(CO)_{16}$ cluster and form a π-complex, the vinyl group in **II** is in the plane of the pyridine ring and does not interact with the rhodium cluster. The length of the double C=C bond is within its normal range (1.32(3) Å.

Spectral parameters of compounds **II** and **III** are listed in Table 1. The frequencies and relative intensities of IR absorption bonds in the carbonyl region of compounds **II** (2104, 2068, 2038, 1788 cm^{-1}) and **III** (2090,2056, 2028, 1760 cm^{-1}) are the same as the relevant parameters for the derivatives of the parent cluster.[8] ^1H NMR spectra of **II** and **III** contain multiplet signals from the α- and β-protons in the pyridine cycle AA′BB′ spin system) and relevant signals from the vinyl protons; the overall ratio of intensities is 2:2:1:2 (Table 1).

Preparation and Structure of $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$ (IV)

The reaction of selective replacement of the CO group in **I** by $AllPPh_2$ was performed in two stages. At the first stage, by analogy with a know procedure,[9] the $Rh_6(CO)_{16}$ cluster in chloroform in the presence of acetonitrile was converted into its monosubstituted derivative containing a labile ligand, *viz.*, acetonitrile, under photochemical excitation

Table 1.
Spectral characteristics of $Rh_6(CO)_{15}$(4-VPy) (**II**) and $Rh_6(CO)_{14}(4\text{-}VPy)_2$ (**III**).

Compound	IR spectrum ($CHCl_3$)		^1H ($CDCl_3$)
	ν(CO), cm^{-1}	ν(C=C), cm^{-1}	δ
II	2104(w), 2068(s), 2038(av), 2010(sh), 1788(av.w)	1619(av)	7.39 (m, 2 H-α); 8.88 (m, 2H-β); 6.68 (dd, 1H, $-CH{=}CH_2$, J = 10.74, 17.58 Hz); 6.10 dd 1H, $-CH{=}CH_2$, J = 17.54 Hz); 5.68 (dd, 1H, $-CH{=}CH_2$, J = 10.81 Hz)
III	2090(w), 2056(s), 2028(av), 1760(av.w)	1619(av)	7.35 (m, 2H-α); 8.81 (m, 2H-δ); 6.65 (m, 1H, $-CH{=}CH_2$); 6.06 (dd, 1H, $-CH{=}CH_2$, J = 10.89 Hz); 5.63 (dd, 1H, $-CH{=}CH_2$, J = 10.89 Hz)

(UV radiation, $\lambda > 300$ nm).

$$Rh_6(CO)_{16} + MeCN \xrightarrow{h\nu} Rh_6(CO)_{15}NCMe + CO \ (V)$$

Photoreaction made it possible to prepare $Rh_6(CO)_{15}NCMe$ (V) in quantitative yield. As expected, at the second stage of the synthesis, the reaction of $AlPPh_2$ with **V** proceeded under mild conditions at room temperature:

$$Rh_6(CO)_{15}NCMe + PPh_2CH_2CH{=}CH_2 \rightarrow Rh_6(CO)_{15}PPh_2CH_2CH{=}CH_2{+}MeCN$$

The IR-spectroscopy and TLC-monitoring of the reaction showed that at first the intermediate complex $Rh_6(CO)_{15}(\eta^1\text{-}PPh_2CH_2CH{=}CH_2)$ (**VI**) was formed. Thus, the carbonyl region of the IR spectrum of the reaction mixture had absorption bands at 2104, 2068, 2039, and 2017 (t-CO) and 1790 cm^{-1} (μ-CO) corresponding to the monosubstituted derivative **I**. In addition, a band at 2294 cm^{-1} corresponding to the CN stretching vibration of the coordinated acetonitrile molecule disappeared. The presence of the reactive $AlPPh_2$ ligand, which exhibits bidentate properties owing to the presence of the double bond, in the coordination sphere of the carbonyl cluster resulted in the formation of the final product $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$ **IV** with an additional coordination.

The molecular structure of compound **IV**[10] is shown in Figure 1.

Compound **IV** is an octahedral Rh cluster containing ten terminal and four μ_3-bridging CO ligands. The $PPh_2CH_2CH{=}CH_2$ ligand is attached to the Rh(2) atom (Rh(2) –P 2.311(3) Å). This ligand is also coordinated to the cluster through the Rh(4)...C=C interaction between the unoccupied d-orbital of the Rh atom and the bonding π-orbital of the double bond (Rh(4) – C(232) 2.37(1) Å and Rh(4) –C(233) 2.32(2) Å).

