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Platinum catalyst on polysiloxane microspheres with N-chelating groups

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ABSTRACT

Elastic and durable, magnetic and non-magnetic polysiloxane microspheres containing a large number of SiOH groups were obtained by a simple and cheap emulsion process. N-chelating ligands were grafted on these microspheres by the condensation of their silanol groups with N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane. A platinum catalyst was immobilized on these microspheres. At every stage of the microspheres modification they were characterized by spectroscopy methods as well as by SEM microscopy. The catalyst appears only in the form of Pt(II) complex. The Pt(0) form was obtained by reducing this complex using sodium borohydride. The catalytic activity of the obtained catalysts was compared using model reactions, which were the hydrosilylation of phenylacetylene and hydrogenation of cinnamaldehyde. In both of these reactions the new platinum catalysts were recycled several times with the retention of their high catalytic activity. The hydrogenation of cinnamaldehyde leads to two products hydrocinnamaldehyde (HCA) and 3-phenyl-1-propanol (PP). The comparison of the rate of formation of the products with the rate of HCA and cinnamyl alcohol (CA) hydrogenation indicates that neither HCA nor CA are intermediate in the main pathway of the formation of PP.

1. Introduction

The transition metal catalysts such as complexes of palladium, platinum, rhodium or ruthenium, play an important role in many industrial processes. Among them, platinum catalysts have been commonly used for years. In these catalysts platinum can exist in an oxidation state 0, II and IV. All these forms are used in many organic syntheses in both industrial processes and research laboratories. Platinum is well-known as the catalyst of isomerization, cyclization, dehalogenation, hydrogenation and continues to be number one in hydrosilylation [1–3]. The last two reactions are particularly important. Hydrosilylation is one of the basic reactions in organosilicon chemistry making the synthesis of great number of organosilicon compounds relevant to modern technology and medicine possible [4,5]. Hydrogenation, in turn, is a very important reaction in manufacturing oil, fats pharmaceuticals and petrochemical products [6,7].

There are, at least, two main problems in the use of platinum catalysts, one is their allergic and carcinogenic action and the other is their price [8,9]. That is why a lot of research has been done in industrial and academic laboratories to improve the activity, selectivity, recoverability and recyclability of platinum catalysts. One way to achieve these goals is the immobilization of a homogenous catalyst on solid support also known as heterogenization. In parallel, scientists continue to explore a design of new ligands to obtain more active and selective catalysts.

Polymers are often considered as catalyst carriers because they allow to achieve the two aforementioned goals, being supports with well-defined structure and containing functional groups used as ligands [10–13]. Considering forms of polymer topology a cross-linked network seems to be the best choice for a catalyst carrier [14]. Bidentate nitrogen ligands are attractive for the application in transition metal catalysts, such as a platinum complex, because of a high affinity of nitrogen to these metals [15]. Polysiloxanes used as support for these catalysts give many advantages. The flexibility and mobility of polysiloxane chain allow to adjust its conformation to environment thus giving reactants a better access to catalytic centres. They are also easily modified by the introduction of functional groups which can work as ligands for transition metals [8,16].

The polymer microspheres are a suitable form for catalyst carriers because the shape of particles, their size and chemical structure

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give them valuable hydrodynamic properties and the ease of isolation from a reaction mixture. Among spherical particles used as catalyst supports the most common are TiO_2, Al_2O_3 and Fe_3O_4, coated silica or modified silica alone [17–21] while among the polymer particles the most often explored are polystyrene and chitosan [22–24]. Many works were devoted to composite microspheres whose construction allows to improve their thermal resistance and give them magnetic or hydrophobic-hydrophilic properties. Microspheres exclusively built from polysiloxane chains are a new interesting material which may find many uses [25–27]. The ability for an easy modification on their synthesis level e.g. forming magnetic particles, smooth introduction of functional groups and the aforementioned properties of polysiloxanes provide an attractive multi-purpose material which can be successfully used as catalyst carriers.

