Preparation and characterization of polysiloxane networks containing metallic platinum particles

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ABSTRACT: Polysiloxane networks obtained via cross-linking of D_4/V_4 polysiloxane served as matrices for incorporation of metallic Pt particles. D_4/V_4 polymer used in the crosslinking was synthesized by equilibrium cationic ring-opening polymerization of the corresponding cyclotetrasiloxane monomers. Linear ($^HMM^H$) or cyclic (D_4^H) hydrosiloxanes, at different hydrosiloxane to D_4/V_4 molar ratios, were applied as crosslinking agents. Platinum species were introduced into the crosslinked products from $PtCl_4$ solution in THF or in isopropyl alcohol via the reduction of Pt^{4+} to Pt^0 in the presence of active Si-H sites. Various analytical techniques: UV-vis and FTIR spectroscopy, swelling measurements, XRD, SEM, and thermogravimetric analysis were applied to control the progress of the reaction or to characterize the intermediate or final products. IR spectroscopy allowed to determine the efficiency of crosslinking process and to investigate the consumption of un-reacted Si-H groups accompanying the reduction of platinum ions. XRD studies confirmed the incorporation of metallic platinum into all systems. Good thermal stability of obtained products was found using thermogravimetric analysis. According to SEM investigations, the applied network as well as the solvent used in the reduction process influenced the dispersion of metallic particles on the surface of the matrices. The obtained Pt-systems exhibited mainly redox activity in catalytic isopropyl alcohol conversion used as a test reaction. Significant differences in catalytic properties between systems containing different matrices were observed. The promoting effect on the catalytic activity was found in the case of C-P type support, i.e. the polysiloxane network obtained using the cyclic hydrosiloxane as the crosslinking agent. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43096.

INTRODUCTION

Incorporation of transition metal particles into polymer systems plays recently a significant role in the preparation of active materials for homogeneous or heterogeneous catalysis. The use of polymer templates allows the stabilization of metal particles in a solvent. Protective agents control particle size and prevent them from agglomeration.[1–3] Application of the appropriate support for insoluble heterogeneous catalytic systems enable better dispersion of active sites on the surface of a matrix and better contact with the reagents in catalytic reaction.[4]

Polysiloxanes are particularly well suited to be used as catalysts supports. They exhibit good chemical and thermal stability, show high flexibility, and also fast diffusion velocity of organic molecules.[5,6] They can also be easily separated from the reaction mixture or—depending on the application—easily soluble in

many solvents. They can provide appropriate functional groups for the attachment of catalytic species or for modification of topology of a chain to change the catalytic properties of the systems.[7] Soluble polysiloxane of various topologies, i.e., linear, star-shaped and hyperbranched with pendant vinyl, butylthioethyl or diphenylphosphinoethyl side groups were used as supports for palladium catalysts in the Mizoroki-Heck reaction. The influence of different polymer structures as well as different ligand densities on catalyst stability in such systems was investigated.[8,9] Chauhan *et al.* devoted some works to the synthesis of soluble transition-metal nanoclusters with polymethylhydrosiloxane (PMHS) as a template.[10–14] These works concerned preparation and characterization of polysiloxane-encapsulated metal nanoparticles, mainly Pd ones, and their applications in catalysis. Pd-polysiloxane nanocomposites were synthesized by reduction of metallic salt with PMHS, which acted as a reducing

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Additional Supporting Information may be found in the online version of this article.

agent and as a capping agent for the generation and stabilization of metal-nanoclusters. Polysiloxane-wrapped soluble metal nanoclusters were used as a recyclable catalyst for macromolecular grafting via alcoholysis, silaesterification and chemoselective hydrogenation reactions of PMHS. This polymer was also used for preparation of polysiloxane-stabilized silver nanoparticles from silver acetate.[10] Motoyama et al. applied ruthenium-catalyzed cross-linking of PMHS with amides or diols, which resulted in formation of polysiloxane gels containing ruthenium.[15,16] These insoluble gels were used as reusable heterogeneous catalysts for isomerization of alkenes. The same authors proposed also the synthesis of polysiloxane gels, into which platinum species were incorporated by treatment of polymethylhydrosiloxane with alkenes in the presence of Karstedt's catalyst. These gels acted as recyclable catalysts for reduction of nitro compounds to the corresponding amines.[17]

Differently from previously mentioned works, the key issue in our study was the preparation of polysiloxane network-platinum systems. The main aim of present work was to examine these materials in view of application of the cross-linked polysiloxane compounds as potential supports for platinum metal catalysts in heterogenous catalysis. The preparation of networks involved cross-linking of D_4/V_4 polymer obtained by equilibrium cationic ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V_4), with selected hydrosiloxane compounds using hydrosilylation process.[18] The hydrosilylation reaction is a catalytic addition of a hydrosilane group (Si-H) to multiple carbon-carbon or carbon-heteroatom bond. It can be applied in the synthesis of monomers and in the formation of much bigger, extended products, such as three-dimensional networks via the cross-linking reaction of multifunctional silicon hydride polymers with multifunctional silicon vinyl polymers.[19–22] One of the most commonly used catalysts for the hydrosilylation reaction is the Karstedt's catalyst.[23,24]

As mentioned above, selected hydrosiloxanes, i.e. linear 1,1,3,3-tetramethyldisiloxane ($^HMM^H$) or cyclic 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) at different hydrosiloxane to D_4/V_4 molar ratios were used as crosslinking agents for the preparation of polysiloxane networks. The application of crosslinking agents of a different structure and functionality gave the possibility to obtain matrices with various topologies. Introduction of platinum species was carried out via reduction of Pt^{4+} ions from THF or from isopropyl alcohol solution in the presence of obtained cross-linked products, which served both as reducing agents and simultaneously as matrices for incorporation of metallic Pt particles.

This study is focused on efficiency of cross-linking and reduction processes, incorporation of metallic species and investigation of their distribution in the matrix depending on the applied type of network and, furthermore, on examination of catalytic properties of selected systems. The reduction of platinum ions was controlled using UV-vis spectroscopy.

Polysiloxane matrices and network-platinum systems were characterized by IR spectroscopy, swelling investigations, X-ray diffraction measurements, scanning electron microscopy, and thermogravimetric studies. The catalytic investigations were carried out with the use of isopropyl alcohol conversion as a test reaction.

EXPERIMENTAL

Chemicals

Octamethylcyclotetrasiloxane (D_4) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V_4) (ABCR Germany) were dried by heating over calcium hydride at 60°C under reduced pressure for two days and subsequently distilled directly into the reaction flask. Trifluoromethanesulfonic (triflic) acid (Sigma-Aldrich), hexamethyldisiloxane (HMDS) (Merck), chloromethane and methanol (POCh, analytical grade) were used as supplied. Triethylamine (Sigma-Aldrich) was dried over P_2O_5 and then distilled in the flow of argon.

1,1,3,3-Tetramethyldisiloxane ($^HMM^H$), 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H), ABCR Germany, were used as received. Platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) solution in xylene (2% Pt) was purchased from Aldrich. Toluene (POCh, analytical grade) was initially dried over $CaCl_2$ and subsequently distilled over P_2O_5 in the flow of argon. THF (Sigma-Aldrich) was treated with KOH for two days to remove peroxides, subsequently dried over metallic Na and benzophenone mixture and finally distilled in the flow of argon. Isopropyl alcohol (POCh, analytical grade) was heated over magnesium and then distilled in the flow of argon. $PtCl_4$ (Alfa Aesar) was applied during the syntheses as supplied.

D_4/V_4 Polymer Synthesis

D_4/V_4 polymer was synthesized by equilibrium cationic ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) (15.4 g) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V_4) (7.3 g). The starting molar ratio of monomers D_4 to V_4 was equal to 2. The reaction was conducted in the presence of triflic acid as catalyst (ca. 3.7%, w/w) and hexamethyldisiloxane, HMDS (0.62 mmol), as a molecular weight regulator. The expected theoretical molecular weight of the polymer was 25,000. The reaction was carried out for 4 days at the temperature of 60°C. After that time, Et_3N—in equimolar quantity with respect to the amount of triflic acid used—was added to the reaction mixture to neutralize the catalyst. The polymer was purified using threefold precipitation by addition of methanol to its dichloromethane solution and then dried by heating under high vacuum for several hours. The product was a colorless and transparent, viscous liquid.

