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Rhodium(I) complex catalysts immobilized on polyamides having a pyridine moiety Effect of the polymer structure

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Abstract

A series of polyamides have been synthesized by low-temperature interfacial condensation of 2,5- and 2,6-pyridinedicarboxylic chlorides and aliphatic diamines $H_2N(CH_2)_nNH$, where $n = 2$ and 6, and used as the model supports for immobilization of the Rh(I) complex catalyst. Physical characterization of these materials has involved the measurements of the structural parameters in the dry and swollen states by WAXS, SAXS, DSC, the nitrogen BET adsorption method, ISEC and pycnometry. 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. The relation between the support structure and catalyst activity and selectivity was studied in the model reactions, namely, hydrosilylation of alkenes, dienes and alkynes. It was found that the catalyst activity decreased with increasing polymer crystallinity. A strong impact of support structure on the catalyst selectivity was also revealed. A high regioselectivity of the catalyst in the hydrosilylation of alkenes toward formation of the linear products was achieved due to the favorable microporous structure of the polyamide supports with pore sizes between 10 and 20 Å. It was also demonstrated that the stereoselectivity of the reaction can be reversed to the opposite direction by a proper choice of the donor functions in a polymer support, e.g. the traditional *cis*-selectivity of the rhodium (Rh) catalysts in the hydrosilylation of phenylacetylene was changed to *trans*-selectivity by use of the 2,5-py instead of 2,6-py moiety. The results of the 6–9 times repeated catalytic runs indicated high stability of the polyamide-supported catalysts.

Keywords: Heterocyclic polyamides; Rhodium(I); Supported catalysts; Physicochemical parameters; Microporous structure; Activity; Regioselectivity; Stereoselectivity; Hydrosilylation; Alkene; Diene; Alkyne; Structure-activity/selectivity correlation

1. Introduction

Since the mid-1970s, transition metal complex catalysts heterogenized on solid supports have become a key problem in the research laboratories worldwide, because these type of catalysts can in principle, combine the advantage of easy catalyst recovery with the high activity and selectivity of soluble complexes [1–5]. Several materials including inorganic solids [9,10] and organic polymers [1–8] have been used as supports.

The major advantage of inorganic supports is their good mechanical and thermal stability, while the important advantage of polymeric matrices is their ability of changing the physicochemical structure by simple methods. The enormous interest associated

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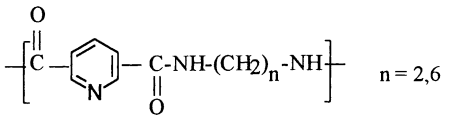
with the field of "heterogenized catalysis" has been documented by a great number of papers, reviews, book chapters, and monographs ([1–15], and the references cited therein).

It has long been recognized that the nature of the polymer support can have a very profound effect on the behavior of supported metal complex catalysts. However, not much information dealing with these problems is available in the literature [16,17]. Recently, a thorough study on the physical and morphological structure of polymer supports and its influence on the activity of the supported catalysts has been presented by an international team [18–21].

An important aspect of studying the correlation between the reactivity of the supported catalysts and the structure of polymer support is a fortunate choice of a model polymeric support and a model reaction. In search for polymeric materials whose physical and chemical structure could be easily modified for our needs we have focused on the use of a family of polyamides containing a pyridine moiety in a polymer mainchain (PApy) of the following formula.



This review paper summarizes the results of our recent studies [22–27] on the catalytic systems supported on polyamide supports.

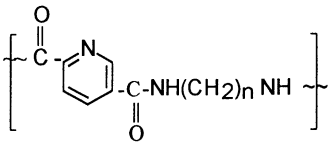
First, we have described the synthesis of PApy supports and supported complex catalysts and their characterization by numerous physico-chemical methods. We have then presented the application of the Papy-supported metal species in catalytic model reactions, namely, hydrosilylation of alkenes, dienes and alkynes. It is worth mentioning here that hydrosililation of carbon–carbon multiple bonds is an important industrial process for which Pt-based species have become the catalysts of choice. There have been many more or less successful attempts to immobilize soluble Pt catalysts and produce more convenient heterogeneous analogues [1,47–49]. Recently, preparation of remarkably active, selective and stable polymer-supported Pt catalysts have been reported for this reaction [28]. The rhodium (Rh) catalysts have been also frequently used among all the metal-based catalysts [1,47–49] and here, in this paper, we present our research that deals with the Rh(I) polymer-supported systems only. Special emphasis has been stressed on the correlation between catalyst activity and selectivity and the support chemical and physical structure. Tests of catalysts stability during their prolonged use have also been described.

2. Synthesis of the polyamide supports PApy and supported catalysts

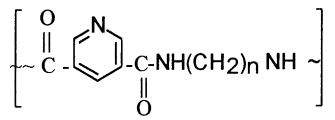
The most widely employed supports for the attachment of active transition metal complexes are styrene and divinylbenzene copolymers [11–15]. Their popularity arises from a rich selection of methods, which can easily incorporate the functional groups and can change their physical structure. However, a drawback of these polymers is their sensitivity to thermooxidation. Therefore, in the past there have also been interest in the use of natural and synthetic polyamides which are more thermally and oxidatively stable and contain inherent coordination sites [29–46].

For our study, we have decided to choose as supports a family of polyamides having a pyridine and aliphatic residues in their repeat units (PApy). Two series of PApy were prepared by low temperature interfacial polycondensation from 2,5- and 2,6-pyridine dicarboxylic acid dichlorides and aliphatic diamines using a toluene–water system with potassium hydroxide as HCl acceptor as insoluble fluffy particulates.

series 2,5-py **E** (n = 2) and **H** (n = 6)



series 2.6-py **E** (n = 2) and **H** (n = 6)



The reason for such a choice was as follows. Firstly, it was possible to tailor the porous structure and control the surface area by variation of the length

of the methylene chain of the diamine and by different placement of a pyridine ring in the mainchain (in the 2,5- and 2,6-positions). Secondly, these polymers contain three potential coordination sites, the pyridine and amide nitrogen, and carbonyl oxygen, which can act as chelating multidentate ligands. Thirdly, the polyamides materials have inherently good thermal stability (over 300°C), and fourthly, they can be prepared by a simple synthetic method. To our knowledge such materials have not been examined as supports for the homogeneous metal complex catalysts prior to our own work [22–27]. The immobilized active metal species were prepared by routine ligand exchange procedure by treating the polyamides, PApy, with a solution of metal complex. In this paper, we shall deal only with the supported Rh catalysts derived from $[RhCl(CO)_2]_2$ as a precursor.