We describe here the synthesis of magnetic or non-magnetic polysiloxane microspheres, their modification by commercially available and cheap 3-(2-amino-ethylamino)propylmethyldimethoxysilane and immobilization of platinum on them. We demonstrated that the obtained Pt(0) and Pt(II) complexes heterogenized on these microspheres are efficient and reusable catalysts in hydrogenation and hydrosilylation reactions.

2. Experimental

2.1. Chemicals

Toluene, acetone, ethanol, polyvinyl alcohol (Mn 7.2×10^4) and dioxane (POCh, analytical grade), cinnamaldehyde (Aldrich, 99%), cinnamyl alcohol (Aldrich, 98%), hydrocinnamylaldehyde (TCI, >93%), dimethylphenylsilane (Fluorochem, 98%), phenylacetylene (ABCR, 98%), potassium tetrachloroplatinate(II) (ABCR, 99.9%), N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (ABCR, 97%), undecane (Aldrich, >99%) were used as received. Iron (III) chloride, Iron(II) chloride, hydrochloric acid (solution 38%) and ammonium hydroxide (solution 25%) (Chempur, analytical grade) were used as received. Polyhydromethylsiloxane (PHMS) was purchased in ABCR under name HMS 991, Mn 4.7×10^3 g/mol as confirmed by SEC. 1,3-Divinyltetramethyldisiloxane (ABCR, 97%). Pt(0) Karstedt catalyst containing 20 w/w% Pt was kindly offered by Momentive Performance Materials GmbH Leverkusen. Magnetite nanoparticles were obtained by coprecipitation of Fe^{2+}/Fe^{3+} in an alkaline solution using known method [28].

2.2. Analytical methods

^{29}Si and ^{13}C MAS NMR spectroscopy, Scanning Electron Microscopy, FIR, XPS spectroscopy and Elemental Analysis were precisely described earlier [29]

2.2.1. Transmission electron microscopy

Transmission electron microscopy (TEM) and scanning-transmission electron microscopy (STEM) analyses were conducted using thin foils utilizing FEI Tecnai G2 20 TWIN microscope equipped with EDS of EDAX. In order to make TEM images of the crosssection of microspheres they were embedded in Araldite 502 (epoxide resin) and cut with an ultramicrotome (Power Tome XL, Boeckeler Instruments, Inc.).

2.2.2. Gas chromatography

Gas chromatographic analysis was performed on a Hewlett Packard 5890 II apparatus (TCD detector) equipped with a HP-50+ column (30 m × 0.53 mm × 1 μm) using helium as a carrier gas. Temperature program for hydrogenation: the column was kept at 60 °C for 4 min, then heated to 240 °C at a rate of 12 °C/min. Temperature program for hydrosilylation: the column was kept at 60 °C for 2 min, then heated to 150 °C at a rate of 5 °C/min and then heated to 280 °C at a rate of 10 °C/min.

2.3. Synthesis of cross-linked polysiloxane microspheres (***M1***)

The preparation of polysiloxane microspheres was precisely described earlier [29]. Regular microspheres, of diameters ranging from 3.5 to 30 μm (mean value 14.7 μm), were analyzed by ^{29}Si and ^{13}C MAS NMR, elemental analysis and SEM. They contained 5.1 mmol/g SiOH. ^{29}Si MAS NMR (δ in ppm at maximum): −67.3 $Me\underline{Si}(OSi)_3$; −57.4 $Me\underline{Si}(OH)(OSi)_2$; −37.8 $Me\underline{Si}(H)(OSi)_2$; −21.0 $Me\underline{Si}(CH_2)(OSi)_2$; +7.2 $Me_2\underline{Si}(CH_2)(OSi)$ and $Me_3\underline{Si}O$. ^{13}C MAS NMR (δ in ppm at maximum): −3.5, −0.9, +0.6 $\underline{C}H_3$; +8.5 $\underline{C}H_2$.

Elemental analysis in wt%: C-24.03%, H-7.1.

