

Rhodium(I) Complex Catalyst Immobilized on Terpolymers of *N*-Vinylpyrrolidinone and 1-Vinylimidazole

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ABSTRACT: The hydrosilylation of cyclohexanone and acetone with triethylsilane and diphenylsilane catalyzed by polymer-supported Rh(I) complex has been investigated. Two terpolymers of styrene, divinylbenzene, and 1-vinylimidazole (S/DVB/VI) or *N*-vinylpyrrolidinone (S/DVB/NVP) were used as the catalysts supports. Physical characterization of these materials has involved the measurements of the structural parameters in the dry and swollen states by DSC, the nitrogen BET adsorption method and inverse steric exclusion chromatography ISEC. From these results it can be concluded that the original polymer structure has been changed during the complex attachment giving rise to materials of higher porosity. X-ray photoelectron spectroscopy XPS, IR, and AAS spectroscopy were used to characterization of heterogeneous complexes before and after use. The effect of the morphology

of the support on the catalytic properties of the polymer-supported Rh(I) species was tested in the hydrosilylation of ketones and correlated with the reaction mechanism. It was demonstrated that the high selectivity of homogeneous rhodium complex toward the silyl ethers can be partially reversed to the dehydrogenative silylation products by a proper choice of polymer support with favorable microporous structure. Recycling tests demonstrated high stability of the supported catalysts during prolonged use. The constant selectivity of the supported catalysts demonstrated during recycling experiments showed that they could be useful for practical application. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3538–3546, 2012

Key words: supports; metal–polymer complexes; catalysts; morphology; selectivity

INTRODUCTION

Catalysis using polymer-supported transition metal complexes continues to attract considerable attention. A great numbers of papers, reviews, and monographs covering this field have been published over the past three decades. Also, a thorough study on the chemical, physical, and morphological structure of polymer supports and its influence on the catalytic properties of the supported catalysts have been presented. The main goal is to combine easy separation and recovery of the immobilized catalyst with the high activity and selectivity of soluble metal complex. Polymers of styrene and divinylbenzene, which are insoluble in all solvents, are the most frequently used supports for the attachment of active transition metal complexes. They can be prepared in several forms with a wide range of crosslinking.

A drawback of these copolymers is the nonequivalence of the active sites. This leads to differences in

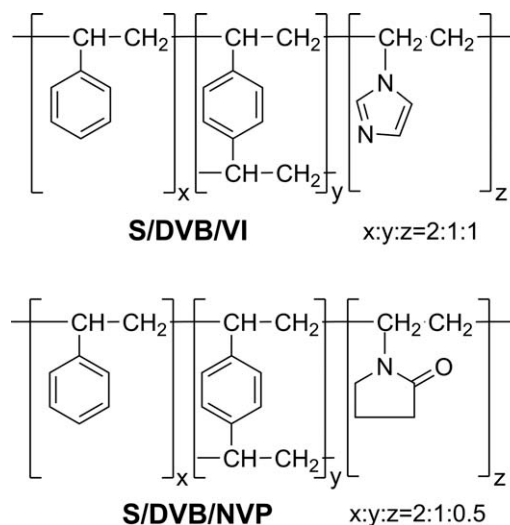
accessibility, microenvironment, stability, and activity. Highly crosslinked networks are very difficult to functionalize, due to presence of dense and thus inaccessible domains. Even if functionalization of such resins is achieved, the access of reactants to the active sites is slow and typically diffusion controlled.¹ Another problem concerned with the application of polymer-supported catalysts for industrial purposes is a costly metal complex leaching from a support to the reaction solutions. For example, the most widely employed for laboratory use phosphinated polystyrene-divinylbenzene supports have serious disadvantages connected with leaching of catalytic active species. Phosphine moiety is easily oxidized by oxygen or peroxides; this will lead to depletion of the phosphine ligand and leaching or deactivation of the catalyst, especially in polar solvents. This problem can be solved by multidentate binding of the metal complex to the polymer matrices containing functional groups which can act as chelating ligands. These strongly binding ligands or chelating units may be incorporated into the polymer during its chemical modification or the polymer itself can have an inherent multidentate character.

In recent years we have carried out investigation of the influence of the polymer structure on the