Preparation of Polysiloxane Networks

All crosslinking reactions were conducted in toluene and reagents were introduced into the reaction flask in the flow of argon. The experiments were performed at two different molar ratios of the Si-H groups (from hydrosiloxane) to vinyl groups (from the polymer): equal to 1 or 2. In a typical hydrosilylation procedure, 2.5 g of D_4/V_4 polymer diluted with toluene (5 ml) and the appropriate amount of a selected hydrosiloxane ($^HMM^H$ or D_4^H) were introduced into the reaction flask. Subsequently, necessary Karstedt's catalyst solution volume, corresponding to the molar ratio of Pt to Si-H groups equal to 1×10^{-5}, was added to the reaction mixture. The syntheses were

Table I. Symbolic Descriptions of Products Obtained via Crosslinking Process and after Incorporation of Platinum Particles

Crosslinking agent	Si-H: vinyl ratio	Symbol of	
		Polysiloxane network	Network-Pt system
$^HMM^H$	1:1	L-P_(1:1)	L-P_(1:1)-Pt$_{thf}$
			L-P_(1:1)-Pt$_{iso}$
D_4^H	1:1	C-P_(1:1)	C-P_(1:1)-Pt$_{thf}$
			C-P_(1:1)-Pt$_{iso}$
$^HMM^H$	2:1	L-P_(2:1)	L-P_(2:1)-Pt$_{thf}$
			L-P_(2:1)-Pt$_{iso}$
D_4^H	2:1	C-P_(2:1)	C-P_(2:1)-Pt$_{thf}$

thf, iso:- The abbreviations for the samples obtained from $PtCl_4$ in THF or isopropyl alcohol solution during the reduction process.

carried out with stirring the reagents at the temperature of 60°C for three days. Final products were dried under vacuum until constant mass in order to remove the solvent and un-reacted substances. All products of cross-linking reaction were colorless solids, more elastic in the case of those obtained with linear hydrosiloxane. The symbols ascribed to the prepared networks are collected in Table I.

Network-Pt Systems Preparation

In all cases, incorporation of platinum particles was performed by reduction of Pt^{4+} ions from $PtCl_4$ solution in THF in the presence of the cross-linking products (see Section Preparation of polysiloxane networks) containing un-reacted active Si-H groups (as described further in Section Characterization of the cross-linked products). For comparison, the reduction in iso-propyl alcohol solution was carried out in the presence of networks obtained by cross-linking with the linear ($^HMM^H$) hydrosiloxane and a selected network obtained with the D_4^H one. In all experiments the concentration of Pt^{4+} ions in the starting solution was equal to 0.0054 mol dm^{-3} and the amount of $PtCl_4$ solution used for the reduction was calculated to obtain 1 wt % of Pt in all final products.

A typical preparation procedure of network – Pt systems was as follows: 0.5 g of a cross-linked product was introduced into the reaction flask and subsequently 4.7 ml of $PtCl_4$ solution was added with simultaneous magnetic stirring and in the flow of argon. The color of solution changed from yellow to gray-brown during the process. Moreover progress of the reaction was accompanied by emission of a gaseous product, presumably H_2. Simultaneously, the initially colorless solid was changing its color as well. Color changes was observed almost immediately after addition of the solution containing linear hydrosiloxane ($^HMM^H$), while in the case of the solution with the cyclic one (D_4^H) changes started with distinct delay (up to 1 min). The stirring was continued at room temperature for 24 h. After that time the black-gray products were filtered, washed with the appropriate solvent and dried. The UV-vis spectra of the filtrate solutions were measured and compared with the spectra of the initial ones. Symbols ascribed to the obtained products are collected in Table I.

Characterization Methods

UV-vis spectra in the range of 190-1100 nm were recorded on a Hewlett-Packard HP 8453 spectrophotometer equipped with a diode array detector.

FTIR measurements in the middle infrared range (400–4000 cm^{-1}) in the transmission mode were performed on a BioRad FTS60v spectrometer using KBr pellet technique. The resolution of the measurements was equal to 4 cm^{-1}. Quantitative analysis was performed using baseline-corrected spectra.

X-ray diffraction studies were carried out on a Philips X'Pert XRD diffractometer using Cu K_α radiation. Reflections positions were determined using Panalytical X'Pert HighScore software.

SEM investigations were carried out on a Nova Nanosem 200, FEI Co. microscope equipped with the back-scattered electrons (BSE) detector and the EDS system. The powders were attached to the SEM stubs using conductive silver paste and then vacuum-sputtered with a thin carbon layer.

Thermogravimetric analyses were conducted on a NETZSCH STA 449 F3 Jupiter® TA instrument in the temperature range of 30°C–1200°C, at a rate of 10 K min^{-1} under argon.

Swelling investigations were carried out in toluene. Before swelling, the samples were weighed, then poured over by a solvent and left to swell. After three days the swollen samples were isolated and weighed again. For each sample weight increase was determined and expressed in weight percent.

Density measurements were performed on a helium pycnometer (Micromeritics, AccuPyc II 1340). Each sample was initially purged with helium (100 times) and subsequently analyzed at room temperature, and 30 single measurements were performed. Calculated standard deviation was lower than 1%.

Catalytic Investigations

The oxidation-reduction and acid-base properties of the examined catalysts were determined using the conversion of isopropyl alcohol. The measurements were performed in a glass flow reactor with a fixed catalyst bed. The inner diameter of the

Table II. Si-H and Si-CH$_3$ Band Area Ratios in the IR Spectra of the Products Presented in Figure 5 and Supporting information Figure S1

Product	SiH/SiCH$_3$[a] area ratio	Product	SiH/SiCH$_3$[a] area ratio
L-P_(1:1)	0.202	L-P_(1:1)-Pt$_{thf}$	–
		L-P_(1:1)-Pt$_{iso}$	–
L-P_(2:1)	0.243	L-P_(2:1)-Pt$_{thf}$	–
		L-P_(2:1)-Pt$_{iso}$	–
C-P_(1:1)	0.373	C-P_(1:1)-Pt$_{thf}$	0.167
C-P_(2:1)	0.747	C-P_(2:1)-Pt$_{thf}$	0.191

[a] Area ratio of bands due to Si-H bond at 2120 cm^{-1} or 2170 cm^{-1} (depending on cross-linking product) and C-H bond from SiCH$_3$ groups at 1261 cm^{-1} (in the spectra denoted with the asterisk), which remain unchanged during the reaction.
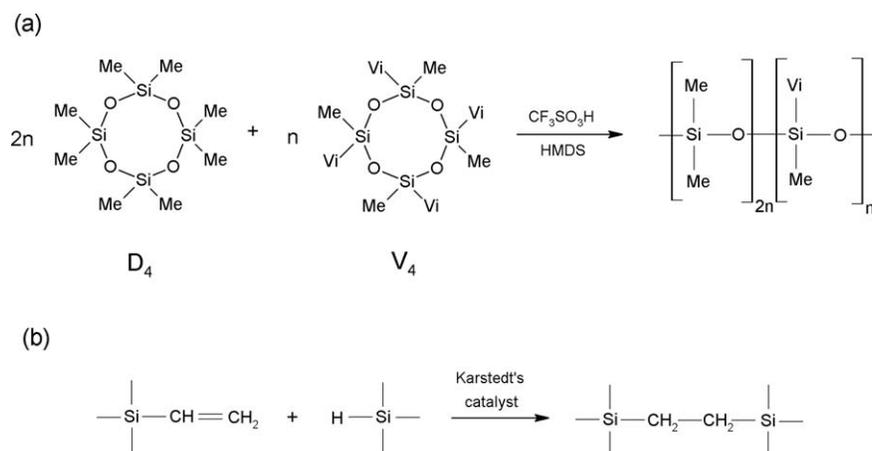
Figure 1. Scheme of: (a) synthesis of D_4/V_4 polysiloxane, (b) hydrosilylation of vinyl compounds.

reactor was 18 mm. Isopropyl alcohol was diluted with nitrogen. The mole fraction of the alcohol in nitrogen was 0.0179. The flow rate of the mixture was 20 dm^3 h^{-1}. The GHSV was 10,000 h^{-1} in all measurements. The temperature was measured inside the catalyst bed. In each experiment approximately 0.5 g of the sample was used. The measurements were performed in the kinetic region of the reaction (conversion below 20%). To preserve steady state conditions of the experiments, after each increase of temperature, several samples of the product mixture were analyzed. The main measurements were performed, when there was no further increase in the concentration of the products. The products of the reaction were separated using the capillary column type: DB FFAP with the diameter 0.32 mm and the length 60 m, the thickness of the film was 0.25 μm. The products were analyzed *in situ* using the gas chromatograph (Agilent 7890A) with a flame ionization detector (FID). Before the reaction all catalysts were standardized in the reactor at 400 K for 1 h in the nitrogen flow.

The experimental data were used to determine the selectivities, the apparent activation energies and the rates of the reaction. The results are presented in a form of Arrhenius plots of log (r) versus 1000/T. This simplification is justified by the fact that the rate constant is directly proportional to the rate in this case.[25] The linear character of all Arrhenius plots is preserved in the examined temperature range.

RESULTS AND DISCUSSION

Characterization of the Crosslinked Products

Polysiloxane D_4/V_4 containing vinyl groups, the product of equilibrium cationic ring-opening polymerization [Figure 1(a)], was hydrosilylated using two different hydrosiloxanes: linear $^HMM^H$ or cyclic D_4^H, according to the scheme [Figure 1(b)]. The structural formulas of the selected hydrosiloxanes are presented in Figure 2.

Applying two types of cross-linking agents, which differ both in the structure and in the number of reactive Si-H groups should result in various efficiency of cross-linking process and formation of different cross-linked polysiloxane networks. The use of D_4^H, containing four reactive sites causes polysiloxane chains

linked by cyclic siloxane bridges through ethylene spacers should induce formation of higher cross-linked products than those obtained applying the linear, more flexible compound $^HMM^H$, containing two Si-H groups in the molecule. Moreover, the application of different hydrosiloxane to D_4/V_4 molar ratios may result in different efficiency levels of cross-linking process and, simultaneously, in different amounts of un-reacted Si-H groups, remaining in the obtained networks.