It should be noted that this coordination of vinylphosphine ligands is observed in many carbonyl cluster complexes. Interestingly, this coordination bond can be readily cleaved, for example, upon heating or treatment with CO, as was observed in the case of the vinylphosphine isomers

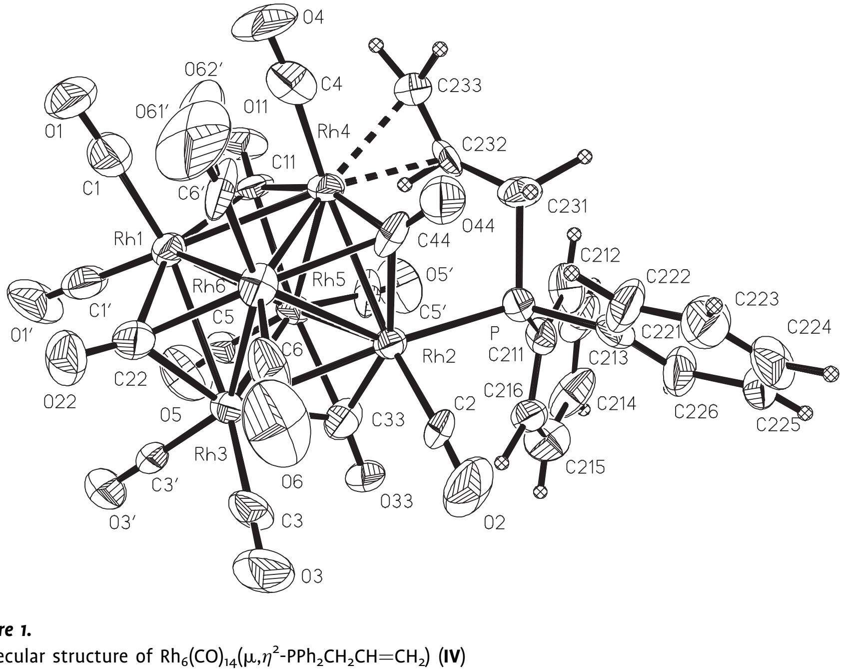


Figure 1.
Molecular structure of $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$ (**IV**)

$[Co_3(\mu_3\text{-}CR)(CO)_7(\mu\text{-}PPh_2CH{=}CH_2)]$.[11] Analogous conversions as well as other types conversions also occur in a solution of compound **IV** apparently, due to activation of the ligand in the coordination sphere of the rhodium atom. Thus, the ^1H NMR spectrum of complex **IV** was complicated, which made its interpretation rather difficult.

Copolymerization of Cluster-Containing Monomers with Styrene

The specific character of cluster-containing monomers reveals through polymerization reactions. As a rule, the homopolymerization proceeded hardly. Only oligomer products of low yields were formed. At the same time, these monomers were very active in copolymerization reactions with common monomers (styrene, methylmethacrylate, acrylonitrile). Here we consider the copolymerization reactions of cluster-containing monomers **II-IV**.

Copolymerization of $Rh_6(CO)_{15}(4\text{-}Vpy)$(II) with Styrene

Radical copolymerization of $Rh_6(CO)_{15}(4\text{-}VPy)$ **(II)** with styrene in benzene in the presence of azobisisobutyronitrile (AIBN) resulted in copolymer products with rhodium content of 0.29 to 3.3 wt.% and relatively low yield (25%) (Table 2).

IR spectra of copolymers obtained revealed the bands corresponded to stretching frequencies of terminal (t-CO) (2101 w., 2063 s., 2038 m., 2010 sh, cm^{-1}) and bridge (μ-CO) (1793 m.br. and 1601m, cm^{-1}) carbonyl groups of the molecule **II** that proved the retention of a cluster skeleton of the starting cluster monomer during copolymerization.