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catalytic properties of immobilized metal complex catalyst.²⁻⁴ Recently we have focused our attention on using a two novel microporous functional resins as supports for palladium nanocluster catalyst. These supports were prepared by copolymerization of styrene and divinylbenzene with *N*-vinylpyrrolidinone and 1-vinylimidazole monomers.⁵ Because of their chemical structure, vinylpyrrolidinone and 1-vinylimidazole polymers form complexes with numerous low molecular weight compounds as well as with many polymers. *N*-vinyl-2-pyrrolidinone moiety has been attractive in the chemical and material fields because of the combination of properties including solubility both in water and in a range of organic liquids, high complexing ability toward many types of organic and inorganic compounds, very low toxicity, protective-colloid action, film-forming ability, and adhesive qualities.^{6,7} Vinylpyrrolidinone units contain a highly polar disubstituted amide group coupled with apolar methylene and methine groups, bearing this respect a structural similarity to amphiphilic solvents as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and *N*-methylpyrrolidinone. The 1-vinylimidazole moiety contains two active centers: a lone electron pair of N atoms, which exhibits donating properties, and an unsaturated π -system of heterocycle, which is characterized by withdrawing properties.^{8,9} Such combination of acidic and basic units in a polymer chain imparts the macromolecules highly interesting acid-base and complexing properties.¹⁰ Although an extensive literature on the application of 1-vinylimidazole and *N*-vinyl-2-pyrrolidinone functionalized polymers as polymeric dyes, ion-exchange resins, biologically active macromolecules, drug carriers and quenching media, few studies have been published in which such polymers are employed as catalysts supports.¹¹⁻¹⁷

We now extend our studies on the application of these supports in the catalytic reactions, where catalytic sites are not present in the reduced form. Our aim was to evaluate the usefulness of rhodium(I) complex supported on above copolymers as the catalysts for hydrosilylation of ketones. Another objective was to study the influence of the polymer structure and morphology on the reaction activity and selectivity, and to assess the catalyst stability. The X-ray photoelectron spectroscopy (XPS) was used to gain more information about the mode of bonding between the metal atom and the functional groups of the copolymers. We were particularly interested to learn about microporous structure of these supports. Such polymeric materials can offer the potential for selectivity based on molecular size. In this article, we describe the results of the structural analysis of the supports and supported catalysts in the dry and swollen state. The results of thermal analysis of the selected copolymers and immobilized catalyst are also reported.



Scheme 1 Structures of polymer supports.

EXPERIMENTAL

Materials

Unless otherwise noted, materials were obtained from commercial suppliers (Sigma-Aldrich, Fluka) and used without further purification. Toluene was dried over and distilled from sodium. The complex $[\text{RhCl}(\text{CO})_2]_2$ was obtained from ABCR. Acetone, cyclohexanone, and all hydrosilanes were distilled under nitrogen, and stored over molecular sieves.

Terpolymers S/DVB/VI and S/DVB/NVP (Scheme 1) were synthesized under conditions of free-radical initiation in the presence of 2,2'-azobis(2-methylpropanitrile) (AIBN). The S : DVB : VI and S : DVB : NVP molar ratios were 2 : 1 : 1 and 2 : 1 : 0.5, respectively. Details of the materials and the synthetic procedure have already been described.⁵

Catalyst preparation

A typical procedure was followed. To a known amount of polymer matrix (0.1 g) in a round-bottom flask, a known amount of $[\text{RhCl}(\text{CO})_2]_2$ dissolved in 10 cm³ of toluene was added. The mixture was stirred at room temperature for 2–3 days until all the Rh complex was extracted by the polymer. The color of the solution changed from yellow to colorless. The product was filtered off, extracted with toluene under nitrogen to remove complex that was non-chemically bound to the polymer and finally dried under vacuum. For all supported catalysts the Rh content was fixed at ~ 0.064 mmol g⁻¹, which was below the metal uptake capacity for a polymer. IR analysis of the filtrates confirmed that all soluble complexes were absorbed by polymer matrices. The Rh content was determined by AAS spectroscopy.

Catalytic tests

All the reactions were carried out under nitrogen using freshly distilled solvent and liquid reagents. A typical procedure for hydrosilylation of ketones was as follows. The appropriate mass of supported catalyst with the required level of Rh was placed in a dried reaction vessel. A solvent—toluene (0.5 cm^3), silane (1 mmol), and ketone (1 mmol), were added successively with syringe. In all experiments the silane : ketone : Rh molar ratio was $1 : 1 : 2 \times 10^{-4}$. The mixture was stirred at 80°C . The progress of the reaction and product distribution were routinely and quantitatively analyzed by gas chromatography (GC) on a Hewlett-Packard 5990 II gas chromatograph equipped with a thermal conductivity detector. The GC column was HP-50+ (crosslinked 50% Ph Me silicone) $30 \text{ m} \times 0.63 \text{ mm} \times 1.0 \text{ }\mu\text{m}$ film thickness. The products were identified by matching their retention times with those of authentic samples.

Catalyst recycling

In the recycling tests, after a reaction was complete, the catalyst was filtered off from the reaction mixture, washed with $3 \times 25 \text{ cm}^3$ of hot toluene, dried under vacuum and used for the next reaction.

Morphology studies

The specific surface area of terpolymers and supported catalysts was measured using a dynamic nitrogen desorption method on a Sorptomatic 2000 (Carlo Erba) instrument.

Inverse steric exclusion chromatography (ISEC) was used to characterize the morphology of the samples swollen in toluene. The measurements were performed using a HP 1100 series liquid chromatograph system consisting of HP G1310A pump, Rheodyne 7725i injector, and HP G1314A RID detector. The polystyrenes of molecular weight 400–150,000 g mol^{-1} (Fluka) were used as calibration standards; $100 \times 3 \text{ mm}$ columns were loaded with the sample to be studied just before the measurements.