2.4. Synthesis of magnetic cross-linked polysiloxane microspheres (***M2***)

The preparation of polysiloxane microspheres was carried out according to the procedure similar to that described previously [30]. The suspension of iron oxide nanoparticles in isopropanol was added to the mixture before emulsification. The exact description of the synthesis was placed in Supporting information. The microspheres (6.4 g–82.8% yield) with diameters in the range of 4.2 to 52.5 μm (mean 18.9 μm) were acquired. They were analyzed by ^{29}Si and ^{13}C MAS NMR, IR, elemental analysis and SEM. They contained 3.8 mmol/g SiOH. ^{29}Si MAS NMR (δ in ppm at maximum): −67.8 $Me\underline{Si}(OSi)_3$; −58.5 $Me\underline{Si}(OH)(OSi)_2$; − 38.5 $Me\underline{Si}(H)(OSi)_2$; −21.4 $Me\underline{Si}(CH_2)(OSi)_2$; +5.9 $Me_2\underline{Si}(CH_2)(OSi)$ and $Me_3\underline{Si}O$. ^{13}C MAS NMR (δ in ppm at maximum): −5.2, −3.6, −2.2, −1.0 $\underline{C}H_3$; +6.6 $\underline{C}H_2$, +23.5 C-$\underline{C}H_3$, +74.2 $\underline{C}H$. Elemental analysis in wt%: C-23.64, H-5.61

2.5. Preparation of 3-(2-aminoethyl)aminopropyl functionalized microspheres (***M1N***, ***M2N***)

The microspheres with pendant aminoethylamino groups were obtained by condensation reaction of silanol groups in microspheres with N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane. The reaction was carried out using the procedure similar to that described in Ref. [30]. Microspheres (**M1**-8.12 g, **M2**-1.54 g) were suspended in the toluene (20 and 10 mL respectively) and the methoxysilane (10 and 2 mL respectively) was slowly added by syringe to the stirred mixture and the stirring was continued for 48 h. The microspheres were separated and repeatedly washed with toluene, dried in vacuum and analyzed. The [3-(2-aminoethyl)aminopropyl]siloxane groups replaced almost completely the initial hydroxyl groups, as shown by ^{29}Si MAS NMR.

2.5.1. ***M1N*** microspheres

^{29}Si MAS NMR (δ in ppm at maximum): −69.2 $Me\underline{Si}(OSi)_3$; −60.9 $Me\underline{Si}(OH)(OSi)_2$; −23.8 $Me\underline{Si}(CH_2)(OSi)_2$; +5.6 $Me_2\underline{Si}(CH_2)(OSi)$ and $Me_3\underline{Si}O$. ^{13}C MAS NMR (δ in ppm at maximum): −4.4, −2.8 $\underline{C}H_3$; +7.1, +13.1 Si-$\underline{C}H_2$, +21.0 C-$\underline{C}H_2$-C, 39.6 H_2N-$\underline{C}H_2$, 50.7 NH-$\underline{C}H_2$, OCH_3.

2.5.2. ***M2N*** microspheres

^{29}Si MAS NMR (δ in ppm at maximum): −69.5 $Me\underline{Si}(OSi)_3$; −60.7 $Me\underline{Si}(OH)(OSi)_2$; −23.9 $Me\underline{Si}(CH_2)(OSi)_2$; +5.2 $Me_2\underline{Si}(CH_2)(OSi)$ and $Me_3\underline{Si}O$. ^{13}C MAS NMR (δ in ppm at maximum): −5.2, −3.7 $\underline{C}H_3$; +6.1, +11.9 Si-$\underline{C}H_2$, +20.7 C-$\underline{C}H_2$-C, 38.3 H_2N-$\underline{C}H_2$, 49.6 NH-$\underline{C}H_2$, OCH_3,