In the present work, the efficiency of cross-linking reaction, which is related to the efficiency of the hydrosilylation process, has been studied using IR spectroscopy. IR spectrum recorded for starting polysiloxane as well as the spectra for the cross-linked products are collected in Figure 3. The characteristic set of bands corresponding to vinyl groups (-CH=CH$_2$), located at 3055 cm^{-1} and 3016 cm^{-1} (C-H stretching vibrations), at 1598 cm^{-1} (C=C stretching vibrations) and at 960 cm^{-1} (C-H bending vibrations) observed in the spectrum of starting polysiloxane is not present in the spectra of all but one cross-linked products. The only exception is the spectrum recorded for the sample C-P_(1:1) where some of these bands, of a very low intensity, are still seen. On the other hand, characteristic bands attributed to the

–CH$_2$-CH$_2$- linkages between Si atoms appear in the spectra of all cross-linked products. They are located at about 2910 cm^{-1} and 2870 cm^{-1} (C-H stretching vibrations) and at 1138 cm^{-1} (C-H bending vibrations).[26–28] These results have confirmed the successful occurrence of hydrosilylation reaction in the systems studied.
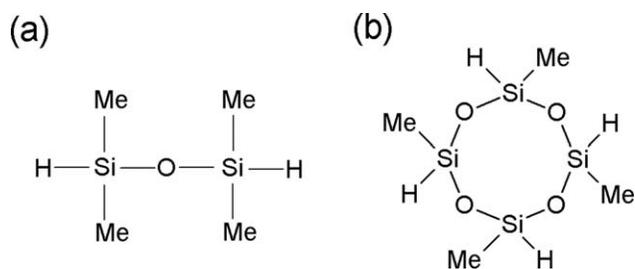

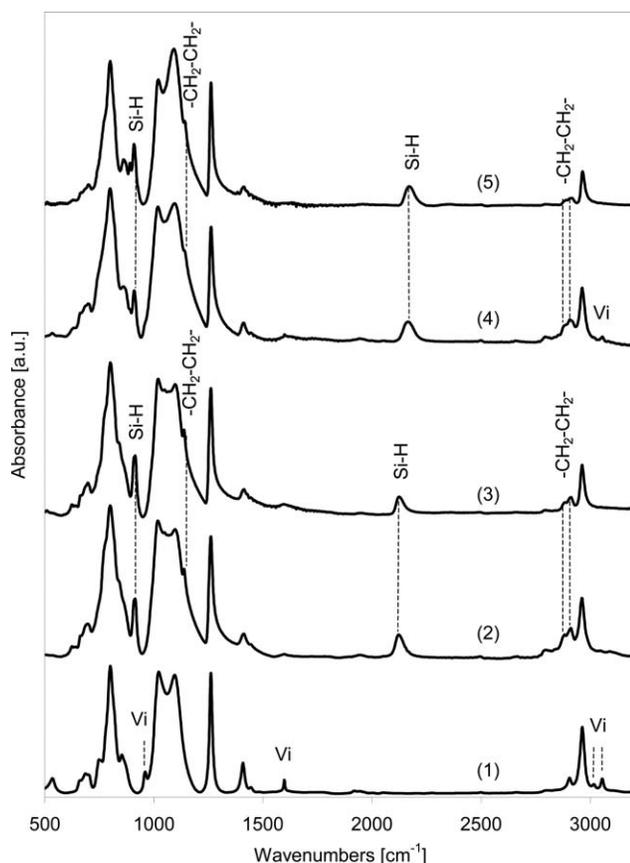**Figure 2.** Structures of compounds used as the cross-linking agents: (a) $^HMM^H$, (b) D_4^H.

Figure 3. FTIR spectra of D_4/V_4 polysiloxane (1) and the cross-linked products: (2) L-P_(1:1), (3) L-P_(2:1), (4) C-P_(1:1), (5) C-P_(2:1).

Table III. The Results of Swelling Measurements for Crosslinked Products and Values of Crosslinking Density and Average Molecular Weight between Crosslinks (Calculated on the Basis of Swelling Measurements)

Cross-linking product	Swelling in toluene : weight increase (%)	nRF (mol cm^{-3})	Mc (g mol^{-1})
L-P_(1:1)	455	7.77×10^{-5}	12,548
L-P_(2:1)	546	5.22×10^{-5}	17,817
C-P_(1:1)	231	5.63×10^{-4}	1823
C-P_(2:1)	216	6.79×10^{-4}	1552

Hence, IR studies show clearly the various efficiency of cross-linking process and, simultaneously, different amounts of un-reacted Si-H groups remaining in the obtained networks, depending on the type and amount of cross-linking agent.

The results of swelling tests (Table II) show significant difference between products obtained via cross-linking of the starting polysiloxane with linear $^H MM^H$ or cyclic D_4^H hydrosiloxane. The obtained data clearly indicate that C-P_(1:1) and C-P_(2:1) samples are higher cross-linked networks than L-P_(1:1) or L-P_(2:1) ones. Much higher increase of the sample mass after contact with the solvent in the case of L-P_(1:1) and L-P_(2:1) samples in comparison with C-P_(1:1) and C-P_(2:1) ones has been observed. This effect could be expected because of differences in the structure of hydrosiloxanes used in the hydrosilylation process. Application of an excessive amount of $^H MM^H$ with respect to the number of vinyl groups in the starting polymer gives a less cross-linked product (sample L-P_(2:1)), when comparing both L-P types of networks. Most probably, a smaller number of hydrosiloxane molecules create bridges between the polysiloxane chains in the case of L-P_(2:1) network than in L-P_(1:1) one. However, the presence of un-reacted Si-H groups in both networks indicates that in the case of part of hydrosiloxane molecules only one Si-H group participate in the hydrosilylation reaction, while the other one remains "pendant". The results of swelling measurements obtained for C-P_(1:1) and C-P_(2:1) samples show that the application of an excess of the cyclic hydrosiloxane in the hydrosilylation reaction does not influence cross-linking degree so significantly, as in the case of L-P networks. However, the increase of the sample mass for C-P_(2:1) network is smaller than for C-P_(1:1), which can indicate that this latter product is rather lower cross-linked than C-P_(2:1) one.

Based on swelling measurements, the cross-linking density (n^{FR}) for all crosslinked products was estimated using the Flory-Rehner equation:

$$n^{FR} = - \left[v_2 + v_2^2 \, \chi + \ln(1 - v_2) \right] / V_1 \left(v_2^{1/3} - 0.5 \, v_2 \right)$$

where v_2 corresponds to the polymeric volume fraction in the swollen mass; V_1 is the molar volume of the solvent (cm^3 mol^{-1}); χ is the polymer-solvent interaction parameter (the value used for this estimation was 0.48).[29,30] The average molecular weight between cross-links, which is defined as $M_c = \rho/n^{FR}$ [where ρ (g cm^{-3}) - the density of the polymer] was also calculated. The density values determined for the particular networks

IR spectra of all obtained networks contain the bands corresponding to Si-H groups (originating from the appropriate hydrosiloxane compounds), which are of particular interest as active sites in the hydrosilylation reaction and in further reduction process. Depending on hydrosiloxane used they are located at 2120 cm^{-1} (Si-H stretching vibrations) and 910 cm^{-1} (Si-H bending vibrations) for $^H MM^H$, while in the case of D_4^H the bands attributed to the mentioned vibrations are observed at 2170 cm^{-1} and 914 cm^{-1} respectively.

Independently of hydrosiloxane to D_4/V_4 ratio, Si-H-attributed bands are observed in the spectra of all crosslinked products. However, as mentioned previously, only in the case of the C-P_(1:1) sample the presence of vinyl groups indicates, that the hydrosilylation process has not been completed. Comparing the spectra of C-P_(1:1) and C-P_(2:1) networks it can be seen that bands due to Si-H bonds are more intensive in the case of the product prepared using excessive amount of hydrosiloxane with respect to the number of vinyl groups in the starting polymer. Such differences are less evident in the spectra obtained for L-P_(1:1) and L-P_(2:1) networks. Additionally, according to the data presented in Table III, the Si-H and Si-CH$_3$ band area ratios indicate significant differences in amount of un-reacted Si-H groups in the networks. These differences are much higher in the case of products obtained using cyclic cross-linking agent than those obtained with the use of the linear one.

(0.9753, 0.9297, 1.0255, 1.0537 for L-P_(1:1), L-P_(2:1), C-P_(1:1), C-P_(2:1), respectively) **were used to estimate the corresponding M_c values. The results of these calculations are presented in Table** II.

According to n^{FR} values, the differences in cross-linking density between both types of networks, i.e. L-P and C-P ones, are clearly seen. As expected, the latter networks were higher cross-linked than the former ones. Moreover, the M_c values for networks of C-P type are significantly lower than for the L-P ones. Twofold increase of the amount of the cyclic cross-linking agent resulted in lower M_c value and in increase of the cross-linking density (sample C-P_(2:1)). On the contrary, the results for L-P_(2:1) sample, where the linear cross-linking agent was applied, have shown the higher value of the average molecular weight between cross-links and decrease in the cross-linking density. Above observations stay in good agreement with the results of TG measurements, as described further in this paper.