Study of Rh leaching

The amount of rhodium loaded in the support was analyzed by AAS method with a Perkin Elmer 3030 atomic absorption spectrometer. A sample of a polymer supported catalyst was heated up to 600°C and then dissolved in aqua regia. The resulting solution was diluted and assayed by AAS.

Spectroscopy characterization

The FT-IR spectra were measured by BIORAD spectrophotometer in an air atmosphere. For the infrared

measurements a small portion of the polymer was ground cryogenically to a fine powder, mixed with KBr powder and pressed into a pellet.

XPS measurements were made on a VG ESCALAB 210 spectrometer with Mg $K\alpha$ ($h\nu = 1253.6 \text{ eV}$) excitation from an X-ray tube (reduced power 10 kV, 10 mA). The pressure in the spectrometer chamber was about $5 \times 10^{-9} \text{ mbar}$. Samples were pressed to pellets under a pressure of 100 kbar for 10 min before these measurements. The C 1s, N 1s, O 1s, Cl 2p, and Rh 3d core level spectra were recorded. The analyzer pass energy was set at 20 eV. A take off angle of 90° was used in all XPS studies. Curve fitting was performed using the ECLIPSE data system software. This software describes each of the components of a complex envelope as a Gaussian–Lorentzian sum function. The background was fitted using nonlinear model function proportional to the integral of the elastically scattered electrons (Shirley backgrounds). All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV.

Thermal studies

DSC measurements were performed on a differential scanning calorimeter—Mettler Toledo DSC 1 at a heating rate of $10^\circ\text{C min}^{-1}$ in the nitrogen atmosphere, and the temperature range from 25 to 500°C .

RESULTS AND DISCUSSION

Characterization of the polymer supports and immobilized Rh catalysts

Two types of polymer supports functionalized with imidazole and pyrrolidinone groups were prepared by free-radical polymerization of styrene, divinylbenzene, and 1-vinylimidazole (S/DVB/VI) or *N*-vinylpyrrolidinone (S/DVB/NVP) in the presence of 2,2'-azobisisobutyronitrile initiator (Scheme 1). The synthesis and characterization of chemical composition of these terpolymers has previously been described.⁵ The immobilized active metal species were prepared by routine ligand exchange procedure by treating the polymer supports, with a solution of rhodium complex. In this article, we will deal only with supported Rh catalysts derived from $[\text{RhCl}(\text{CO})_2]_2$ as a precursor.

To characterize physicochemical properties of the polymer matrices and polymer-supported catalysts in the dry and swollen states we used a variety of analytical methods. These included the IR and X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), the nitrogen BET adsorption method, and inverse steric exclusion chromatography (ISEC).

Infrared spectroscopy and XPS measurements were used to study the mode of bonding the Rh

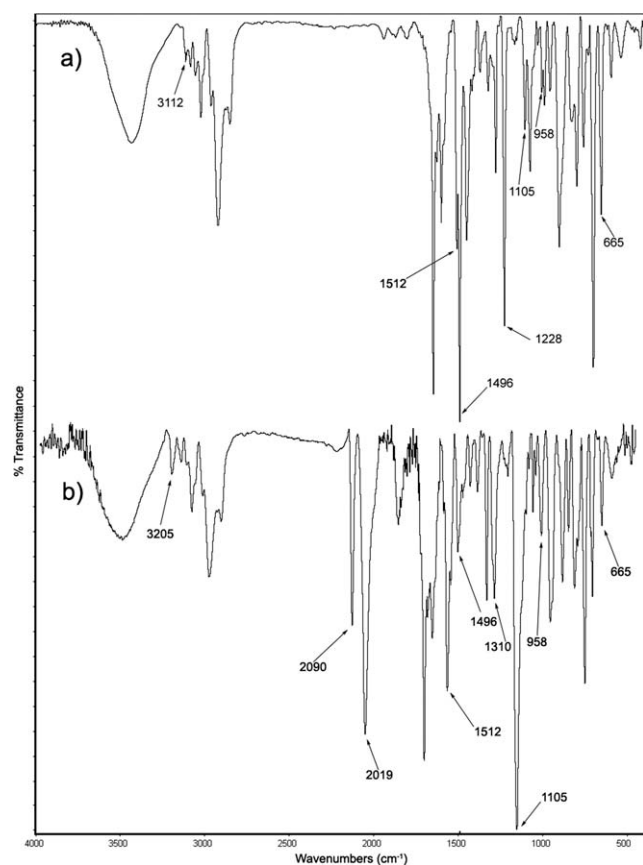
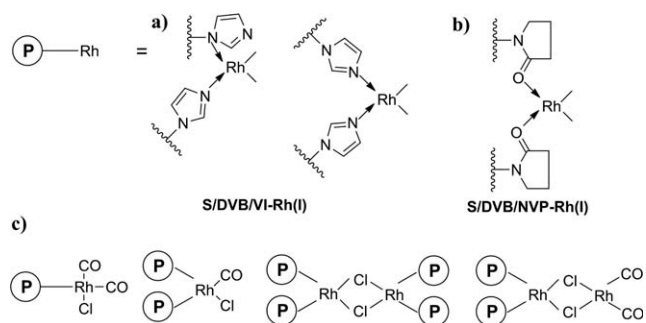