Copolymerization of $Rh_6(CO)_{14}(4\text{-}VPy)_2$ (III) with Styrene

Copolymerization of $Rh_6(CO)_{14}(4\text{-}VPy)_2$ **(III)** with styrene in benzene yielded copolymers containing rhodium of 2.1 to 9.3%. The products obtained were characterized by elemental analysis and IR spectroscopy. Thus, IR spectra have the bands corresponded to stretching frequencies of pyridine ring (1602 s, 1452, 757, 689 cm^{-1}), μ-CO (1785 cm^{-1}) and t-CO (2052 cm^{-1}) groups. The composition of copolymers depended on the composition of the starting monomer mixture (Table 3). The products were soluble in tetrahydrofuran, toluene.

Molecular-weight characteristics for copolymer **5Rh** was found to be $\overline{M}_n = 46100$, $\overline{M}_w = 109100$, $M_w/M_n = 2.37$.

Copolymerization of $Rh_6(CO)_{14}P(C_6H_5)_2CH_2CH{=}CH_2)$ (IV) with Styrene

As shown in Tables 2 and 3, copolymerization of styrene with the monomers **II** and **III** gave the products with relatively high content of Rh. With aim to obtain the low percent rhodium catalysts, Rh- containing monomers bearing polymerizable allylic groups can be used. Copolymerization of styrene with the cluster monomer $Rh_6(CO)_{14}PPh_2Allyl$ **(IV)** was carried out in bulk, the concentration of **IV** in a monomer mixture did not exceed 1 mol. % from its poor solubility in styrene. The analysis of kinetic curves showed the cluster monomer within the studied concentration range had no effect on the rate of styrene polymerization (Figure 2).

The molecular weights of the copolymers decreased with the increase of the cluster comonomer content in the reaction mixture (Table 4).

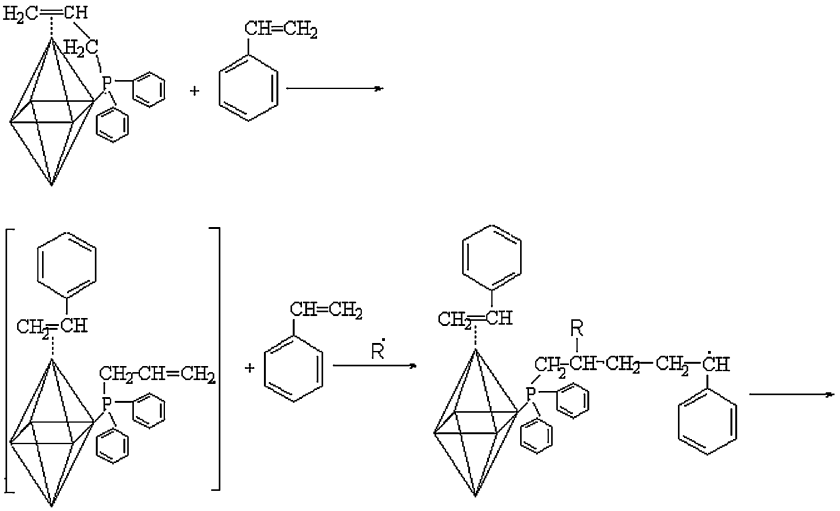
Table 2.
The content of $Rh_6(CO)_{15}(4\text{-}VPy)$ (**II**) in a monomer mixture and copolymers (60 °C, 2 wt.% AIBN, benzene).

Copolymer	The content of **II** in a monomer mixture (mol. %)	The content of cluster units in copolymer (mol. %)	The content of Rh in copolymer (wt. %)
1Rh	0.04	0.05	0.29
2Rh	0.24	0.15	1.03
3Rh	2.90	0.18	1.10
4Rh	4.90	0.57	3.27

Table 3.
The compositions of the monomer mixture and copolymers.

Copolymer	The content of **III** in a monomer mixture (mol. %)	The content of cluster units in copolymer (mol. %)	The content of Rh in copolymer (wt. %)
5Rh	3.0	2.0	9.3
6Rh	1.2	0.7	4.2
7Rh	0.7	0.4	2.1

This is apparently caused by a specificity of chain transfer reaction due to a cluster nature of comonomer. Styrene can be also an agent of chain transfer reaction. The ratio of growth and chain transfer reaction rates was equal to 0.2–0.4. Copolymerization of **IV** with styrene allowed one to demonstrate the specificity of polymerization transformations of cluster-containing monomers. As shown, the double bond in the molecule **IV** took part in π-coordination with Rh atom of a cluster skeleton. Such a bond may be involved in polymerization, if its "liberation" occurs in a coordination sphere of the cluster core, for example, on the route of π-intercoordination with styrene molecule:



It should be noted the yield of copolymer was decreased but the content of cluster units in the copolymer chain was increased (from 0.4 to 1.4 wt.% Rh) when the copolymerization reaction of **IV** with styrene was carried out in solution. In principle the similar results were obtained at copolymerization of cluster-containing monomers with another monomers such as acrylonitrile, methylmethacrylate, acrylic acid. The presence of bands at stretching frequencies 1792 (μ-CO), 2058 (t-CO), 1942, 1439, 1004 cm^{-1} (P-C) in the IR spectra indicated that no changes of the cluster monomer were observed after its incorporation into copolymer chain.