3. Physical characterization of the PApy supports and PApy-supported rhodium catalysts

A full knowledge of the physicochemical characteristics of the polymer support itself and the polymer-supported catalyst are essential in designing the catalytic properties of the polymer-supported systems for a given reaction.

We used a variety of analytical methods to study the PApy matrices and Papy-supported Rh catalysts in the dry and swollen states. These included the wide and small angle X-ray diffraction scattering, IR and X-ray photoelectron spectroscopy, differential scanning calorimetry and thermogravimetry, the nitrogen BET adsorption method, pycnometry and inverse steric exclusion chromatography.

3.1. Crystallinity studies

The exent of crystallinity in the polyamides was examined by wide angle X-ray diffraction. The prepared polyamides possess a semi-crystalline character and show various degrees of crystallinity depending on the length of the aliphatic spacer (Table 1). As expected, polyamides of the 2,5-py series which are more prone to close packing, show a greater crystallinity than those of the 2,6-py series. The presence of crystallites makes the PApy polymer behave as though it was a crosslinked network.

3.2. Porous structure studies

The morphology of a polymer support can greatly affect the activity and selectivity of the polymer attached complex catalysts. Therefore, we were particularly interested to learn more about the microporous structure of the PApy matrices and supported catalysts in the range of pores <20 Å, being of the same order of dimensions as those of the reacting molecules. Several techniques were applied to study the morphology of those materials in the dry and swollen states.

Fig. 1 [27] and Table 1 [25] summarize the results determined by small angle X-ray scattering (SAXS) and nitrogen BET adsorption methods, respectively. They indicate that regardless of the chemical structure, the polyamide supports can be divided into two groups. Both of the E-type matrices, 2,5-py E and 2,6-py E, with a short ethylene spacer have a higher surface area and similar distribution of pores with a maximum around 15 Å. Similarly, both of H-type polymers, 2,5-py H and 2,6-py H, with a longer hexamethy-

Table 1
Characteristics of PApy and PApy/Rh catalysts deduced from N_2 sorption and BET analysis [25]

Sample symbol	2,5-py E	2,6-py E	2,6-py E/Rh	2,5-py H	2,6-py H	2,6-py H/Rh
Crystallinity (%)	30	20		35	26	
Surface area (m^2/g)	91.7	47.9	43.2	19.0	4.4	7.7
Volume of pores (%)						
Macro w > 500 Å	45.7	46.3	50.6	0	0	0
Meso 20 Å < w < 500 Å	40.3	42.1	38.8	72.5	75.8	77.0
Micro w < 20 Å	14.0	11.6	10.6	27.5	24.2	23.0
Pore specific volume (cm^3/g)	0.36	0.22	0.22	0.042	0.012	0.022
Porosity	0.35	0.22	0.35	0.051	0.015	0.026

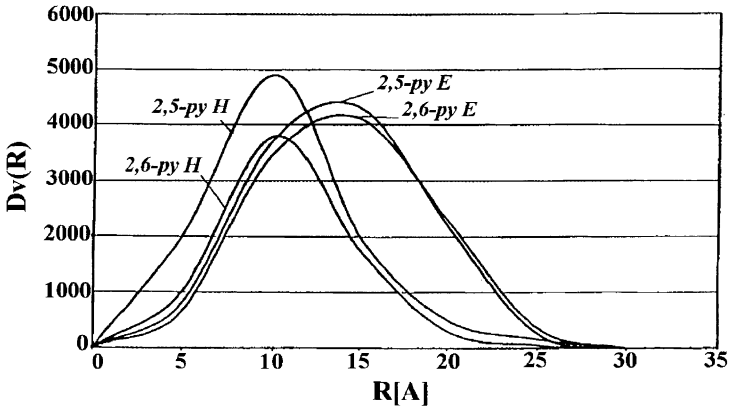


Fig. 1. The micropore size distribution of the polyamide PApy supports by the SAXS method [27].

lene chain show a lower surface area, no macropores, and display a pore distribution with a maximum around 10 Å.

The data given in Table 1 reveal that the original microporous structure of the polymer supports has been changed after the attachment of the Rh complex. A significant increase of the total porosity was found, namely, 59% for 2,6-py E/Rh and 73% for the 2,6-py H/Rh type matrix. This is consistent with the decrease of the surface area for 2,6-py E/Rh. Only for the 2,6-py H sample does the complexation process bring about an increase of surface area because this particular polymer has the lowest surface area, the lowest pore specific volume and porosity. An example of the changes that occur during a complex immobilization is given in Fig. 2 [25]. It shows a shift of the pore size distribution to lower values going from pure to metal supported polymers.

We were aware of the poor accuracy of the N_2 sorption and BET method and have applied additional techniques such as inverse steric exclusion chromatography (ISEC) and pycnometry to study of PApy polymers and attached Rh catalysts in the swollen state. As presented in Fig. 3 the ISEC comparative measurements of 2,6-py E and 2,6-py E/Rh, indicate an increase of microporosity from 19 to 47% after the Rh immobilization and a shift of the pore size distribution toward smaller pores. The profile of this function is in excellent agreement with those determined for samples in the dry state.

Morphological parameters determined by pycnometry [25] show that the porosity, specific pore volume

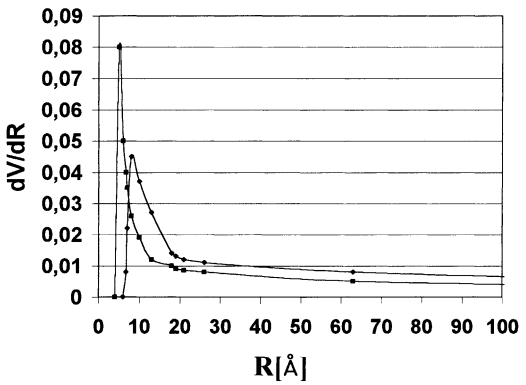


Fig. 2. The micropore size distribution of the 2,6-py H and 2,6-py H/Rh systems by the BET method [25].