Figure 1 IR spectra of (a) S/DVB/VI terpolymer; (b) S/DVB/VI-Rh(I) catalyst.

species with the functional sites of terpolymers. The IR spectrum of S/DVB/VI complexed with the Rh carbonyl dimer (Fig. 1), $[\text{RhCl}(\text{CO})_2]_2$, reveal a change in the intensity of the characteristic imidazole ring peaks at 1496, 1512 cm^{-1} (C—C/N—C stretching), strong increase of vibration bands at 1105 cm^{-1} (in-plane ring C—H bending) and 958 cm^{-1} (out-of plane ring C—H bending), and decrease of peak at 665 cm^{-1} (torsion stretching).¹⁸ Two band at 3112 cm^{-1} (C=C—H/N=C—H stretching) and 1228 cm^{-1} (ring vibration), were shifted to 3205 and 1310 cm^{-1} , respectively. These changes may suggest that both nitrogen atoms in imidazole ring can participate in the metal coordination to the polymer matrix [Scheme 2(a)]. Such mode of coordination for Rh(I) was also confirmed by XPS measurements (Table I). The observed at XPS spectra, differences in the BEs components attributed to the amine (—N—H—) and imine (=N—) nitrogen are similar and indicate for two the two possible coordination sites.

The incorporation of Rh(I) into S/DVB/NVP polymer caused the shift of the absorption band of C=O lactame ring at 1680 to 1697 cm^{-1} , and the formation of two new absorption peaks at 1805 and 1860 cm^{-1} (Fig. 2). This indicates that the rhodium complex is bonded to S/DVB/NVP terpolymer through the car-



Scheme 2 Mode of coordination of Rh(I) complex catalyst by polymer supports.

bonyl oxygen [Scheme 2(b)]. However, contrary to previously reported data for the palladium complex bonded to S/DVB/NVP, no changes of C—N group vibration at 1287 cm^{-1} were observed.⁵ Also, XPS results did not reveal any distinct change in the BE of N 1s, which shows that nitrogen atom cannot participate in coordination with rhodium complex (Table I).

Two new strong bands observed in the carbonyl region at 2019 and 2090, after Rh complexation of both polymers, are typical for the *cis*-Rh(CO)₂ moiety. The far IR spectra of both catalysts show a new strong intensity bands in the region 280–240 cm^{-1} attributed to the bridging chlorine atoms, and a band at 301 cm^{-1} consistent with the terminal $\nu(\text{Rh—Cl})$. This indicates that both mono $[-\text{RhCl}(\text{CO})_2]$ and dinuclear $[-\text{RhCl}(\text{CO})_2]_2$ species are formed at the surface of polymers [Scheme 2(c)].

Porous structure studies

The morphology of a polymer support can greatly affect the activity and selectivity of the polymer attached complex catalysts. Conventional techniques have been used to study the porosity of the support and supported catalysts in the dry and swollen states. The support microporous structure with a narrow size pore distribution can influence the selectivity of reaction at a given site. The steric demands

TABLE I
Binding Energy Values for Supported Rhodium Catalysts and Pure Polymer Supports

Sample	Binding energy (eV)			
	N 1s		Rh 3d _{5/2}	Cl 2p _{3/2}
	N _{imine}	N _{amine}		
S/DVB/VI	398.4	399.6	309.3	198.4
S/DVB/VI-Rh(I)	398.9	399.9		
	N 1s	O 1s		
S/DVB/NVP	399.8	532.8	309.8	198.1
S/DVB/NVP-Rh(I)	399.9	533.4		

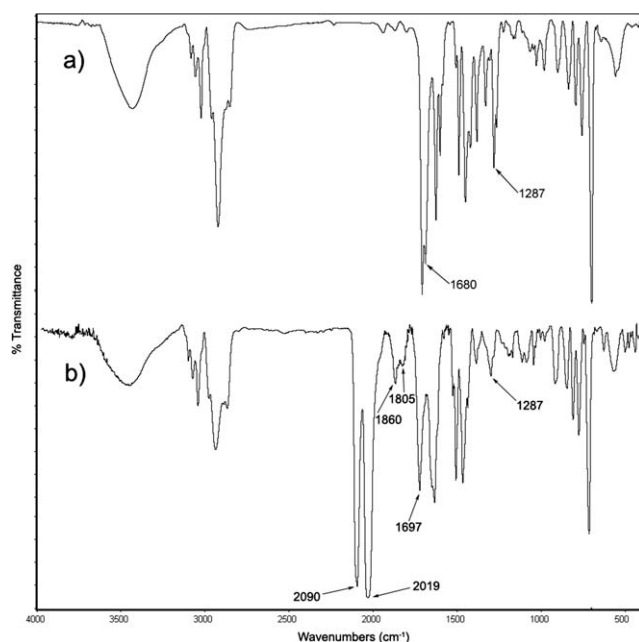


Figure 2 IR spectra of (a) S/DVB/NVP terpolymer; (b) S/DVB/NVP-Rh(I) catalyst.