Incorporation of Platinum Particles

The presence of unreacted Si-H groups in all hydrosilylation products, confirmed by the results of IR spectroscopic studies, has enabled the use of obtained polysiloxane networks both as reducing agents and as matrices for the introduction of platinum particles.

Incorporation of platinum particles has occurred by reduction of platinum ions from $PtCl_4$ in THF or isopropyl alcohol solutions. This process was carried out in the solution of one of two different solvents: THF, which makes the networks swollen, or isopropyl alcohol - a poor solvent for the starting polymer and poor swelling agent of the cross-linking products.

The results of UV-vis measurements supplied the preliminary evidence of the Pt^{4+} ions reduction in the presence of cross-linked products. The selected spectra of $PtCl_4$ in THF or isopropyl alcohol solutions, recorded before and after the reduction process are collected in Figure 4. Pt^{4+} ions in both initial solutions show distinct and characteristic absorption effects in the UV-vis spectral range. The absorption maxima in the visible range are not observed. Strong absorption effects can be seen mainly in the UV range, with the slight shoulders at about 350 nm or 295 and 340 nm (for THF or isopropyl alcohol solution, respectively) extended up to visible range. The UV-vis spectra recorded for the filtrate solutions after the separation from the solid products show considerable decrease of the characteristic absorption peaks in comparison with the spectra of initial ones, which is most evident in the THF- containing solutions. These results clearly indicate the significantly lower content of Pt^{4+} ions in the solution after the reduction. However, the decrease of intensity of absorption maxima for the isopropyl alcohol solution after contact with the C-P_(1:1) sample is less significant, which may indicate the lower than expected platinum content in that product. Presumably, the use of both higher cross-linked network and isopropyl alcohol solution causes the limitation of reduction of platinum ions to the most accessible parts of the network surface (i.e. the least cross-linked places containing Si-H groups). In such case the reduction—most probably—does not occur completely and some amount of Pt^{4+} ions in the solution can remain unreduced.
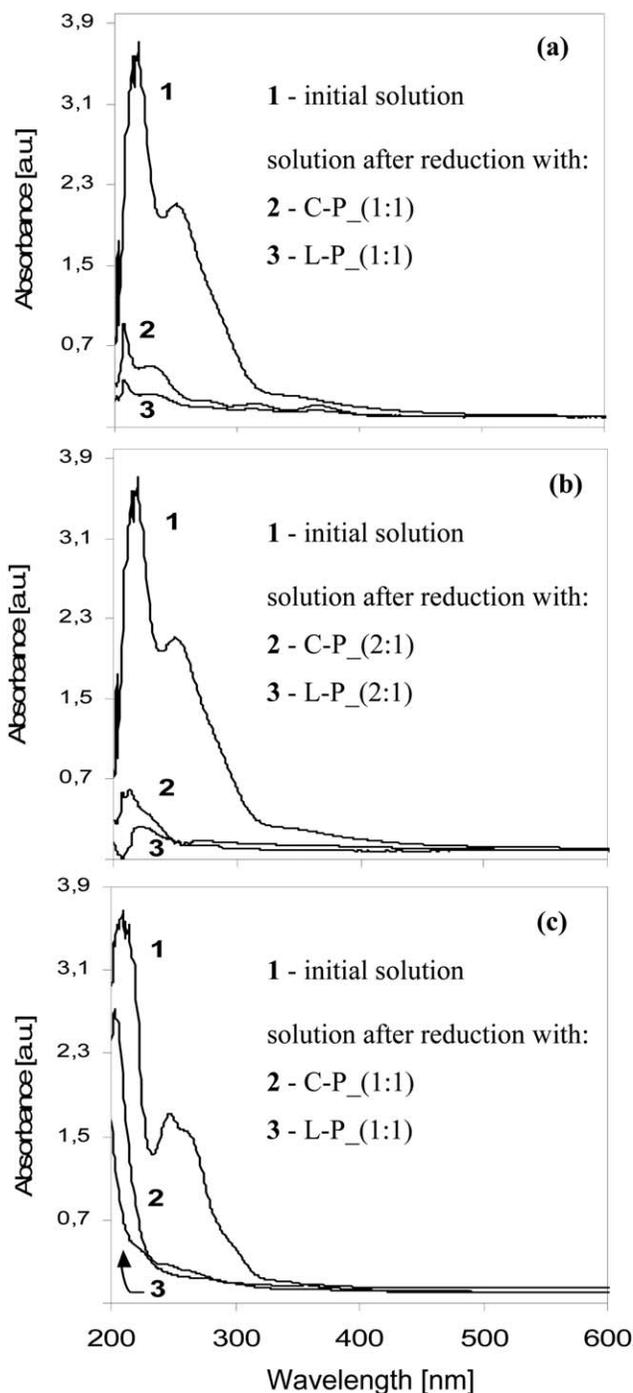

Figure 4. UV-Vis spectra of the $PtCl_4$ solutions before and after reduction with different polysiloxane networks: (a) in THF, in contact with C-P_(1:1) or L-P_(1:1), (b) in THF, in contact with C-P_(2:1) or L-P_(2:1), (c) in isopropyl alcohol, in contact with C-P_(1:1) or L-P_(1:1)

Characterization of Network-Platinum Systems

All products obtained after the reduction process were examined using IR spectroscopy. Recorded representative spectra are shown in Figure 5 and Supporting Information Figure S1. These investigations were focused on the examination of consumption of Si-H groups, accompanying the reduction of Pt ions. This process was manifested in decrease or even lack of characteristic
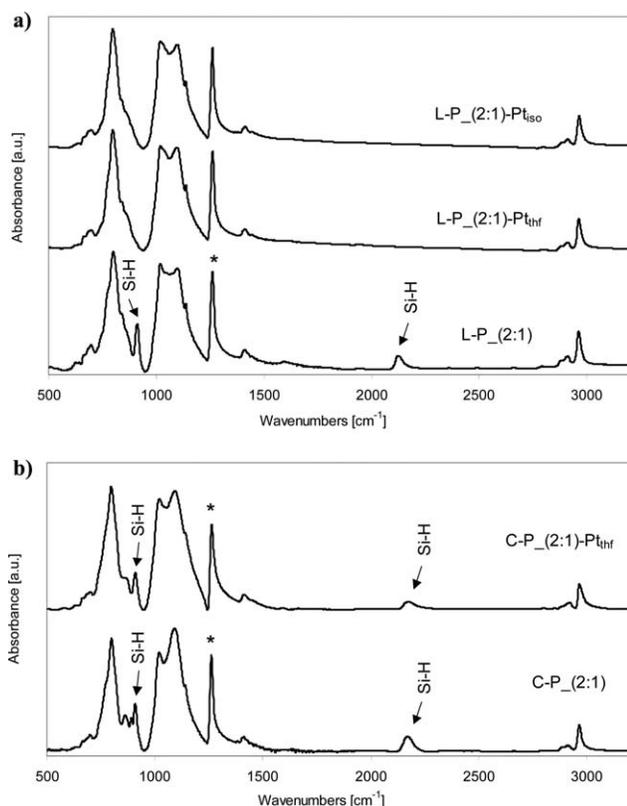
Figure 5. FTIR spectra of selected networks before and after the introduction of platinum: (a) L-P_(2:1) type; (b) C-P_(2:1) type.

Si-H bands in the IR spectra of the obtained products - in comparison with the spectra of the starting networks. No Si-H bands at 2120 cm^{-1} and 910 cm^{-1} are observed in the IR spectra of both networks obtained with the linear cross-linking agent after the reduction of platinum ions, independently of the applied solution [Figure 5(a), Table III]. This indicates that all Si-H groups remaining in the network participated in the reduction process and were accessible even for the isopropyl alcohol, penetrating mainly the least cross-linked areas. Incomplete consumption of Si-H groups is observed in the case of C-P type networks. According to the spectra of C-P_(1:1)-Pt$_{thf}$ and C-P_(2:1)-Pt$_{thf}$, Si-H groups are still present in these samples, but intensity of the characteristic Si-H bands, at 2170 cm^{-1} and at 914 cm^{-1}, decreases (in comparison with the starting networks) [Figure 5(b) and Table III]. However, higher intensities of these bands, are observed in the case of C-P_(2:1)-Pt$_{thf}$ sample. On the basis of above results, it can be supposed, that in C-P_(1:1) and C-P_(2:1) networks, the incorporation of higher amount of platinum is possible, especially in the materials obtained with the excess of the cross-linking agent.