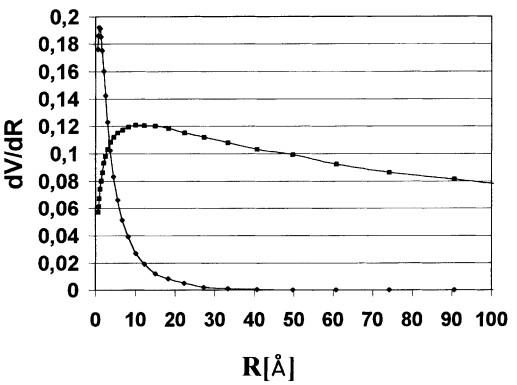


Fig. 3. The micropore size distribution of the 2,6-py E and 2,6-py E/Rh systems by the ISEC method [25].

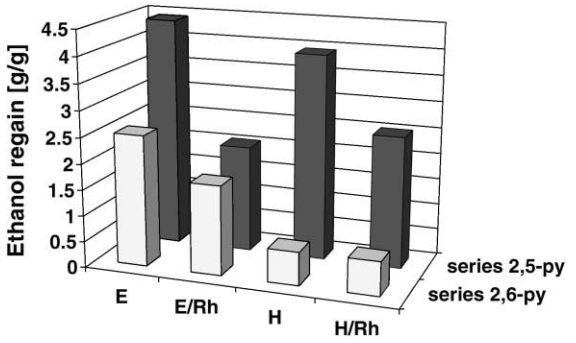


Fig. 4. Swelling in ethanol of the 2,5- and 2,6-py E and H polyamide supports and supported Rh catalysts [25].

and solvent regain of pure matrices decrease after the Rh complex loading. Fig. 4 shows a significant lowering of swelling of PApy-attached Rh catalysts in ethanol in comparison with pure, unloaded polymers.

The structural rearrangements of the polymer chains that take place during complexation were also confirmed by differential scanning calorimetry [25]. The most characteristic feature of the DSC profiles of the PApy-supported systems was the appearance of new endothermic transitions with low enthalpy values (Table 2 and Fig. 5) when compared with the pure polymers. We ascribe the observed changes in the microporous structure of the PApy supports to the formation of crosslinks between polymer chains and metal species through coordination bonds. Thermal analysis has shown that the introduction of the metal species into the PApy polymers only slightly reduces the inherent thermostability of these materials which are stable in air up to 300°C.

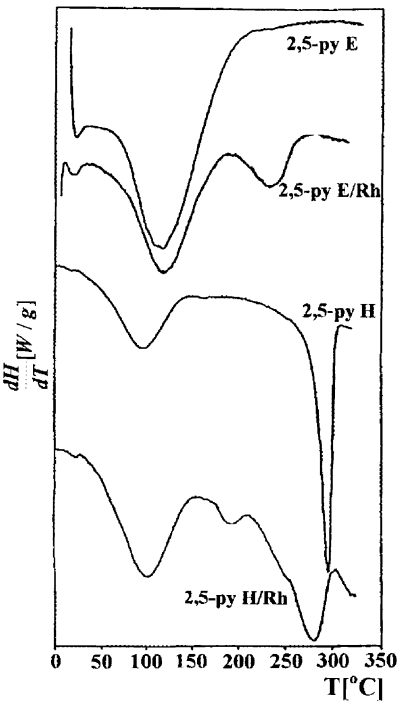


Fig. 5. Collective DSC curves of the 2,5-py E and H polyamide supports and supported Rh catalysts at a heating rate of 20°/min. [25].

4. Characterization of the PApy-supported rhodium catalysts by spectroscopic methods

4.1. Infrared spectroscopy

Infrared spectroscopy was used to study the mode of bonding of the Rh species with the functional sites

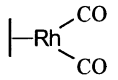
Table 2
The temperature of endothermic transitions and enthalpy values of polyamide PApy matrices and Papy-supported rhodium systems from DSC analysis [25]

Sample	$T_{H_2O\,peak}$ (°C)	ΔH (J/g)	$T_{new\,peak}$ (°C)	ΔH (J/g)	$T_{melt.\,peak}$ (°C)	ΔH (J/g)
2,5-py H	94	66			297	60
2,5-py H/Rh	97	53	243 sh, 187	30, 3	279	31
2,5-py E	119	103				
2,5-py E/Rh	113	75	233	16		
2,6-py H	119	63				
2,6-py H/Rh	98	49	227	2		
2,6-py E	119	102			275	44
2,6-py E Rh	115	102	222	5	259	10

of the polyamide PApy supports. Since the detection sensitivity for metal coordination to the polymer support was very poor, due to the low metal concentration and strong absorptions of the PApy itself, we synthesized and used two low-molecular-weight model compounds to mimic the polymer repeat unit, namely, di-*n*-butyl-2,5-pyridinedicarboxamide and di-*n*-butyl-2,6-piridinedicarboxamide (a) (2,5- and 2,6-$[CH_3(CH_2)_3HNCOpy\text{-}CONH(CH_2)_3CH_3]$ [22].

The IR spectra of the model compounds complexed with the Rh carbonyl dimer, $[RhCl(CO)_2]_2$, reveal the disappearance of the I and II amide bands at 1627 cm^{-1} (νC=O) and 1530 cm^{-1} ($\nu CN + \delta NH$) and appearance of the new band at 1585 cm^{-1} (Fig. 6). Spectra in the far-infrared region show the presence of bands between 274 and 240 cm^{-1} characteristic of bridging chlorine atoms, and a band at 308 cm^{-1} consistent with the terminal ν(Rh–Cl). A decrease in the intensity of the pyridine bands of the model compounds after Rh complexation is also observed. New bands appear in the range 245–220 cm^{-1} assigned to the Rh–py stretching vibrations.

In the N–H stretching region, no new band appears, which suggests no formation of a Rh–NH bond. The two strong IR bands, in the carbonyl region at 2093 and 2032 cm^{-1} are typical for the Rh *cis*-dicarbonyl moiety.



The results from the infrared studies indicate that the Rh species are bound to PApy supports through the carbonyl oxygen and pyridine nitrogen and form a mixture of mono- and di-nuclear surface structures.

4.2. X-ray photoelectron spectroscopy

The XPS data summarized in Table 3 show that three possible coordination sites participate in binding the Rh to the polyamide support [26]. This is indicated by the increase of the binding energy BE for N_{py}, N_{amide} and $O_{C=O}$ 1s electrons after the Rh attachment. It is also clear that the BE for the Rh $3d_{5/2}$ attached to the 2,6-py type polymers is lower by 0.31–1.03 eV than that observed for the Rh-supported on the 2,5-py polymers. (Table 3, entries 2, 6, 10 and 12). These results can be explained by the electronic effects of the polymeric ligands. The pyridine ring substituted in the 2,6-positions is considered as the better electron donating moiety than that substituted in the 2,5-positions, where the electron density is more dispersed. This was confirmed by the semi-empirical PM3 method.