of a catalytic centre bound to a support can be very different to those of its homogeneous analogue. Porous structure of the support affects the accessibility of the interior of the swollen resin and so enhances the selectivity by increasing diffusional restrictions for reaction species. Therefore, we were particularly interested to learn about the porous structure of these materials in the range of micropores (<2 nm) and mesopores (>2 nm, <50 nm), being of the same order of dimension as those of reacting molecules. Table II summarizes the results determined by nitrogen BET adsorption method. They indicate that two studied supports have different distribution of pores. These materials show different ratio of meso- to micropores and similar volume of macropores. The pores of S/DVB/NVP terpolymer were concentrated in a large, narrow band ~ 35 nm. The S/DVB/VI polymer exhibits the lower value of pore specific volume, the lower surface area and porosity than S/DVB/NVP. This sup-

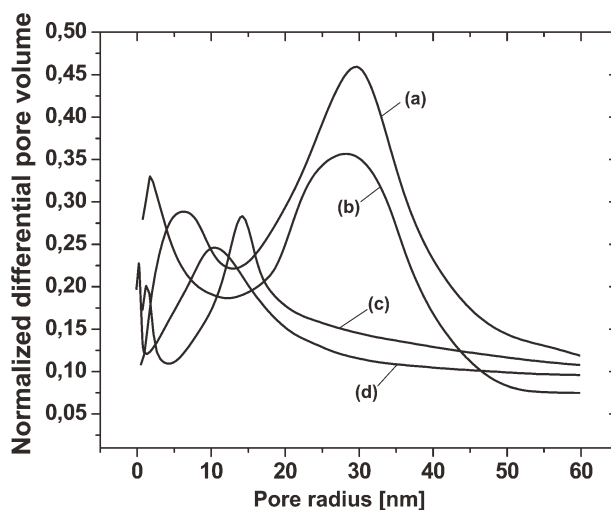


Figure 3 Pore size distribution in swollen state obtained by ISEC. (a) S/DVB/NVP; (b) S/DVB/NVP-Rh(I); (c) S/DVB/VI; (d) S/DVB/VI-Rh(I).

port had pore size distribution with the majority of the pores with a maximum about 18 nm as well as some micropores of radii about 2 nm. The lower ratio of meso- to micropores for this polymer was also confirmed by inverse steric exclusion chromatography (ISEC) measurements. The effect of swelling and porosities of polymers and polymer-supported rhodium catalysts in the swollen state were determined by ISEC. Significant differences of porosities in the dry and swollen state were observed. Because of swelling of the both terpolymers a clear decrease in the mean pore diameter was found (Fig. 3). The BET data reveal that the original porous structure of the polymer supports have been changed after the attachment of the Rh complex. In general an increase of total porosity was found after complexation with the $[\text{RhCl}(\text{CO})_2]_2$, namely, 14.7 % for S/DVB/NVP and 14.3% for S/DVB/VI matrix. For both studied supports we observed a shift of the pore size distribution to lower values going from pure to metal supported polymers. However, in the case of S/DVB/VI increasing of micropores of radii below 2 nm was not as distinct as for S/DVB/NVP. Presumably,

TABLE II
Characteristics of Polymer Supports and Supported Rh Catalysts by the BET Methods

Sample symbol	S/DVB/NVP	S/DVB/NVP-Rh(I)	S/DVB/VI	S/DVB/VI-Rh(I)
Surface area ($\text{m}^2 \text{g}^{-1}$)	220	196	170	82
Mean pore diameter (nm)	7	2	2	1.8
	35	30	18	16
Volume of pores (%)				
. macro $w > 50 \text{ nm}$	12.6	10.4	11.8	10.2
. meso $2 < w < 50 \text{ nm}$	71.8	62.6	56.9	55.0
. micro $w < 2 \text{ nm}$	15.6	27.0	31.3	34.8
Pore specific volume ($\text{cm}^3 \text{g}^{-1}$)	0.33	0.35	0.25	0.31
Porosity	0.34	0.39	0.28	0.32