In order to check the presence of metallic Pt particles in the reduction products, X-ray diffraction investigations were carried out. XRD patterns of cross-linked products as well as materials obtained after incorporation of platinum are collected in Figure 6 and Supporting Information Figure S2. The position of the broad reflection at *ca.* $2\theta = 12°$ (*d*-spacing value ca. 7.4 Å) can be ascribed to the distance between the chains in cross-linked products,[31–33] and its shape indicates the amorphous nature of
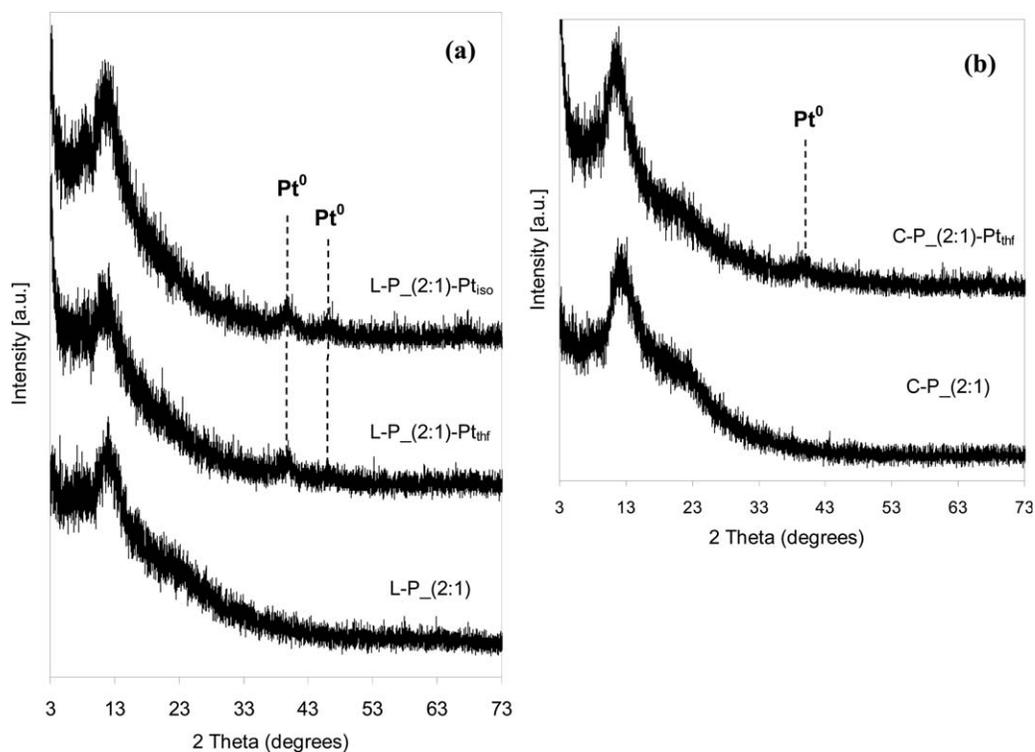

Figure 6. XRD patterns of selected networks and products after incorporation of Pt species: (a) L-P_(2:1) type; (b) C-P_(2:1) type.

these products, with only short-range ordering existing in obtained networks. The patterns of systems after incorporation of platinum show additional reflections at $2\theta = 39.8°$ and $2\theta = 46.2°$ ascribed to Pt (111) and Pt (200) planes, respectively,[34] which confirms the presence of Pt^0. Comparison of patterns of starting compounds with those after incorporation of platinum, leads to the statement that reflections ascribed to metallic Pt are present in diffractograms of all Pt-containing systems. The reflections corresponding to the metal phase exhibit rather low intensity as compared with those related to the networks, but it is obvious since only a small amount (not higher than 1 wt %) of platinum was incorporated into the samples. Unfortunately, so weak reflections do not allow the calculation of an average size of Pt crystallites. Thus, XRD diffraction studies confirmed the reduction of Pt^{4+} ions with the remaining Si-H groups in the cross-linked products resulting in the formation of two-phase systems in which metallic platinum particles are dispersed into polysiloxane networks.

SEM investigations were carried out in order to determine the influence of the applied network as well as the solvent used in the reduction process on the dispersion of the incorporated platinum species. SEM images of selected samples (only of these used later in the catalytic tests – see Section Catalytic investiga-tions), obtained with the application of BSE detector, are presented in Figures 7–10. Distinct white inclusions are visible in the micrographs of Pt-network systems. They are present as separate spots of different shape and size or form large, white areas covering matrice's surface (Figures 7 and 8). As established by EDS (Figure 9), these inclusions contain mainly Pt atoms. These images clearly indicate, that in the obtained systems, independently on the applied type of matrix (or solvent used in the reduction), exist both regions distinctly enriched in platinum and regions showing deficit or even absence of this metal. However, some differences in metal dispersion between particular samples can be observed. Distinct white separated spots of different size observed in Pt-deficient regions, are especially seen in C-P_(2:1)-Pt$_{thf}$ sample (Figure 8). They are observed as bigger spots (size of about 0.5-0.8 μm) of irregular shape - indicating that the metal particles may be agglomerated – or as much smaller spherical ones in the 20-50 nm size range. Such separated inclusions are not so evident in systems containing L-P matrix, particularly in L-P_(2:1)-Pt$_{thf}$ sample, which contain mainly smaller or larger Pt-covers (Figure 7). On the other hand BSE images of these last samples show significant differences in platinum coverage depending on the solvent contacting with the same type of matrix during the reduction process
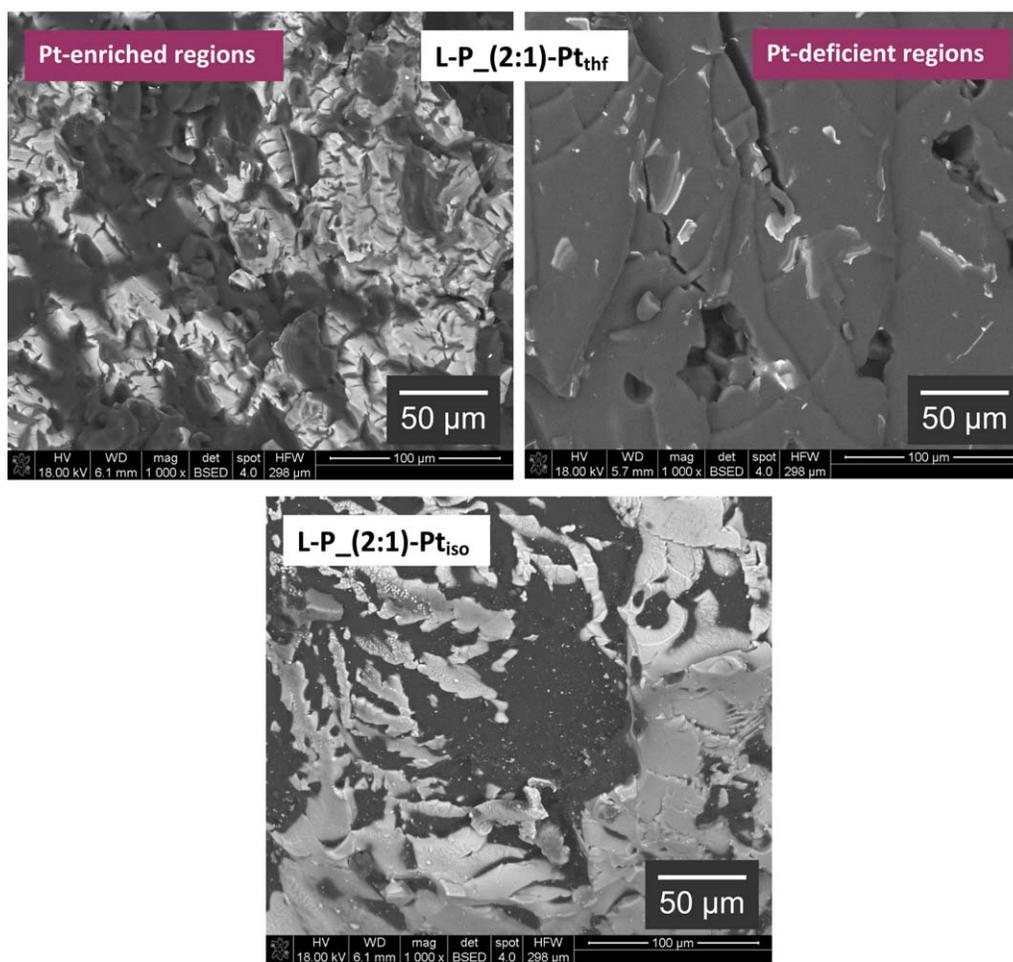