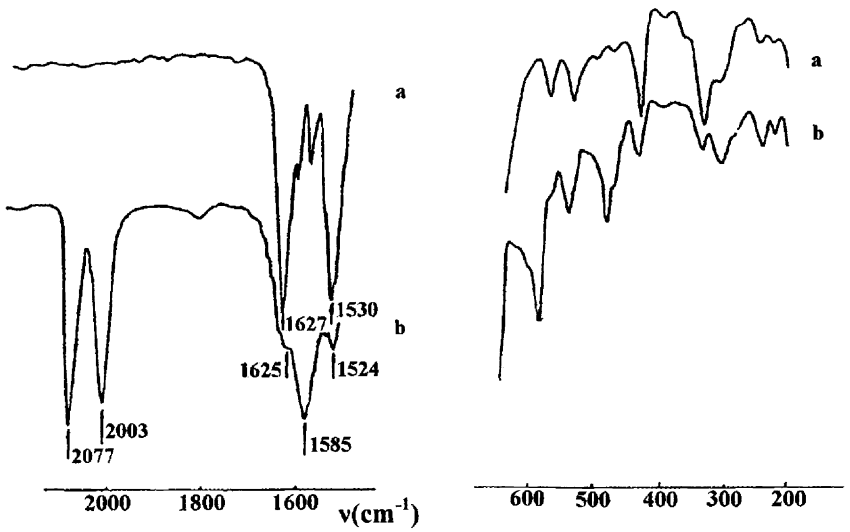


Fig. 6. IR spectra of (a) the model low-molecular-weight compound and (b) when complexed with the precursor complex $[RhCl(CO)_2]_2$ [22].

Table 3
Binding energy values of the pure polyamide PApy supports and PApy-supported Rh(I) catalysts from XPS measurements [26][a]

Entry	Sample	N 1s		O 1s	Cl $3p_{3/2}$	Rh $3d_{5/2}$
		N_{py}	N_{amide}			
1	2,6-py E	399.36	399.88	531.47		
2	2,6-py E/Rh before use	399.50	400.02	531.63	198.05	309.57
3	2,6-py E/Rh after first run	399.29	399.81	531.35	197.95	309.06
4	2,6-py E/Rh after several runs	399.50	400.02	531.59	198.10	309.56
5	2,6-py H	399.35	399.87	531.58		
6	2,6-py H/Rh before use	399.54	400.05	531.64	198.27	309.27
7	2,6-py H/Rh after 1st run	399.26	399.78	531.44	197.96	309.00
8	2,6-py H/Rh after several runs	399.34	399.86	531.49	198.25	309.11
9	2,5-py E	399.22	399.74	531.33		
10	2,5-py E/Rh before use	399.36	399.88	531.46	197.26	309.88
11	2,5-py H	399.39	399.91	531.67		
12	2,5-py H/Rh before use	399.82	400.34	531.97	198.43	310.30

[a] All binding energy values referenced to C 1s = 287.90 eV of the >C=O group FWHM values ranged from 1.5 to 2 eV.

5. Catalytic properties of the PApy-supported rhodium catalysts

To study the effect of the support structure on activity and selectivity of the PApy-supported Rh catalysts, we have chosen as a model reaction hydrosilylation, which formally is the addition of hydrosilanes to unsaturated bonds. As this reaction often leads to different isomers and side products, it gives the opportunity for a thorough examination of factors that can make a reaction selective. In this study, we deal with silanes having alkyl, aryl or alkoxy substituents, but not with chlorosilanes which often turn to be the difficult reactants.

5.1. Activity studies

Since the major effect of the crystallite in a polyamide matrix is to act as a crosslink, we first investigated the activity of the PApy-supported catalysts in relation to the degree of the support crystallinity. The model reaction for this study was the hydrosilylation of hexene-1 which gives the addition product and some amount of hexene-1 isomers [22].

$$X_3SiH + CH_2{=}CH(CH_2)_3CH_3 \rightarrow X_3Si(CH_2)_5CH_3 + \text{alkene isomers},$$

$$X_3Si = Me_2PhSi$$

From the results presented in Fig. 7, it is evident that the activity of the supported catalysts expressed in TOF closely correlate with the polymer structure dependent on the amount of crystalline order. In general, the activity decreases when the crystallinity of the PApy polymers increases. These changes are in agreement with the expected trends, i.e. that the activity of the catalysts supported on polyamides of the 2,5-py series is lower than that on the polymers of 2,6-py series. The decrease of the catalyst activity we ascribe to fewer Rh sites being accessible to the

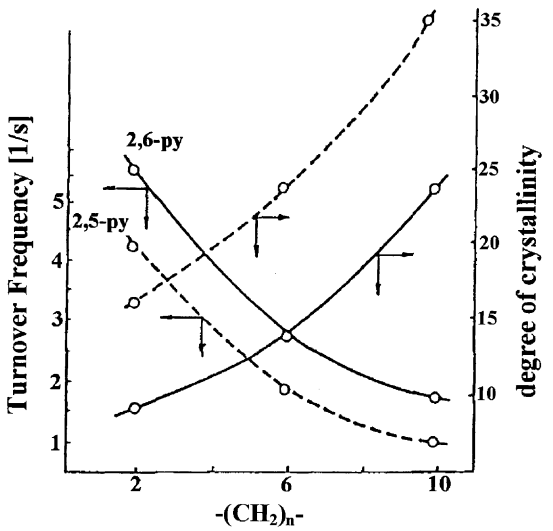


Fig. 7. Dependence between activity in TOF (s^{-1}) of the 2,5- and 2,6-py-polyamide supported Rh catalysts and polymer crystallinity in the hydrosilylation of hexene-1 in benzene [23].

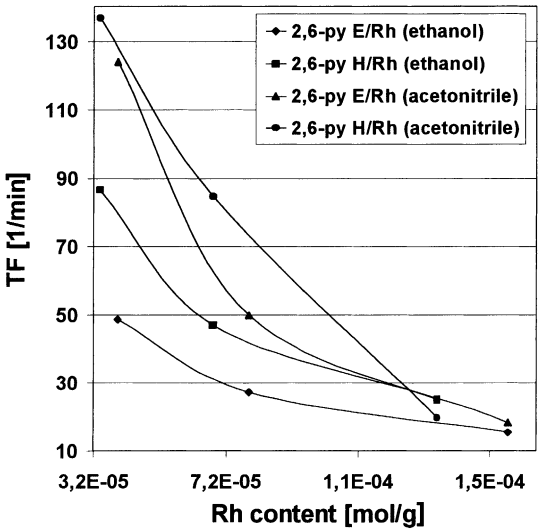


Fig. 8. Dependence between activity in TOF (min^{-1}) of the 2,6-py E and H polyamide-supported Rh catalysts and the rhodium content in hydrosilylation of hexene-1 [27].

reactants when these are attached to the polymer of higher crystallinity.