Synthesis of Cluster-Containing Polymers via Polymer-Analogous Reactions

The synthesis of cluster-containing monomers is often coupled with difficulties, therefore the alternative ways for preparation of cluster-containing polymers, namely, known methods of polymer-analogous transformations of macroligands containing reactive functional groups are also used.[12] These reactions concern only the side

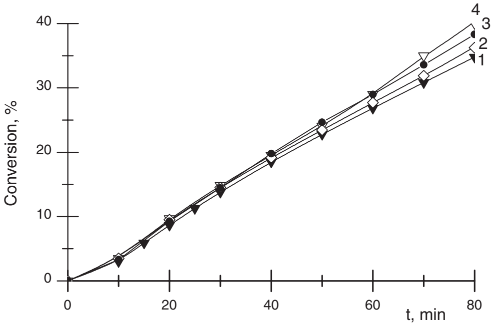


Figure 2.

Percentage conversion versus time plot for polymerization of styrene (1) and comonomer mixture of styrene with 0.1 (2), 0.5 (3) and 1 mol.% (4) of $Rh_6(CO)_{14}(\mu,\eta^2\text{-}CH_2CH{=}CH_2)\,P(C_6H_5)_2$. The conditions of polymerization: in bulk, 60 °C, 0.6 mol.% of AIBN.

groups not backbone of polymer chain. As for binding rhodium clusters the methods of competing ligands are utilized, the functional groups of macroligands can substitute one of the groups in the cluster $Rh_6(CO)_{15}NCMe$ (**V**). With this aim, the copolymers of styrene with 4-vinylpyridine or diphenylphosphoallyl as macroligands to bind the rhodium cluster were synthesized.

Copolymerization of 4-vinylpyridine with Styrene

Copolymers of 4-vinylpyridine with styrene were obtained by radical copolymerization in bulk in the presence of AIBN. The products were light-beige and soluble in tetrahydrofuran. The composition of copolymers depends on the composition of the starting monomer mixture (Table 5).

Copolymerization of Allyldiphenylphosphine with Styrene

The copolymers were obtained by radical copolymerization of the monomers at temperature 58 °C in the presence of AIBN (0.5 wt.%) (Table 6).

Synthesis of Polymer-immobilized Complexes

Synthesis of polymer-immobilized clusters via polymer-analogous reactions of copolymers of styrene with 4-VPy. Macrocomplexes

Table 4.

Copolymerization of the cluster monomer $Rh_6(CO)_{14}(\mu,\eta^2\text{-}CH_2{=}CHCH_2PPh_2)$ (**IV**) with styrene (in bulk, 70 °C, 0.6 mol.% AIBN).

Copolymer	The content of **IV** in the monomer mixture (mol. %)	The content of cluster units in copolymer (mol. %)	The content of Rh in copolymer (wt. %)	$\overline{M}_n$
8Rh	0,04	0.02	0.09	56600
9Rh	0.08	0.1	0.6	33000
10Rh	1.0	1.0	0.5	**
11Rh*	1.0	1.4	1.4	**

*In toluene.
**No measured

Table 5.

The molar ratio of 4-vinylpyridine (VPy) (m_1) and styrene (m_2) units in the copolymer and molecular-weight characteristics of the products obtained.

Copolymer	The 4-VPy: styrene in copolymer (mol. %)	$\overline{M}_n$	$\overline{M}_w$	M_w/M_n
1VPy	60:40	208000	349000	1.68
2VPy	30:70	148000	261000	1.76
3VPy	22:78	168000	327000	1.95
4VPy	8:92	150000	286000	1.91

Table 6.
The molar ratio of allyldiphenylphosphine ($AllPPh_2$) (m_1) and styrene (m_2) units in the copolymer and molecular-weight characteristics of the products obtained.