Figure 7. BSE images of: L-P_(2:1)-Pt$_{thf}$ and L-P_(2:1)-Pt$_{iso}$ at magnification 1,000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
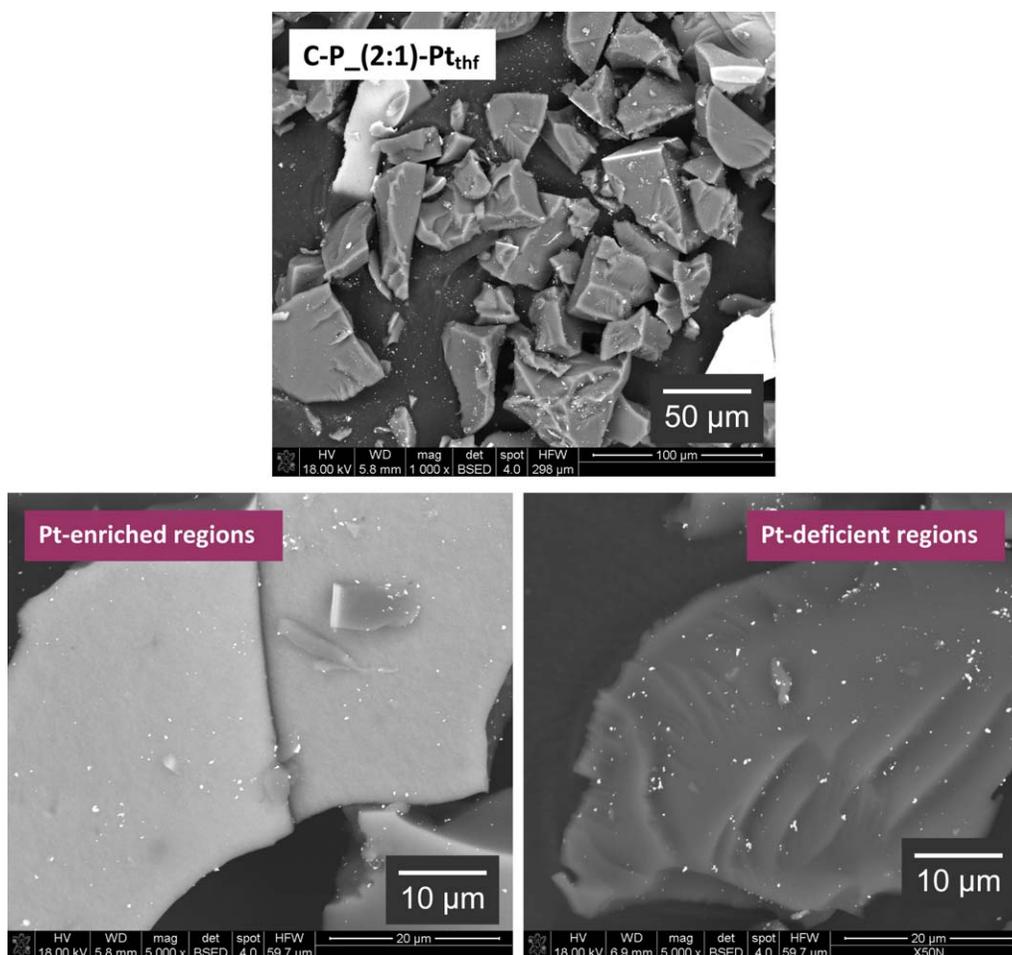
Figure 8. BSE images of C-P_(2:1)-Pt$_{thf}$ at magnification: 1,000—overall look, or 5,000—selected regions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Figure 7). These micrographs indicate much higher coverage with platinum particles in the case, when isopropyl alcohol - a solvent remaining in contact mainly with the most accessible parts of a network surface - has been used (L-P_(2:1)-Pt$_{iso}$). In the same sample some separated spots of irregular shape (agglomerated Pt-particles) can also be observed (Figure 9). Differences in platinum coverage in Pt-enriched regions can be observed in all investigated systems. More information about that reveal BSE images obtained at magnification of 100,000 (Figure 10). In L-P_(2:1)-Pt$_{thf}$ sample metal particles cover the surface forming the areas tightly occupied with small (size of about 20 nm), separated particles. Application of the isopropyl alcohol solution strengthens the agglomeration of the very small particles, with the estimated size of the aggregates in the range of 0,3-1 μm. Comparing systems containing different matrices (reduction conducted in THF solution), obtained BSE images indicate a higher Pt-coverage in C-P_(2:1)-Pt$_{thf}$ system than in the case of L-P_(2:1)-Pt$_{thf}$ one. According to micrographs presented in Figure 10, Pt-enriched large areas covering a surface of C-P matrix, are very tightly occupied (tighter than in the case of L-P one) with small metal particles, but no agglomeration is observed. The size of platinum particles in these "porridge-like" covers is about 20 nm and smaller, but the accurate determination of the size of such small particles using this microscopic method is rather difficult.

Differences in platinum coverage and particles dispersion result, undoubtedly, from the differences in cross-linking degree of particular networks as well as the location of active Si-H sites, participating in the reduction process. In the case of L-P type networks the presence of the more accessible active sites due to the higher M_c values (see Section Characterization of the cross-linked products) and the presence of Si-H group only in "pendant" hydrosiloxane molecules, accelerates the reduction process. However, the formation of metal particles may occur both on Si-H groups "enriched" surface areas and in a bulk of the low cross-linked matrix, where the active groups are also accessible for the well penetrating solvent (as THF, in this case). The use of a solvent (isopropyl alcohol) penetrating mainly the most accessible parts of a network surface, results in a higher platinum coverage, but, on the other hand, induces aggregation of metal particles. In the case of C-P type network, the formation of metal particles may occur in the regions containing "more isolated"—or "easier available"—Si-H groups. This can take place due to the structure of the cross-linking agent. Different number of Si-H groups originating from the same molecule, can be consumed during the cross-linking process. This results
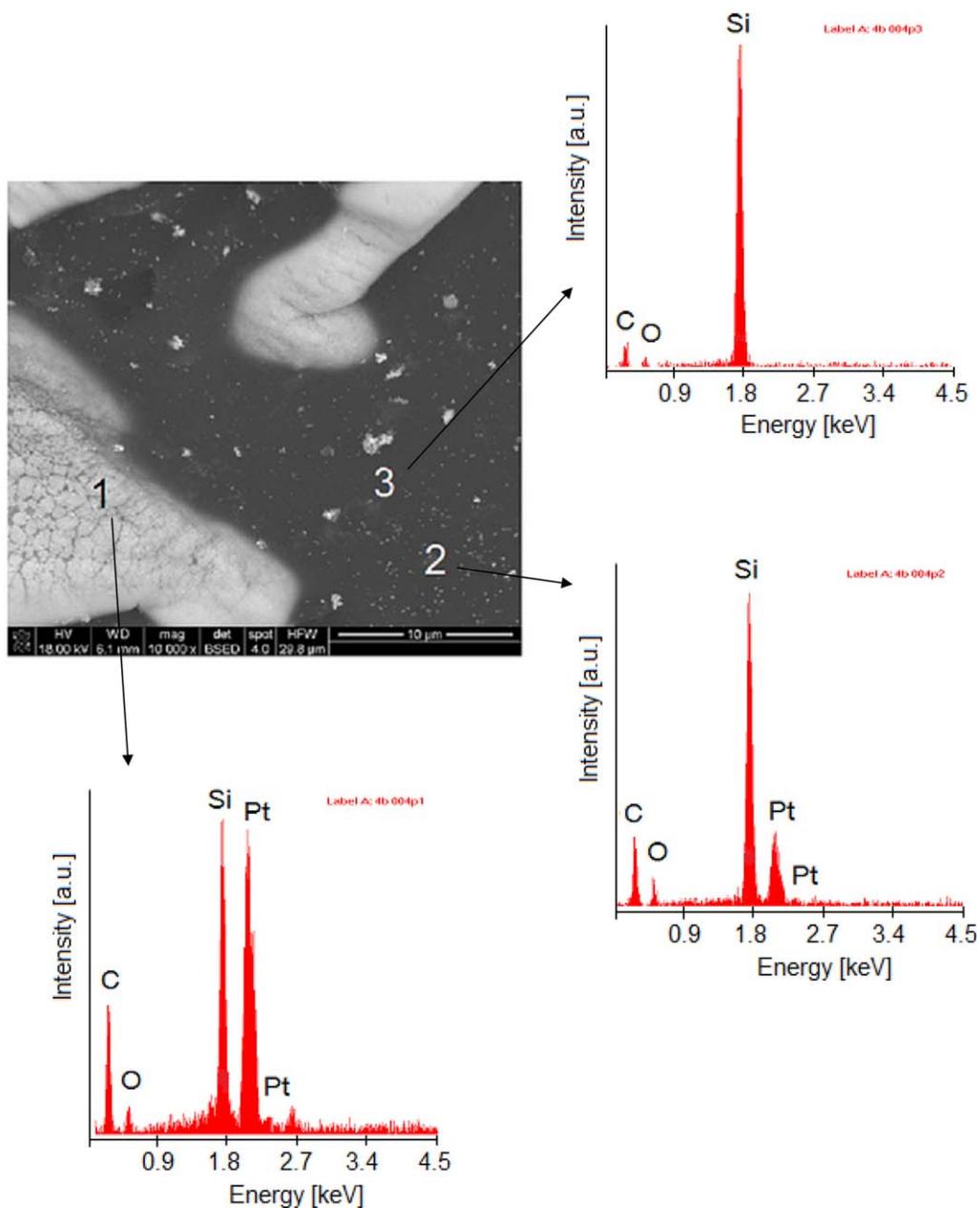
Figure 9. BSE image of L-P_(2:1)-Pt$_{iso}$ and results of EDX analysis performed for selected points of the sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in creation of regions with different cross-linking density and containing higher or lower number of available Si-H groups. Hence, the presence of large Pt-covered areas, indicating a high concentration of Pt particles, or of distinct separated spots in BSE images for C-P matrix. However, because of the relatively low M_c value for C-P matrix (when compared with L-P matrix), the formation of metal particles in places of a higher density is rather difficult. Therefore, it can occur mainly in regions of lower cross-linking density, significantly enriched in these active groups. It can be assumed, that in materials with C-P matrix, formation of platinum particles takes place mostly on the surface. Additionally, effectively higher number of Si-H groups in "pendant" cyclic molecules than in the linear ones, may cause

the creation of a higher coverage of metal particles in the C-P matrix containing sample.