It is also clear that the activity of the Papy-supported catalysts is dependent on the concentration of the Rh loaded. Figs. 8 and 9 [27] shows the relation between catalytic activity and the Rh content for the 2,6-py E/Rh and 2,6-py H/Rh catalysts. The tests were performed in two solvents, ethanol and acetonitrile (Fig. 8), with the catalysts having Rh loading twice and four times lower then that of the standard level, i.e. 0.1 mmol of Rh/g. The results indicate that at higher Rh concentration the activity decreases. The catalyst deactivation can be attributed to the formation of less active dimeric species, whereas, a low metal loading favors site isolation and coordinative unsaturation usually leading to species of higher activity.

5.2. Selectivity studies

Detailed information on the morphological structure of the polyamide materials and PApy-supported Rh catalysts derived from the physical characterization studies, suggest that morphological factors may give rise to catalyst selectivity. We investigated the effects imposed by the PApy matrices on reaction selectivity in three model reactions: the hydrosilylation of alkenes, dienes and alkynes.

5.2.1. Hydrosilylation of alkenes

The homogeneously catalyzed hydrosilylation of vinyl-type alkenes with bulky substituents usually gives a mixture of two regioisomers: linear β- and less desirable inner α-products, and some olefin isomerization products [47–49].

$$X_3SiH + R_1R_2C{=}CH_2 \rightarrow \underset{\beta}{X_3SiCHR_2R_1} + \underset{\alpha}{CH_3(SiX_3)CR_2R_1}$$

where $X_3Si = Me_2PhSi$; $R_2 = H$ for $R_1 = Ph$, $(MeO)_3Si$, $(MeO)_2MeSi$, $(EtO)_3Si$; $R_2 = Me$ for $R_1 = Ph$.

For example, when hydrosilylation, of α-methylstyrene is catalyzed by a soluble Rh complex $[RhCl(CO)_2]_2$, the yield of the β-product is 41% [23]. When the same catalyst supported on the PApy matrices is used the yield of this isomer increases to 98%. A similar shift towards formation of the linear product is observed for styrene and alkoxysubstituted vinylsilanes (Table 4). The highest yields of the β-product are achieved with the catalysts supported on the H-type polymers of both 2,5-py and 2,6-py series.

The high selectivity in this reaction towards the formation of the linear β-products can be attributed to a favorable distribution of the micropores, whose sizes supressed formation of the branched α-products. Calculation shows that the linear dimensions of β-products are within the range of 12–15 Å and that their transverse dimension is two times smaller than that of the α-products. This explains why we observed an enhanced selectivity for the supported catalyst in general, and for the catalysts on the H-type polyamides in particular.

5.2.2. Hydrosilylation of dienes

Hydrosilylation of conjugated dienes leads predominantly to 1,4-addition, but whether the *cis* (*Z*) or *trans* (*E*) isomers is generated depends upon the catalyst used [47,48]. The hydrosilylation of two dienes isoprene and 2-methyl-1,3-pentadiene by two silanes Me_2PhSiH and $HSi(OEt)_3$ promoted by the polyamide PApy-immobilized Rh(I) catalysts were our model reactions [24].

As the results in Scheme 1 show, hydrosilylation of both dienes regardless of the hydrosilane used proceeds highly regioselectively via the 1,4-addition and

Table 4
Hydrosilylation of vinyl compounds with Me_2PhSiH catalyzed by 2,5-py and 2,6-py-supported Rh(I) catalysts [23][a]

Vinyl compound	Product distribution[b] (%)					
	Homogeneous		2,5-py E		2,5-py H	
	α	β	α	β	α	β
$CH_2=C(CH_3)C_6H_5$[c]	59	41	12	88	2	98
$CH_2=CHC_6H_5$[d]	43	57	13	87	4	96
$CH_2=CHSi(OEt)_3$[e]	22	78	14	86	5	95
	Homogeneous		2,6-py E		2,6-py H	
$CH_2=C(CH_3)C_6H_5$[c]	59	41	7	93	5	95
$CH_2=CHSi(OMe)_3$[c]	22	78	10	90	2	98

[a] Conditions: silane (1.5 mmol), alkene (1.5 mmol), polymer catalyst (0.001 mmol of Rh) in benzane (0.5 cm^3).
[b] Determined by GLC.
[c] At 40°C.
[d] At 30°C.
[e] At 30°C.

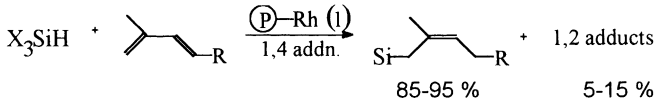
highly stereoselectively giving high yields (85–95%) of the 1,4-*cis* (*Z*) isomers (Ia–d). Essentially the same selectivity is found for reactions under homogeneous conditions (Table 5). These results demonstrate that the microporous structure of the PApy supports do not exert any significant effect on the regioselective and stereoselective course of the reaction although the opposite effect might have been expected.

To account for the absence of an influence of the polyamide structure on the catalyst selectivity, we analyzed the mechanism of this reaction proposed by Ojima et al. (Scheme 2) [50]. This is believed to involve the formation of a π-allylic intermediate I and/or II of the type proposed for most diene reactions which leads to 1,4 head *Z* (1) and/or 1,4-tail adducts (2). It can also yield the *E* isomer (1′) if the intermediate I undergoes isomerization to the intermediate I′. If no effect of support structure is observed, it is because the steric requirements for the formation of the cisoid structure of the π-allylic intermediate are small, i.e. <10 Å and match the dimensions of the micropores. Simple computer modelling calculations confirmed this.

These investigations have shown that in some cases when the support structure does not prevent the correct approach of the reactants to the active sites, the regiospecifity and stereospecifity of the parent homogeneous catalyst can be preserved after immobilization.