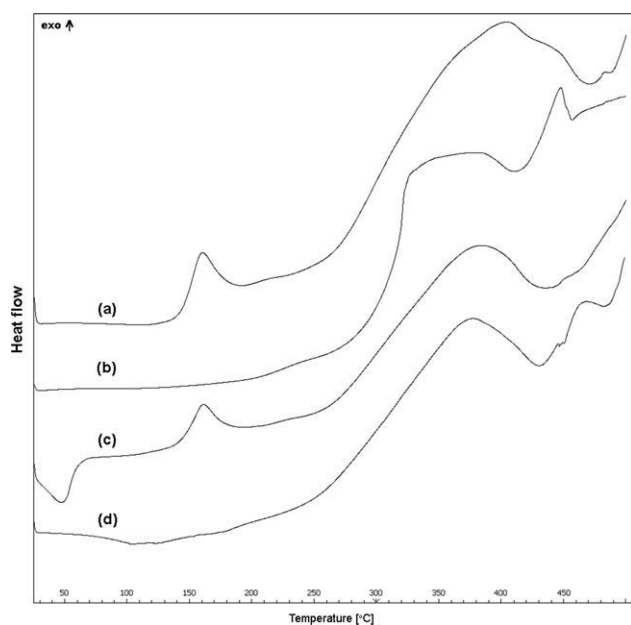


Figure 4 DSC patterns of (a) S/DVB/NVP; (b) S/DVB/NVP-Rh(I); (c) S/DVB/VI; (d) S/DVB/VI-Rh(I).

micropores of this support were blocked by the metal complex, whereas new micropores were formed for S/DVB/NVP. This is consistent with the decrease of the surface area after the catalyst precursor attachment. We observed similar changes when polymer supports and attached rhodium catalysts were studied in the swollen state by ISEC method. As presented in Figure 3 the ISEC comparative measurements of terpolymers and immobilized rhodium catalysts, indicate a shift of the pore size distribution toward smaller pores. Similar changes in the porous structure of polyamide matrices after attaching rhodium complex and the formation of crosslinking between polymer chains and metal species we reported in our earlier works.^{19–21}

Thermal studies

The structural rearrangements of the polymer network that take place during complexation were also confirmed by differential scanning calorimetry. The most characteristic feature of the DSC profiles of both immobilized Rh(I) catalysts was the disappearance of the exothermic peaks at 160°C (Fig. 4) when compared with the pure polymers. One of the rationalizations available at the moment, partially confirmed by SEM analysis (not presented here) and observed morphology changes, is the presence of rhodium complex crystallites inside micropores of polymer support. Such an exotherm can also mean that a chemical reaction without weight change took place. In a similar way to microporous structure differences, we ascribe the observed changes to the formation of additional crosslinks between polymer chains and metal species

through coordination bonds. DSC analysis has shown that the introduction of the rhodium species into the both terpolymers does not change glass temperature (lies in region of decomposition) and the thermostability of these materials which are stable to about 270°C in the presence of nitrogen.

Catalytic tests

The catalytic properties of the Rh(I) complex catalyst attached to the resins via imidazole and pyrrolidone groups were studied in the hydrosilylation of symmetric ketones. As this reaction often leads to side products, it gives the opportunity for thorough examination of conditions that can make the reaction selective.²² The selectivity of this reaction is difficult to control and depends on several factors such as electronic and steric effects of the substituents on the ketone and silane, type and valency of transition metal. Additionally, for the immobilized systems, the rate and selectivity of the reaction can be controlled by tuning the steric and electronic character of metal centres induced by the binding ligands and morphological structure of the support. Hydrosilylation of carbonyl groups is an important synthetic transformation that is widely employed in organic chemistry. This reaction provides a convenient one-step process for converting aldehydes and ketones directly to protected alcohols (silyl ethers), which circumvents the two-step procedure of reduction to alcohol followed by silyl protection. However, selectivity of these processes are not always satisfactory because of side reactions. The main side reaction of carbonyl compounds catalyzed by Rh(I) complexes is dehydrogenative silylation.^{23–26} The resultant silyl enol ethers are also useful reagents in organic synthesis.

From the results presented in Table III, it is evident that the activity of the supported catalysts with comparable Rh content, expressed as a time required for a desired conversion, closely correlate with the polymer morphology. The activity decrease of the S/DVB/VI-Rh(I) catalyst we ascribe to fewer Rh sites located inside micropores, being accessible to the reactants. The S/DVB/NVP-Rh(I) which contains a high quantity of mesopores facilitates contact of reagents and enhances the catalytic reaction. The higher impact of the porous structure of the polymer supports on the activity of the catalysts as compared with the influence of the electronic effects of the polymeric ligands was confirmed by XPS measurements which showed small differences of the BEs for the Rh 3d_{5/2} attached to both types of polymers.