Thermal stability of the cross-linked products and the network-Pt systems was studied using thermogravimetric analysis. Typical TG curves of selected samples are collected in Figure 11. According to these results, for the cross-linked products as well as for all network-Pt systems no significant mass loss took place up to 360°C–380°C. It should be pointed out that the significant differences are observed in the regions of a strong weight loss for both series of products. The highest weight loss in the case of the L-P type networks, as well as of those containing Pt particles, is observed in the region of 400°C–600°C. For the other series, C-P type networks – before and after Pt incorporation - that region is
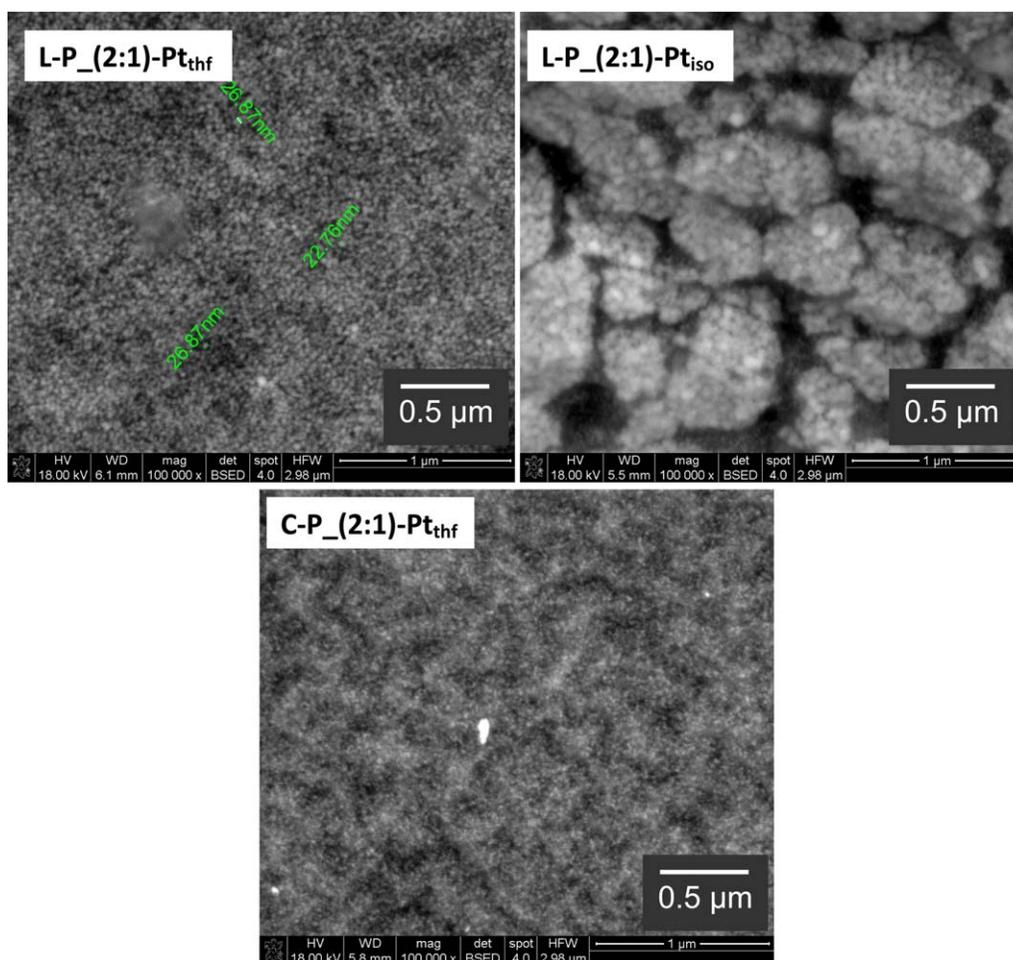
Figure 10. BSE images of samples: L-P_(2:1)-Pt$_{thf}$, L-P_(2:1)-Pt$_{iso}$, C-P_(2:1)-Pt$_{thf}$ at magnification 100,000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

extended up to 800°C. The results of TG analysis show also the considerable differences in weight loss up to 1200°C, which is significantly higher for the networks obtained via cross-linking of the starting polysiloxane with the linear ^{H}MM^H hydrosiloxane than for those obtained with the cyclic D$_4^H$ one. The weight loss is equal to 56% and 68% for L-P_(1:1) and L-P_(2:1) samples respectively, or 30% and 28% for C-P_(1:1) and C-P_(2:1) ones. Such behavior is, most probably, connected with a different cross-linking degree of particular networks (see Section Characterization of the cross-linked products).[35,36]

The incorporation of platinum into the matrices induces the decrease of weight loss in the case of C-P_(1:1)-Pt$_{thf}$ and C-P_(2:1)-Pt$_{thf}$ systems. On the other hand, considerable increase of weight loss is observed for the L-P_(1:1)-Pt$_{thf}$ and L-P_(2:1)-Pt$_{thf}$ samples. However, formulation of final conclusions based on these results requires further studies to clarify the influence of incorporation of platinum species into the networks on their thermal properties. Such studies are currently in progress.

Investigations of Catalytic Properties

Catalytic conversion of isopropyl alcohol can lead to three reaction products, namely acetone, propene and diisopropyl ether.

Acetone - the product of dehydrogenation - is formed on redox or base active sites, whereas the products of dehydration: propene and diisopropyl ether are formed on acid-base centers.[37–39] The results of catalytic tests carried out over examined samples: selected Pt-systems and - for comparison - unmodified matrices are shown in Figure 12. The values of activation energy and selectivity are collected in Tables IV and V respectively.

Comparing the results of dehydrogenation of isopropyl alcohol to acetone [Figure 12(a)] it is well seen that the incorporation of platinum into both types of network matrix upgrades the catalytic properties of these systems. Thus L-P_(2:1)-Pt$_{iso}$ and L-P_(2:1)-Pt$_{thf}$ are more active than L-P_(2:1), and - in the same manner - C-P_(2:1)-Pt$_{thf}$ is more active than C-P_(2:1). This tendency is a logical consequence of introduction of new active redox sites (Pt^0) into the polymer support. Taking into account the type of polymer matrix, the catalysts with C-P type support are more active than these of corresponding L-P ones. It is observed that C-P_(2:1) is more active than L-P_(2:1) and C-P_(2:1)-Pt$_{thf}$ is more active than L-P_(2:1)-Pt$_{thf}$. Focusing on Pt-systems, two major aspects may influence the activity in this case i.e.: the dispersion and the accessibility of active phase of the catalysts. Regarding the results of SEM analysis it is visible that the
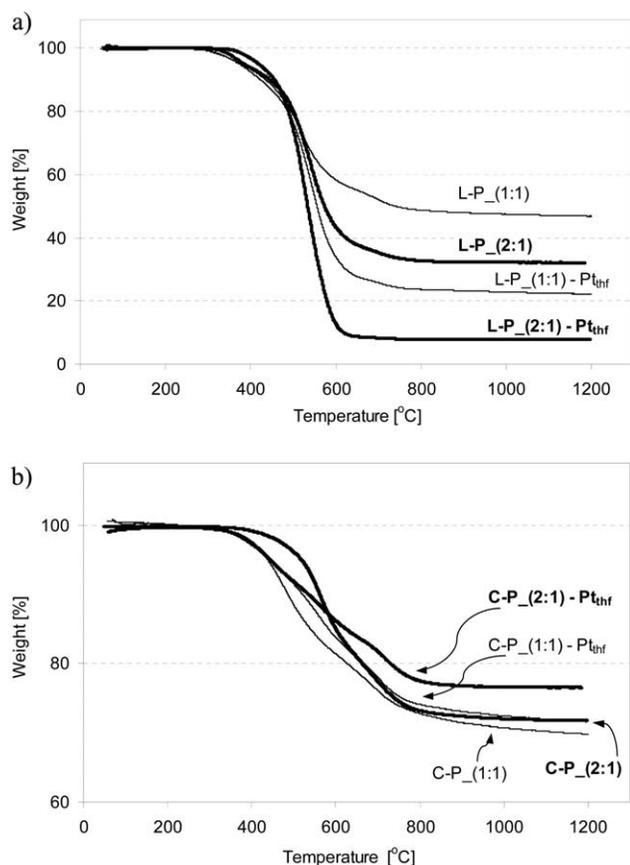
Figure 11. TG curves recorded for: (a) L-P type networks and products containing Pt species, (b) C-P type networks and products containing Pt species.

L-P_(2:1)-Pt$_{iso}$ and L-P_(2:1)-Pt$_{thf}$, into which platinum was introduced using different solvents: THF and isopropyl alcohol. The catalytic measurements for L-P_(2:1)-Pt$_{iso}$ reveal constant concentration of acetone despite the increase of the temperature. It indicates that the reaction proceeds in the diffusion region, which is also confirmed by the value of activation energy equal to 6.6 kJ mol^{-1} (characteristic for diffusion processes). According to SEM analysis (Figure 10) in L-P_(2:1)-Pt$_{iso}$ the effect of coalescence of platinum particles is observed. The Pt^0 agglomeration hinders migration of substrate molecules in the catalyst and, in this case, the rate of the reaction is limited by the diffusion process. Additionally, lower dispersion of active phase (Figures 7 and 10) causes lower activity of L-P (2:1)- Pt$_{iso}$ than L-P_(2:1)-Pt$_{thf}$, especially in higher temperatures [Figure 12(a)].