5.2.3. *Hydrosilylation of alkynes*

A very strong effect of the polyamide structure on the selectivity of the PApy-supported Rh(I) catalysts was found in the hydrosilylation of phenylacetylene with triethoxysilane [26].



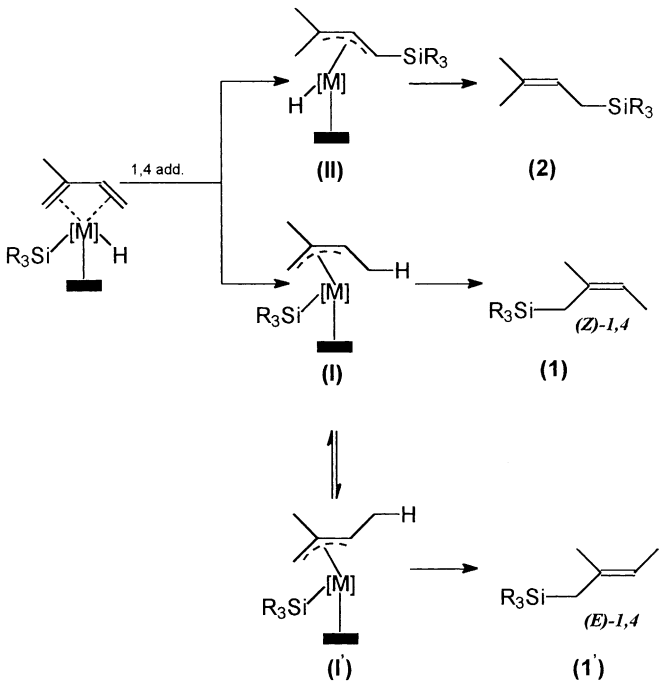
a : $X_3Si = Me_2PhSi$, R = H
b : $X_3Si = (EtO)_3Si$, R = H
c : $X_3Si = Me_2PhSi$, $R = CH_3$
d : $X_3Si = (EtO)_3Si$, $R = CH_3$

Scheme 1.

Table 5
Hydrosilylation of isoprene catalyzed by polyamide-supported Rh(I) complex [24][a]

Catalyst	Silane	Isoprene[b]			
		Product ratio[c] (%)			Yield[d]
		(*Z*)-1,4 addittion		(*Z*)-1,2 addition	
Homogeneous	Me_2PhSiH	**1a**	92	6	98
2,5-py E/Rh			91	9	95
2,5-py H/Rh			89	11	91
2,6-py E/Rh			90	10	93
2,6-py H/Rh			90	8	89
Homogeneous	$(EtO)_3SiH$	**1b**	94	5	94
2,5-py E/Rh			88	9	95
2,5-py H/Rh			95	2	78
2,6-py E/Rh			86	11	90
2,6-py H/Rh			88	9	89

[a] Conditions: silane (3 mmol), diene (3 mmol), polymer catalyst (0.002 mmol of Rh) in benzene (0.5 cm^3).
[b] At 30°C, 120 h.
[c] Isomeric ratios derived from GC area.
[d] Based on diene.



Scheme 2.

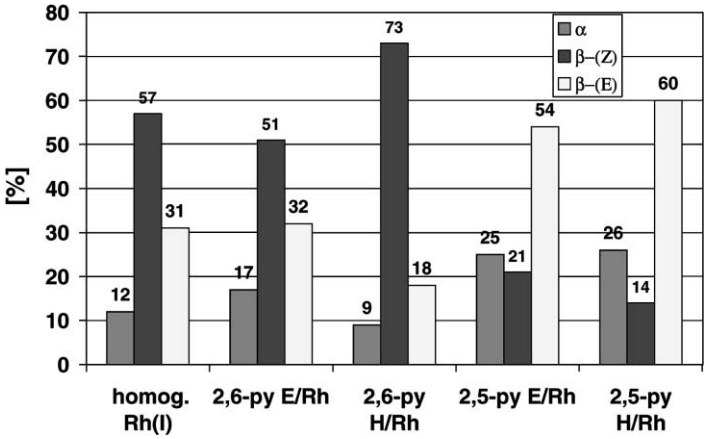
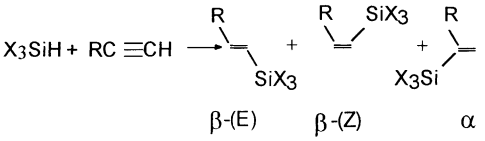


Fig. 9. Selectivity of the 2,5- and 2,6-py polyamide-supported Rh catalysts in the hydrosilylation of phenylacetylene by $HSi(OEt)_3$ in benzene [26].

Hydrosilylation of alkynes usually gives three addition products: α-and two β-stereoisomers β-(*Z*) and β-(*E*) [47,48].



$X_3Si = (EtO)_3Si$; R = Ph

The selectivity of this reaction is difficult to control and depends on several factors such as the electronic and steric effects of the substituents on the alkyne and silane, the catalytic species involved and the type of solvent. When the hydrosilylation of alkynes is catalyzed by Rh(I) complexes, *cis*-vinylsilanes are obtained exclusively.

The most important observation found in this study is that the selectivity of the hydrosilylation is dependent on the chemical structure of the polymers support. The results presented in Fig. 10, show that the Rh catalysts attached to the 2,6-py type polyamide give *cis* (*Z*)-vinylsilane as the major product. Use of the same catalyst supported on the 2,5-py type polymer