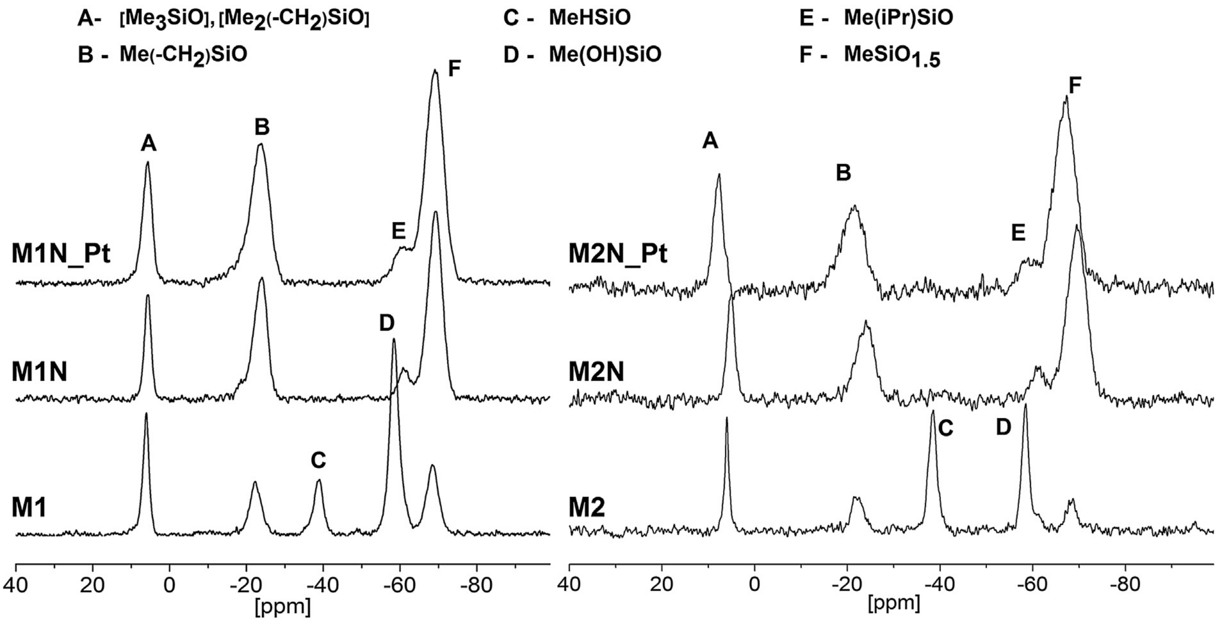
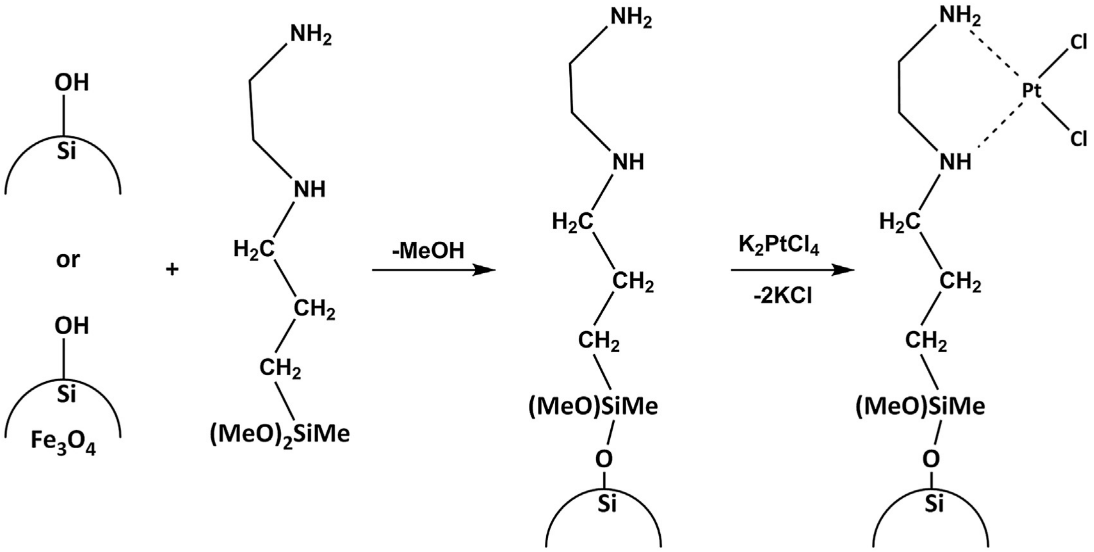


Fig. 1. ^{29}Si MAS NMR spectra of microspheres.