The accessibility of redox sites for the alcohol molecules is determined by the textural parameters of the network and the type of cross-linking agent. The values of M_c (Table II) are much higher for L-P than for C-P matrices. Additionally, L-P based catalysts contain less cross-linked support than these with C-P matrix. Thus, the migration of platinum ions is much easier in L-P matrices, which results in encapsulation of a part of reduced platinum in the bulk of network matrix (see Section Characterization of network-platinum systems). Since alcohol molecules weakly penetrate the network support, the most accessible sites are situated on the surface of the catalysts. Because some platinum sites in L-P-Pt catalysts are localized in the bulk of the support, these centers are not available for substrate molecules. In contrary to L-P based catalyst, in C-P-Pt system penetration of the network by platinum ions (during the process of platinum incorporation) is hindered because of smaller M_c value and a higher cross-linking degree (Table II). In this case more Pt^0 active sites are exposed on the surface of C-P-Pt catalyst and - as a result - are more accessible for the reaction substrate.

The values of activation energy (Table IV) are lower for platinum containing samples than for corresponding unmodified polymer matrices. The selectivities to acetone (Table V) for all Pt-containing catalysts exceed 90%, therefore for these systems the activity of redox sites predominates the activity of acid–base
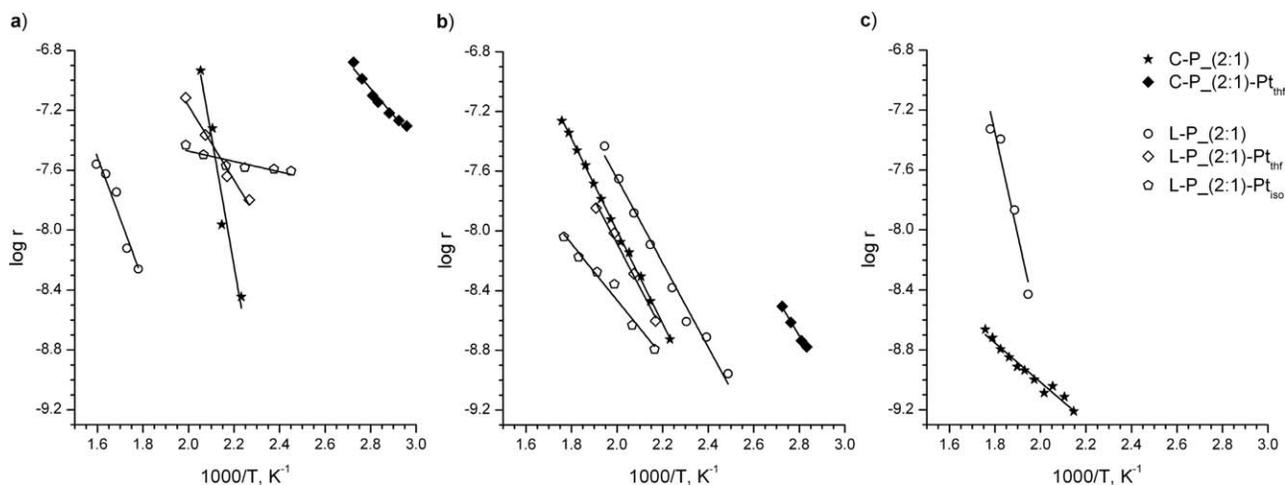
dispersion of platinum particles is different for C-P_(2:1)-Pt$_{thf}$ comparing to L-P_(2:1)-Pt systems (Figures 7 and 10). Higher dispersion of smaller platinum particles, uniform and more spread active phase (Figure 8) favor C-P-Pt system as redox catalyst. The influence of the agglomeration effect is also confirmed regarding the activity in dehydrogenation over samples

Figure 12. Arrhenius plots of isopropyl alcohol conversion to: (a) acetone, (b) propene, (c) diisopropyl ether, conducted over examined samples (selected Pt-systems and matrices). The reaction rate (r) has been expressed in mol g^{-1} s^{-1}.

Table IV. Activation Energies of Isopropyl Alcohol Conversion to Acetone, Propene, and Diisopropyl Ether

Catalyst	Dehydrogenation to acetone	Dehydration to propene	Dehydration to ether[a]
		Ea (kJ mol^{-1})	
C-P_(2:1)-Pt$_{thf}$	34.0 ± 3.0	48.8 ± 2.6	
C-P_(2:1)	166.8 ± 24.0	59.3 ± 0.6	25.0 ± 1.6
L-P_(2:1)-Pt$_{thf}$	47.5 ± 4.4	56.0 ± 3.8	
L-P_(2:1)-Pt$_{iso}$	6.6 ± 1.6	36.1 ± 3.1	
L-P_(2:1)	78.6 ± 11.6	54.0 ± 2.4	130.8 ± 22.2

[a] Diisopropyl ether.

ones. For C-P_(2:1) sample, in the lower temperature range the activities of redox and acid-base sites are comparable, but with the increase of the temperature redox sites become significantly more active. Among all examined samples, L-P_(2:1) catalyst reveals the highest activation temperature and the lowest activity of redox sites.

Regarding the results of dehydration of isopropyl alcohol to propene [Figure 12(b)] for C-P supported catalyst introduction of platinum sites increases activity, whereas for L-P-Pt systems activity decreases when compared with unmodified L-P matrix. The rise of activity for C-P-Pt catalyst is probably caused by the generation of new acid sites in the reaction of the reduction of Pt^{4+} ions by the hydrogen from Si-H groups. As described above, the reduction of platinum ions during catalyst synthesis proceeds mainly on the surface of C-P support, thus most of acid active sites are predominantly generated on the surface of this catalyst. In L-P supported catalysts, platinum ions can penetrate the network more easily, than in the C-P based one, resulting with acid centers localized mostly inside the L-P matrix. As a consequence the accessibility of active sites for the substrate molecules is better in the case of C-P-Pt than of L-P-Pt catalysts.

The reaction of isopropyl alcohol conversion to diisopropyl ether is an intermolecular dehydration of two alcohol molecules involving two adjacent acid sites. The creation of diisopropyl ether is detected only for C-P_(2:1) and L-P_(2:1) samples [Figure 12(c)]. Probably in unmodified matrices the concentration and accessibility of acid sites are high enough to enable intermolecular dehydration.

Summarizing, it is well demonstrated that for both types of network matrix the introduction of platinum active sites increases redox properties of the examined catalysts. Moreover, this modification generates new acid active sites, more accessible in C-P-Pt system.

CONCLUSIONS

The experiments have shown that metallic Pt particles can be incorporated into polysiloxane networks by a chemical reduction of metal ions conducted in the presence of cross-linking products containing active Si-H groups. Matrices prepared with the application of the cyclic hydrosiloxane (D_4^H) as the cross-linking agent are higher cross-linked networks and simultaneously contain more active Si-H groups than products obtained using the linear one (^{H}MM^H). Differences in topology of networks influence the dispersion of Pt particles introduced into the matrices. Furthermore, the reduction of platinum ions carried out in THF solution give the products with better Pt-dispersion, while the use of isopropyl alcohol solution increases the agglomeration of metal particles.

The obtained Pt-systems exhibit mainly redox activity in catalytic isopropyl alcohol conversion. The results of catalytic investigations indicate that the textural parameters of the network and the type of cross-linking agent are essential factors influencing the catalytic properties of obtained Pt-systems. C-P-Pt catalyst exhibit significantly higher activity than L-P supported ones.

Table V. Selectivities of Isopropyl Alcohol Conversion to Acetone, Propene, and Diisopropyl Ether

Catalyst	Acetone	Propene	Ether[a]	Acetone	Propene	Ether[a]	Acetone	Propene	Ether[a]
				Selectivity (%)					
		T = 330 K			T = 340 K			T = 350 K	
C-P_(2:1)-Pt$_{thf}$	98.5	1.5	–	98.3	1.7	–	98.0	2.0	–
		T = 440 K			T = 460 K			T = 500 K	
L-P_(2:1)-Pt$_{iso}$	96.3	3.7	–	94.8	5.2	–	90.7	9.3	–
L-P_(2:1)-Pt$_{thf}$	91.6	8.4	–	90.8	9.2	–	89.2	10.8	–
C-P_(2:1)	42.0	44.7	13.3	73.8	21.9	4.3	90.6	8.3	1.1
		T = 540 K			T = 560 K			T = 580 K	
L-P_(2:1)	–	74.8	25.2	3.5	59.5	37.0	3.2	46.2	50.6

[a] Diisopropyl ether.

It can be concluded, that the cross-linking products of C-P type appear to be more promising matrices than L-P type ones. Two main aspects should be indicated are: (1) the higher dispersion and the accessibility of active phase on the surface of C-P based catalyst, and (2) the possibility of the introduction of a higher amount of metal species (than used in the present work) into C-P matrices because of the remaining unconsumed Si-H sites in them. Particularly promising network appears to be C-P_(2:1) one, the product obtained using the excess of the cross-linking agent.

ACKNOWLEDGMENTS

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