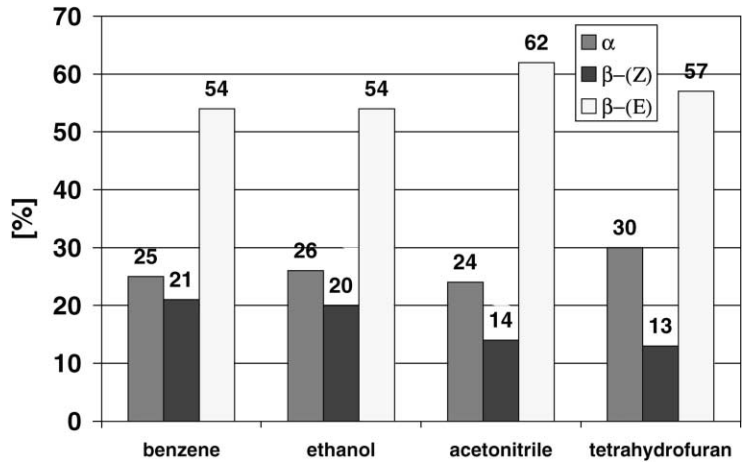
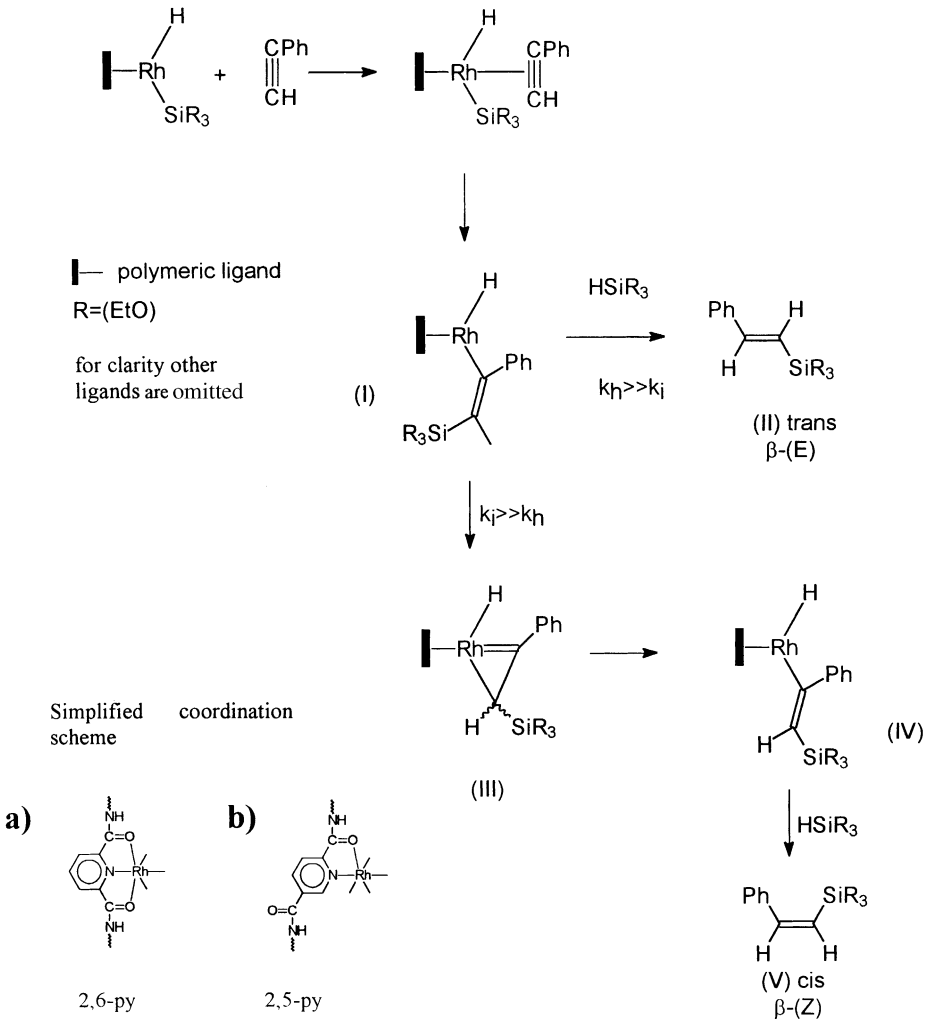


Fig. 10. Hydrosilylation of phenylacetylene with trietoxysilane using the 2,5-py E/Rh catalyst in different solvents [26].



Scheme 3.

results in a reversal of the stereoselectivity and *trans*-(*E*) vinylsilane becomes predominant. This specific selectivity is found to be independent of the nature of the solvent used. Fig. 10 illustrates the 2,5-py E/Rh catalyst behavior in different solvents. In order to explain such a dependence, we have considered the reaction mechanism in relation to the electron density on the Rh centre (Table 3).

According to the accepted mechanism of alkyne hydrosilylation [51–54] (Scheme 3) the intermediate (I) can either undergo isomerization to the intermediate (IV) via the η^2-vinyl carbene complex (III) to give the final β-*cis*-product (V) or can add a hydrosilane molecule to form the β-*trans*-vinyl product (II). The route that will prevail depends on the stabilizing effects of the ligands and the steric hindrance around the metal centre of the intermediate (I).

The XPS measurements [26] show the lower value of the binding energy BE for the Rh 3d5/2 for 2,6-py E and H/Rh catalysts (Table 3, entries 2 and 6). This means that the ligand 2,6-(HNCOpyCONH) as a good electron donor stabilizes the *cis* (*Z*)-vinylrhodium intermediate (I) and at the same time offering a steric hindrance for the metal atom, facilitates the isomerization of (I) to the less congested β-*trans*

(E)-vinylrhodium intermediate (IV) and to the final β-*cis*-product (V) ($k_i > k_h$).

The higher BE values for the Rh $3d_{5/2}$ attached to the 2,5-py type supports (Table 3 entries 10 and 12) are responsible for the lower donating ability of the ligand 2,5-[HNCOpyCONH]. Moreover, the Rh centre on the 2,5-py type support is less crowded and more available to an incoming substrate than on the 2,6-py type matrix (Scheme 3). Such a situation disfavors isomerization of the (I) and favors the addition of the hydrosilane molecule and subsequent reductive elimination of the *trans*-product (II) ($k_h > k_i$).

The results of this study have shown that it is possible to control the stereoselectivity of hydrosilylation and reverse the direction by using a suitable donor ligating group.

5.3. Stability of the PApy-supported catalysts

A serious problem in using polymer-supported catalysts is loss or leaching of the metal from the catalyst. This can be reduced significantly by using chelating ligands. The polyamides studied, containing a pyridine moiety are multidentate in character having three potential coordination sites, N_{amide}, N_y and $O_{C=O}$. Such binding is not completely broken during the catalytic process, thus, allowing the metal to remain attached to the support.

In all tested reactions, the catalytic properties of the PApy-supported Rh catalysts have been fairly stable during repeated use. Fig. 11 shows the stability tests performed during the hydrosilylation of isoprene over six catalytic cycles [24]. Except for the usually observed initial small drop, the activity and selectivity of the polymer catalysts remain essentially constant. We obtained similar positive results when the Rh catalyst 2,6-py H/Rh was tested in the hydrosilylation of acetylene [26]. Its activity and selectevity remained high after nine catalytic cycles in spite of Rh leaching. The Rh content in the polymer determined by atomic absorption sectroscopy AAS dropped from 1.36 to 0.81%. As Fig. 8 shows this drop was still at the safe level of the Rh concentration and does not affect the catalysts activity. A constant 75% yield of the β-*cis*-vinylsilane was obtained over nine catalytic runs after the same reaction times.