Scheme 1. Modification of microspheres by N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane and immobilization of platinum.

Elemental analysis **M1N** (in wt.%): C 32.95, H 8.08, N 7.19; **M2N** (in wt.%): C 31.00, H 7.83, N 4.48.

2.6. Immobilization of platinum onto microspheres

The **M1N** and **M2N** microspheres were dispersed in dioxane/phosphate buffer mixture and solution of platinum salt K_2PtCl_4 (0.103 g) in phosphate buffer (pH-7.2) (7 mL), was added dropwise. The proportion of mol(Pt)/mol(ligands) has been used as 1/6. The suspension was shaken for tens hours at room temperature. The obtained platinum complexes immobilized on microspheres (**M1N_Pt** and **M2N_Pt**) were isolated from the solution by filtration, washed successively with several solvents (water, acetone, toluene) and then dried under vacuum. The complexes **M1N_Pt** and **M2N_Pt** were light grey and brown in colour respectively. These complexes were characterized by ^{29}Si and ^{13}C MAS-NMR spectroscopy, FIR, SEM, XRF and XPS.

2.6.1. ***M1N_Pt***

^{29}Si MAS NMR (δ in ppm at maximum): −69.2 $\text{Me}\underline{\text{Si}}(\text{OSi})_3$; −59.9 $\text{Me}\underline{\text{Si}}(\text{OH})(\text{OSi})_2$; −23.4 $\text{Me}\underline{\text{Si}}(\text{CH}_2)(\text{OSi})_2$; +5.8 $\text{Me}_2\underline{\text{Si}}(\text{CH}_2)(\text{OSi})$ and Me_3SiO. ^{13}C MAS NMR (δ in ppm at maximum): −3.3, $\underline{\text{C}}\text{H}_3$; +6.9, +12.4 Si-$\underline{\text{C}}\text{H}_2$, +19.9 C-$\underline{\text{C}}\text{H}_2$-C, +40.2 H_2N-$\underline{\text{C}}\text{H}_2$, +44.1 OCH_3, +50.6 NH-$\underline{\text{C}}\text{H}_2$; FIR (in cm^{-1} at maximum): 350 Pt-Cl; 267, 243, 208 Pt-N; Elemental analysis (in wt.%): C 20.53, H 6.2, N 4.67.

2.6.2. ***M2N_Pt***

^{29}Si MAS NMR (δ in ppm at maximum): −67.0 $\text{Me}\underline{\text{Si}}(\text{OSi})_3$; −58.8 $\text{Me}\underline{\text{Si}}(\text{OH})(\text{OSi})_2$; −21.5 $\text{Me}\underline{\text{Si}}(\text{CH}_2)(\text{OSi})_2$; +7.9 $\text{Me}_2\underline{\text{Si}}(\text{CH}_2)(\text{OSi})$ and Me_3SiO. ^{13}C MAS NMR (δ in ppm at maximum): −2.3, $\underline{\text{C}}\text{H}_3$; +8.8, +14.6 Si-$\underline{\text{C}}\text{H}_2$, +22.1, +28.5 C-$\underline{\text{C}}\text{H}_2$-C, +42.6 H_2N-$\underline{\text{C}}\text{H}_2$, +50.8 NH-