Copolymer	The $AllPPh_2$: styrene in copolymer (mol.%)	$\overline{M}_n$	$\overline{M}_w$	M_w/M_n
1 $AllPPh_2$	46:54	9600	26200	2.70
2 $AllPPh_2$	22:78	20700	52900	2.55
3 $AllPPh_2$	10:90	25600	95600	3.73
4 $AllPPh_2$	2:98	80000	169000	2.11

were obtained by the interaction of $Rh_6(CO)_{15}CH_3CN$ with copolymers of styrene with 4-VPy in benzene solution. The macrocomplex formed was isolated by the precipitation with methanol, ether or heptane. The copolymers with content of Rh from 3.1 to 6.1 wt.% (Table 7) were obtained.

Synthesis of polymer-immobilized clusters via polymer-analogous reactions of copolymers of styrene with $AllPPh_2$. The immobilized clusters were obtained by similar interactions of $Rh_6(CO)_{15}CH_3CN$ and copolymers of allyldiphenylphosphine with styrene. The reaction was carried out in benzene. The copolymers with content of Rh from 1.8 to 4.1 wt.% (Table 6) were obtained. The molecular weight of macrocomplex was lower than that for the starting copolymer ($\overline{M}_n = 56000$, $\overline{M}_w = 140000$, $M_w/M_n = 2.50$ and $\overline{M}_n = 80000$, $\overline{M}_w = 169000$, $M_w/M_n = 2.11$, respectively).

Catalytic Properties of Rh_6-containing Clusters in Hydrogenation Reactions

The chemical binding of metallocomplexes with polymers is a way for heterogenization of common homogeneous catalysts. The advantages of such an approach are summarized in detail in monograph.[2] Hydrogenation of cyclohexene is a simple model hydrogenation reaction.

Hydrogenation of Cyclohexene in the Presence of Rh_6-containing Copolymers

Hydrogenation of cyclohexene in the presence of the copolymers **12Rh–15Rh** shows that a specific catalytic activity of the catalyst ($1.3{\cdot}10^{-5}$ g-at. of Rh, 0.1mol/L substrate, solvent – isopropyl alcohol, 40 °C) in the first cycle is equal to 0.01 mol/g-at. of Rh s. In the following cycles of hydrogenation the catalyst is “trained”. Such a behavior is typical for common heterogeneous catalysts. In the second cycle the rate of reaction increases up to 0.03 mol/g-at. of Rh s and the catalyst can be easily isolated by filtration from the reaction medium. Practically, the same peculiarities were observed in the case of catalysts based on diphenylphosphoallyl **(8Rh – 11Rh)**.

Hydrogenation of Cyclohexene in the Presence of the Macromolecular Complex on the Base of $Rh_6(CO)_{15}CH_3CN$ and Copolymer of Styrene and $AllPPh_2$

The effectiveness of polymer-immobilized cluster catalysts were compared with traditional heterogeneous catalysts. Thus, the

Table 7.
The composition of macrocomplexes based on the rhodium clusters immobilized onto copolymer styrene with 4-VPy or $AllPPh_2$.

Macro-complex	The 4-VPy: styrene in copolymer (mol. %)	Rh (wt. %)	Macro-complex	The $AllPPh_2$: styrene in copolymer (mol.%)	Rh (wt. %)
12Rh	60:40	12.75	16Rh	46:54	1.8
13Rh	30:70	6.11	17Rh	22:78	2.9
14Rh	22:78	4.15	18Rh	10:90	3.18
15Rh	8:92	3.15	19Rh	2:98	4.16