High stability of the PApy-supported Rh catalysts has been also proved by XPS analysis of the catalyst 2,6-py E/Rh. The BE spectra for the Rh 3d level show that the peaks for the freshly prepared catalysts (a) and those obtained after one (b) and nine catalytic runs (c) are identical (Fig. 12). This is also confirmed by only minor changes of the Rh and Cl content in the surface layer after several catalytic cycles (Table 6). In the case of the chlorine, the Rh:Cl stoichiometry was not preserved. Moreover, the larger width of the Cl $2p_{3/2}$ peak suggests the presence of more than one form of the bound chlorine. This was in agreement with the IR data, which has shown the presence of both terminal and bridging chlorine. These results provide evidence

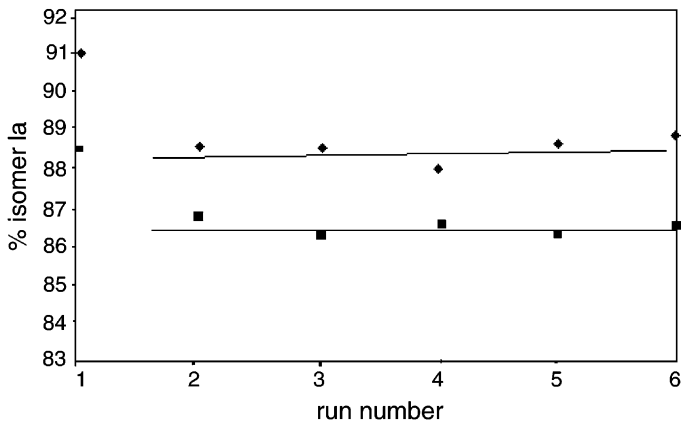


Fig. 11. Selectivity of the 2,6-py E/Rh(II) and 2,6-py H/Rh(II) catalysts during repeated stability tests in hydrosilylation of isoprene by Me_2PhSiH [24].

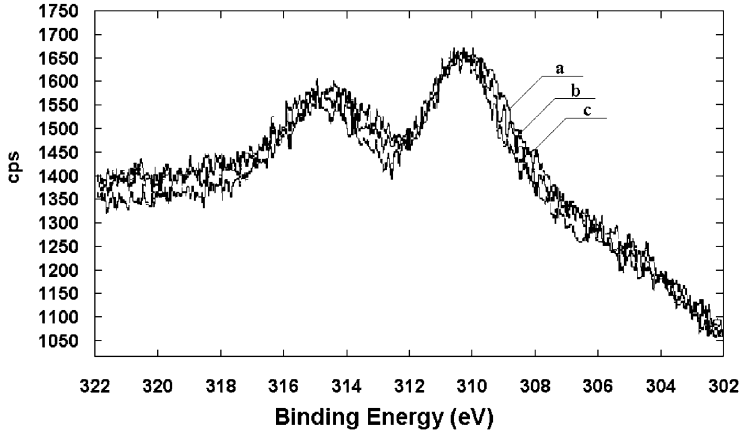


Fig. 12. Rh 3d XPS spectra for the 2,6-py E/Rh catalyst; (a) before use, (b) after one, (c) after nine runs [26].

Table 6
Rhodium and chlorine contents in the surface layer of the polyamide PApy-supported rhodium catalysts during the stability tests determined using ESCA method and Scofield sensitivity coefficients [27][a]

Catalyst	$\%_{at}$ Rh	$\%_{at}$ Cl
2,6-py E/Rh (before use)	0.64	0.51
2,6-py E/Rh (after 1st run)	0.63	0.36
2,6-py E/Rh (after 9th run)	0.60	0.49
2,6-py H/Rh (before use)	0.71	0.45
2,6-py H/Rh (after 1st run)	0.68	0.45
2,6-py H/Rh (after 9th run)	0.60	0.49

[a] The test reaction: hydrosilylation of phenylacetylene by $(EtO)_3SiH$.

that the nature of the metal centre does not change during prolonged use.

6. Conclusions

Our investigations have shown, that the polyamides having a pyridine moiety are very versatile polymeric materials and useful for immobilization of transition metal complex catalysts. The IR and XPS spectroscopy confirmed that their three potential coordination sites participate in binding the metal species.

The polyamides PApy are semi-crystalline materials whose degree of crystallinity depends on the length of the aliphatic spacer between the amide group and the mode of the pyridine placement in the mainchain.

The immobilization process changes the PApy support morphology giving rise to materials of higher microporosity, smaller average pore sizes and narrower pore-size distribution. These were qualitatively evaluated by a combination of several analytical methods in the dry and swollen states such as WAXS, SAXS, the nitrogen BET method, DSC, ISEC and pycnometry.

A close correlation between the polymer PApy support structure and catalytic properties of the supported Rh catalysts was found.

The catalyst activity was dependent on the degree of crystallinity and resulting porous structure. The activity of Papy-supported Rh systems increases when the crystallinity of the polymer decreases. This was ascribed to the better availability of the catalytic sites situated in a polymer having a greater portion of the amorphous domains.

The catalyst activity was found to depend on the concentration of the Rh on the support. The catalyst deactivation at higher Rh loading was attributed to the formation of the less active chlorobridged dimeric species.

The specific microporous structure of the polyamide PApy supports was found to have a strong impact on the selectivity of the supported Rh catalysts. Depending on the type of reaction involved the same polymer matrix can bring about the following different effects:

1. It can improve the catalyst chemoselectivity by serving as a molecular sieve and promoting forma-

tion of the linear products and preventing formation of the branched ones. This was documented in the hydrosilylation of the vinyl-type olefins.

2. It can control the catalyst stereoselectivity, as was shown in the hydrosilylation of phenylacetylene. A choice of the appropriate donor functions in a polymer support makes it possible to change the electron density on the metal centre and by this way reverse the reaction stereoselectivity to opposite direction.
3. It can also preserve the regio- and stereospecificity of a parent homogeneous catalyst, by providing a good match of the dimensions of the key intermediates in the catalytic process to those of the polymer micropores as was indicated in the hydrosilylation of dienes.

The evaluation of the lifetime of the heterogenized catalysts was performed over 6–9 repeated runs. These tests confirmed by the XPS analysis of the catalyst reused several times, demonstrated a very high stability of the polyamide PApy-supported Rh(I) systems. Such characteristics make these catalysts useful for prolonged use.

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