The opposite results of activity studies of the two selected catalysts together with detailed information on their porous structure, suggest that morphological factors may also give rise to catalyst selectivity. Hydrosilylation of acetone and cyclohexanone

TABLE III
Hydrosilylation of Ketones

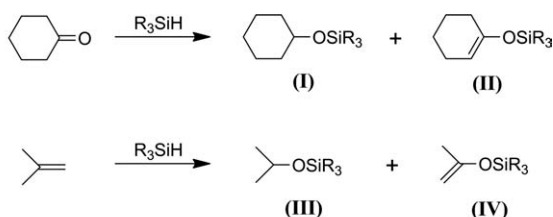
Catalyst	Silane	Time (h)	Conversion (%)	Product distribution (%)	
				I	II
Ketone			cyclohexanone		
Homogeneous Rh(I)		1	89	86.4	13.6
S/DVB/NVP-Rh(I)	Et ₃ SiH	2	82	82.3 (79.0)	17.7 (21.0)
S/DVB/VI-Rh(I)		8	72	71.3 (68.9)	28.7 (31.1)
Homogeneous Rh(I)		1	83	98.1	1.9
S/DVB/NVP-Rh(I)	Ph ₂ SiH ₂	2	87	96.2 (92.3)	3.8 (7.7)
S/DVB/VI-Rh(I)		10	84	75.2 (65.4)	24.8 (34.6)
				III	IV
Ketone			acetone		
Homogeneous Rh(I)		1	83	89.1	10.9
S/DVB/NVP-Rh(I)	Et ₃ SiH	3	74	88.0 (85.2)	12.0 (14.8)
S/DVB/VI-Rh(I)		12	46	58.0 (51.7)	42.0 (48.3)
Homogeneous Rh(I)		1	92	95.7	4.3
S/DVB/NVP-Rh(I)	Ph ₂ SiH ₂	5	89	94.4 (89.5)	5.6 (10.5)
S/DVB/VI-Rh(I)		16	70	60.4 (53.6)	39.6 (46.4)

Reaction conditions: Temperature = 80°C; [silane] : [ketone] : [Rh] = 1 : 1 : 2 × 10⁻⁴; the overall volume: 5 cm³; solvent: toluene; the yield refers to GC analysis; data in parentheses concern the catalysts preswelled in toluene.

(Table III) was carried out with Ph₂SiH₂ and Et₃SiH by using S/DVB/NVP-Rh(I) and S/DVB/VI-Rh(I) catalysts (Scheme 3). The reaction catalyzed by homogeneous complex [RhCl(CO)₂]₂ was also performed for comparison. The selectivity of homogeneous reaction depends on the type of ketone used; e.g., hydrosilylation of cyclohexanone and acetone with Et₃SiH gave 86.4 and 84.1% of silyl ethers, respectively, whereas the hydrosilylation with Ph₂SiH₂ led to almost exclusive formation of these products.

As shown in Table III, the use of polymer supported catalysts in these reactions greatly changed the reaction selectivity when compared with that in the homogeneous system. To account for the dependence of the selectivity of the rhodium systems on the morphology of the catalyst, it is necessary to discuss the reaction mechanism in conjunction with the pore size distribution data. The generally accepted mechanism is presented in Scheme 4.^{27,28}

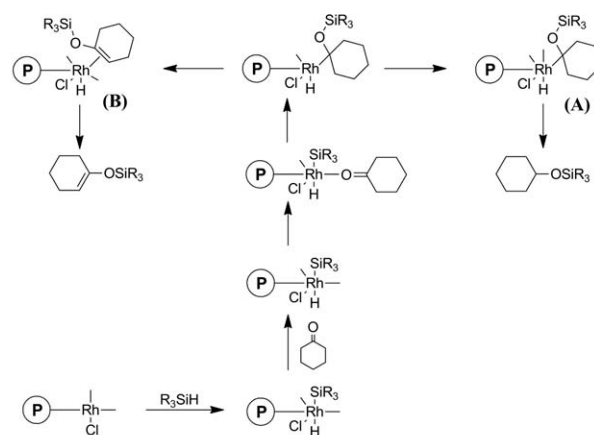
These investigation have shown that in the case of S/DVB/VI support, when microporous structure prevents the formation of intermediate A with higher steric requirements, the selectivity of the parent homogeneous catalyst cannot be preserved after immobilization.



R₃SiH = Et₃SiH, Ph₂SiH₂

Scheme 3 Hydrosilylation of cyclohexanone and acetone.

The steric interactions arising from polymer morphology disfavour the formation of intermediate A, thus allowing the open coordination site at the Rh center in intermediate B that is necessary for β-H elimination. This type of selectivity, where there is not sufficient space in the pores to allow formation of the transition state in a concurrent catalytic cycle, is often described as restricted transition state selectivity.²⁹ For Rh(I) complex catalyst supported with S/DVB/NVP carrier with large surface area and a large pore diameter, the selectivity of the all conducted hydrosilylation reactions were close to those of the homogeneous [RhCl(CO)₂]₂ catalyst. The observed selectivity trend was more distinct for hydrosilylation with Ph₂SiH₂ silane. Less bulky substituents on Et₃SiH, and smaller transversal and linear dimension of intermediate B, verified by the



R₃SiH : Et₃SiH, Ph₂SiH₂

Scheme 4 Mechanism for the hydrosilylation of cyclohexanone catalyzed by polymer-supported Rh(I) catalysts.