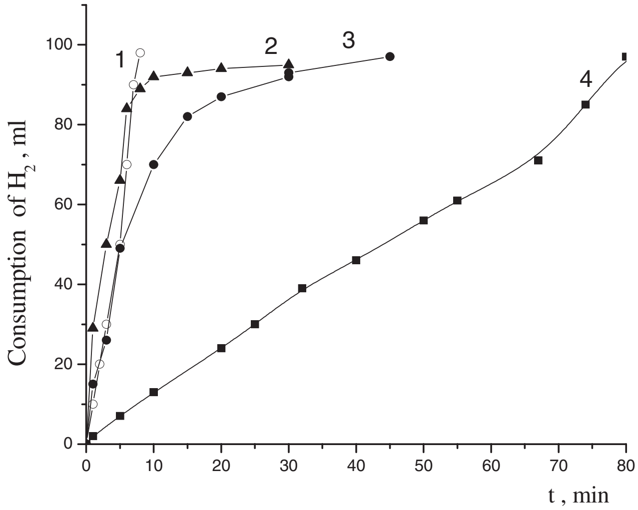


Figure 3.
The kinetic curves of cyclohexene hydrogenation in the presence of catalysts: 1-Rh/C, 2- copolymer of styrene with $Rh_6(CO)_{14}(4\text{-}VPy)_2$ (5Rh), 3- the $Rh_6(CO)_{15}CH_3CN$ immobilized onto copolymer of styrene with $AllPPh_2$ (19Rh), 4 – copolymer of styrene with $Rh_6(CO)_{15}(4\text{-}VPy)$ (4Rh). The reaction conditions: 40 °C, 4.5 mmol of cyclohexene, $P(H_2) = 1$ atm, $3.9 \cdot 10^{-5}$ g-at of Rh, isopropyl alcohol.

special experiments with Rh/C (1% Rh) catalyst showed that its specific activity is 0.1 mol. of H_2/g-at. of Rh s.

As shown, the activity of polymer-immobilized catalysts under studied is comparable with the most active heterogeneous catalysts (Figure 3). The comparison analysis of curves 3 and 4 confirms the well-know fact about the more stabilizing ability of phosphine ligands than for vinylpyridine ones for Rh-intermediates.

Besides, also the low molecular weight analogs – $Rh_6(CO)_{16}$ (**I**) and $Rh_6(CO)_{15}CH_3CN$ (**V**) were tested as catalysts (Figure 4). In the case of **V** the initial specific rate in the first cycle was low (0.006 mol/g-at. of Rh·s), at the second and next cycles the rate increased up to 0.07 mol/g-at. of Rh·s, i.e., an induction time is necessary for formation of catalytic centers. The repeating use of the catalyst led to an increase of the hydrogenation rate and disappearance of the induction time (Figure 4). The hydrogenation of cyclohexene in the presence of **I** proceeded otherwise. In the first loading of the substrate the rate of hydrogenation is 0.05 mol/g-at. of Rh·s and then it does not change.

Catalysts on the base of $Rh_6(CO)_{15}CH_3CN$ immobilized on copolymer of styrene with $AllPPh_2$ revealed a high catalytic activity. Although in the first loading for the catalyst with 4.16% Rh the initial rate was low (0.02 mol/g-at. of Rh·s), in the next cycles the rate increased up to 0.4 mol/g-at. of Rh·s (Figure 5). The polymer catalysts changed in color from beige to gray. As mentioned above the same behavior is typical for polymer-immobilized catalysts[2] and caused by so called "training" of catalyst.

In contrast to homogeneous systems, heterogenation of clusters allowed one to isolate the catalyst from reaction medium and use it again in new catalytic cycles. Also, that is very important, it is possible to give some experimental proofs concerning the character of catalytic intermediates. IR spectra of polymer cluster after hydrogenation exhibit the bands corresponded to (t-CO) 2066; (μ-CO) 1794, 1802, (P-Ar) 1452 cm^{1} stretching. The repeat using of washed and dried catalyst showed that its activity was well preserved and even increased. It should be noted the same peculiarities were observed in the case of Os_3 polymer-immobilized clusters in

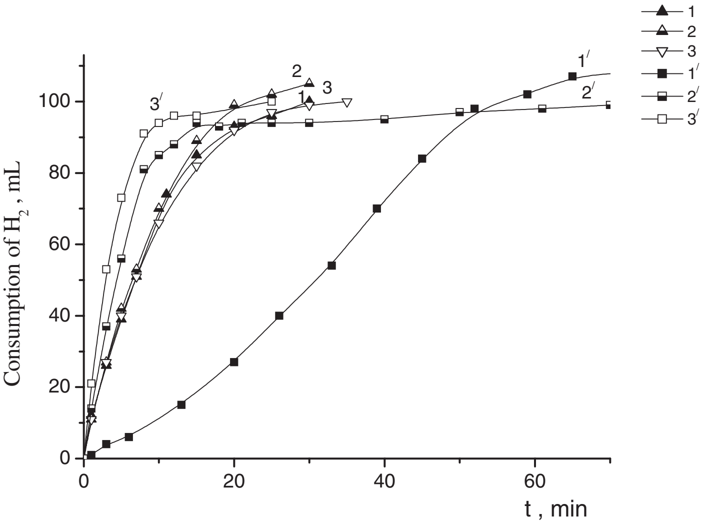


Figure 4.
The kinetic curves of cyclohexene hydrogenation in the followed cycles in the presence of $Rh_6(CO)_{16}$ ($1.2 \cdot 10^{-4}$g-at. of Rh) (1,2,3) and $Rh_6(CO)_{15}CH_3CN$ ($1.2 \cdot 10^{-4}$ g-at. of Rh (1′,2′,3′). The reaction conditions: 40 °C, 4.5 mmol. of cyclohexene, $P(H_2) = 1$ atm, 3.9 10^{-5} g-at. of Rh, isopropyl alcohol. The number of curves corresponds to the run.

oxidation of cyclohexene.[13] These results permit one to suppose the mechanism of hydrogenation with systems analyzed. Thus, the presence of induction period, training of catalyst in subsequent cycles, changing in its color as well as the possibility to use the catalyst in repeat cycles can indicate that cluster undergoes the fragmentation during hydrogenation with formation of high active particles of low concentration, and apparently, of high nuclearity (nano-scale) which may be true

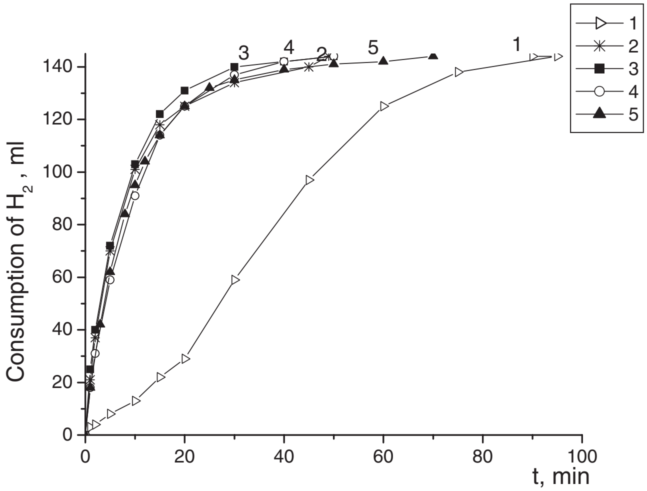


Figure 5.
The kinetic curves of hydrogenation of cyclohexene in the presence of the $Rh_6(CO)_{15}CH_3CN$ immobilized onto copolymer of styrene with $AllPPh_2$ (19Rh). The reaction conditions: 40 °C, 4.5 mmol. of cyclohexene, $P(H_2) = 1$ atm, 3.9 10^{-5} g-at. of Rh, isopropyl alcohol. The number of curves corresponds to the run.

catalysts. Such assumption is also based on that Rh_6 carbonyl clusters have no coordination vacancies to bind hydrogen or substrate. In accordance with the modern concepts, the active centers in immobilized catalysts are localized on the boundaries of cluster formations and stabilized by their electron systems.[2] It should be noted, such systems are dynamical species, their concentration can be varied in the course of activation of the immobilized complex. Thus, the activity of polymer-immobilized mononuclearic complex of Rh increased with decarbonylation degree of Rh and formation of metal centers including $Rh^0{}_n$.[14] Under favorable conditions (for example, the presence of macromolecular ligands prevented the aggregation of cluster particles) super-equilibrium concentration of the active states can occur. This is indirectly confirmed by comparison of the IR spectra of copolymer complexes before and after hydrogenation: the decrease of intensity and shift of stretching in the range of terminal and bridge carbonyl groups frequencies were observed.