semiempirical PM3 calculation using Gaussian 03W, are responsible for the increase of dehydrogenative silylation products yield. It seems to confirm our hypothesis that the key factor responsible for silyl ether selectivity deterioration must be the narrow structure of the pores in S/DVB/VI terpolymer. However, we are not ruling out that such difference in selectivity can be also ascribed to the type of binding groups in terpolymer. The strong metal-support interaction that exist between rhodium and imidazole functionality, which is considered as better electron donating moiety than pyrrolidinone ring was confirmed by XPS data which show that the BE for the Rh 3d_{5/2} attached to S/DVB/VI was lower than that observed for S/DVB/NVP-Rh(I) catalyst. Higher electron donation from vinylimidazole ligands to the metal should facilitate the β-H elimination.^{30,31} Additionally, participation of both nitrogen atoms in imidazole ring in the metal coordination increase the steric hindrance around the Rh center and induces better silyl enol selectivities.

To get more information on the influence of polymer swelling on the reaction selectivity, experiment were carried out where supported catalysts were preswelled in toluene for 24 h prior the reaction. The results of all catalytic tests (Table III) clearly show that the product distribution is greatly influenced by the polymer morphology changes. For example, for the S/DVB/VI-Rh(I) catalyst with smaller pores, preswelling exerted more distinct effect on the selectivity of all reactions than for S/DVB/NVP-Rh(I) with larger pores. Presumably in the preswelled state the steric factor is becoming more significant and creates better conditions for the formation of the dehydrogenative silylation product.

Catalyst stability

The immobilization of metal complex onto polymer supports without reducing their activity due to leaching of the metal, is of great importance for practical utilization of the catalysts.

The recycling efficiency of the anchored catalysts was determined by reusing, four more times, previously used catalyst, and checked its catalytic activity and selectivity on independent experiment under the same conditions. In all tested reactions, the catalytic properties of supported Rh catalyst have been fairly stable during repeated use in spite of Rh leaching determined by atomic absorption spectroscopy AAS (Fig. 5). Also, the solution, left after each catalytic run, was analyzed by AAS, and the trace of rhodium was detected. This drop was still at the safe level of the Rh concentration and essentially did not affect the activity and selectivity of the polymer catalysts except the first two run. Usually observed initial drop of the activity and selectivity fluctuations

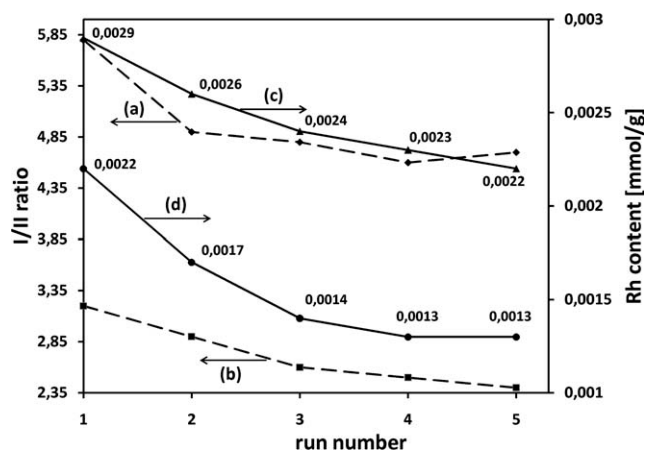


Figure 5 Selectivity and Rh content as function of runs in hydrosilylation of cyclohexanone with Et₃SiH. Products I/II ratio for (a) S/DVB/NVP-Rh(I); (b) S/DVB/VI-Rh(I). Rh concentration determined by AAS for (c) S/DVB/NVP-Rh(I); (d) S/DVB/VI-Rh(I).

mostly come from the detachment of the weakly bound complex species via, for example physical forces (Fig. 5). These are still present after washing the catalyst during the preparation procedure. Based on these results all presented catalytic properties data in Table III concern the 4th run. High stability of studied catalysts was also proved by XPS analysis. Their BE spectra for the Rh 3d level (not presented here) for the freshly prepared catalysts and those after five catalytic runs were almost identical and did not show any peak that can be attributed to the metallic state.

CONCLUSIONS

The results of this study have demonstrated that the prepared terpolymers meet the requirements for organic supports in that they can be used for the preparation of rhodium hydrosilylation catalysts. Our experiments have shown that the microporous structure of the polymer supports in the hydrosilylation of ketones seems to have higher impact on the reaction activity and selectivity as compared with the influence of the type of binding groups of the polymer support. The morphology parameters such as pore size distribution and specific surface area have been changed after complex attachment. This effect was ascribed to structural rearrangements of chains of polymer network around metal species acting as crosslinking centres. Based on the recycling efficiency tests, it was found that the both polymer-supported rhodium catalysts have a high catalytic stability, in terms of both activity and selectivity, for five consecutive runs.

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