The formation of such active intermediates was also confirmed by XPS study. Thus, after first cycle of the catalytic reaction the shift of low-energy line in $Rh3d_{5/2}$ spectra of macromolecular cluster **19Rh** to 308.2 eV and appearance of a new line at 311 eV were observed. In accordance with,[15] the line of E_{bond} $Rh3d_{5/2}$ 308.2 eV may be attributed to Rh atoms bonded with the H(CO) group. An appearance of the line at 311 eV indicated that the Rh atoms with more large positive charge were originated after 1-st cycle of hydrogenation. It should be noted that hydrogenation led to a decrease of the intensity of the major line ($E_{bond} = 309.9$ eV) in $Rh3d_{5/2}$-spectra and growth of a low-energy component of the spectra with $E_{bond} = 308.2$ eV. The relative intensity of the low-energy line for the starting polymer-immobilized cluster 19Rh before hydrogenation was equal to 22%, in the first cycle it was 32%, after the second cycle – 57%. The catalytic activity of the complex analyzed changes simbate with the number of Rh atoms both ones bonded with the H(CO) group and having the more large charge. It is important the polymer chain itself bonded with the cluster fragment, apparently, does not undergo any changes. This is confirmed by molecular-weight characteristics of the macrocomplexes before ($\overline{M}_n = 56000$, $\overline{M}_w = 140000$, $\overline{M}_w/\overline{M}_n = 2.50$) and after hydrogenation ($\overline{M}_n = 54000$, $\overline{M}_w = 127000$, $\overline{M}_w/\overline{M}_n = 2,34$).

Conclusion

The rhodium clusters with unsaturated ligands $Rh_6(CO)_{14}(4\text{-}VPy)_2$ and $Rh_6(CO)_{14}P(C_6H_5)_2CH_2CH{=}CH_2$ are octahedron in which ligands occupy coordination sites of carbonyl groups. An unsaturated ligand have no noticeable effect on the geometry of the starting cluster $Rh_6(CO)_{16}$ and allyldiphenylphosphine is additionaly coordinated with a metal center with formation of π-bond. Such clusters are convenient monomers for copolymerization with styrene, they retained the ability to opening the double bond. Radical polymeization of such monomers resulted in copolymers with rhodium contents of 0.29 to 3.3 wt.%. The remaining of carbonyl skeleton at incorporation of monomer into a polymer chain was confirmed. An alternative way is polymer-analogous reactions with participation of rhodium clusters containing easily substituted ligand. Immobilized catalysts based on Rh_6 showed a high catalytic activity in cyclohexene hydrogenation. In contrast to homogeneous systems, heterogenation of clusters allowed to isolate the catalyst from a reaction medium and use it again in new catalytic cycles as well as to obtain some proofs about the catalytic intermediates.

Experimental Part

Syntheses were performed under argon. Solvents were purified by standard methods prior to use. Infrared spectra were recorded in $CHCl_3$ or from KBr pellet on a Specord

M-80 spectrometer. ^{1}H NMR spectra were obtained on a Bruker AC-200 instrument using $CDCl_3$ as solvent. Preparative thin-layer chromatography (TLC) was carried out on commercial Silufol plates (Chemapol). XP spectra were registered on a ES-2401 spectrometer with the Mg anode. The power of XR-tube was 200 W, vacuum in analysis camera – 10^{-6} Pa. The spectrometer was calibrated on the line $Au4f_{7/2} = 84$ eV. The energy of band (E_{band}) of the C1s for alkyl group was taken on 285.0 eV. The molecular-weight characteristics ($\overline{M}_n$ and $\overline{M}_w$ are the number and weight average molecular masses) was measured by gel-penetration chromatography) "Waters-200". The eluent was tetrahydrofuran.

Radical copolymerization was carried out in bulk and toluene. The needed amounts of AIBN, monomer and solvent were placed into ampoule and degassed under reduced pressure. Then the ampoule was sealed and put in thermostat at 70 °C. The yield product was isolated by precipitation from benzene solution with methanol in argon and dried.

Catalytic hydrogenation was carried out in a thermostatically controlled reactor of the 'duck' type under stirring. 0.01-0.1 g of catalyst ($3.9 \cdot 10^{-5}$ g-at. of Rh) was placed into a reactor, then a stream of hydrogen was passed through the reactor and 15 mL of degassed isopropyl alcohol added. After activation of the system (15 min) 4.5 or 6.5 mmole of cyclohexene was added. The reaction was carried out at 40 °C and stirring (300–400 swings/min). The rate of reaction was estimated from kinetic curves on the consumption of hydrogen in time. Divergences in different experiments did not exceed 5%. The common 1%Rh/C catalyst was prepared by impregnation method. 50 mg of $RhCl_3 \cdot 4H_2O$ from water solution was adsorbed into a previously activated carbon with $S_{sp} = 850$ m^2/g (1.32 g) followed by reduction with excess of $NaBH_4$. The yield product was dried at 100 °C.

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