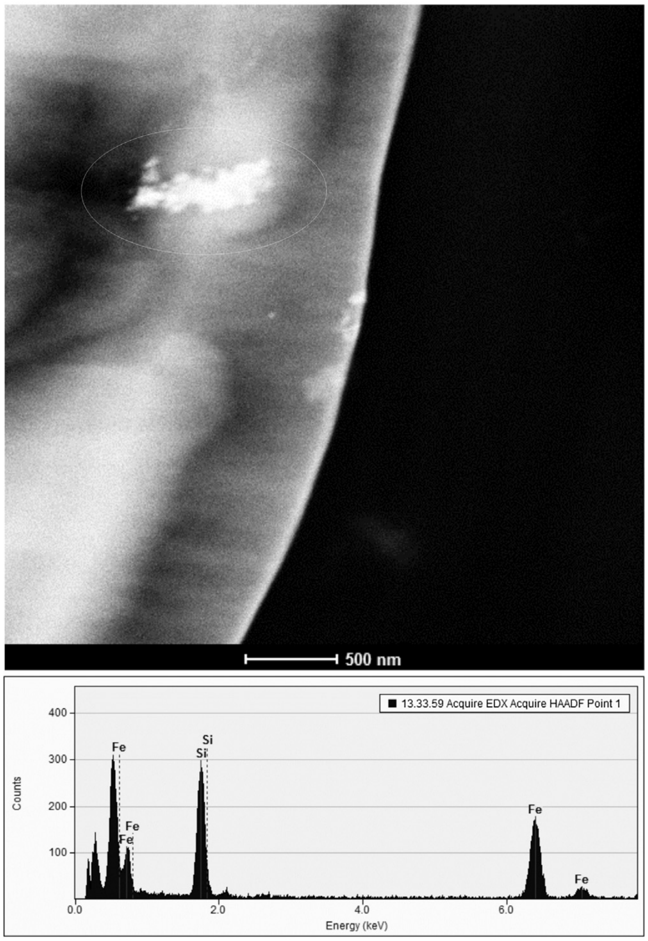


Fig. 2. HAADF-STEM image of the investigated area and EDX spectra from the area of the particles.

$\underline{C}H_2$, +76.6 $\underline{C}H_2$, FIR (in cm^{-1} at maximum): 339 Pt-Cl; 259, 240, 208 Pt-N. Elemental analysis (in wt.%): C 24.18, H 6.78, N 3.42.

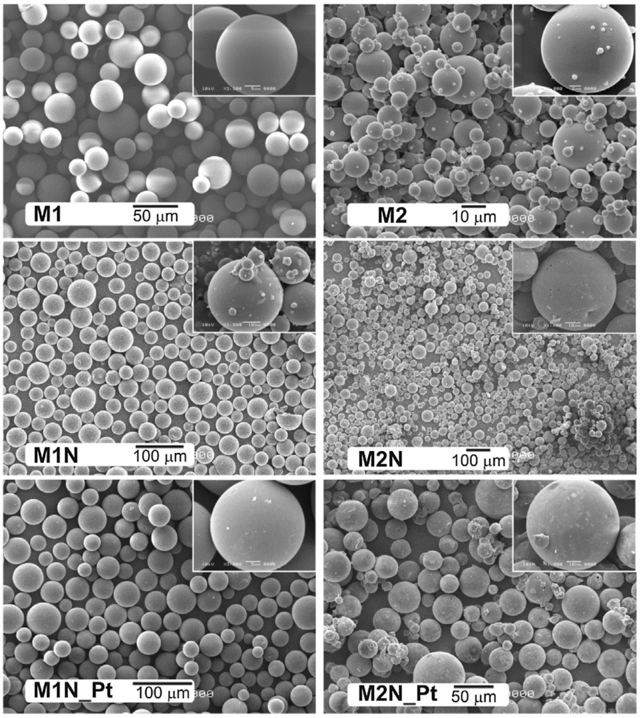


Fig. 4. SEM photograms.

2.7. *Reduction of Pt(II) complex (**M1N_Ptr**)*

M1N_Pt catalyst was reduced to convert Pt(II) complex into Pt(0) similar to the procedure described in Ref. [31]. **M1N_Pt** (0.1 g) was dispersed in ethanol (1 mL), then mixed with $NaBH_4$ (0.1 g) in deionized water (7 mL) and shaken at room temperature for two days. The resulting product was filtered, washed with water and EtOH respectively and dried under vacuum to obtain the dark grey platinum(0) complex.

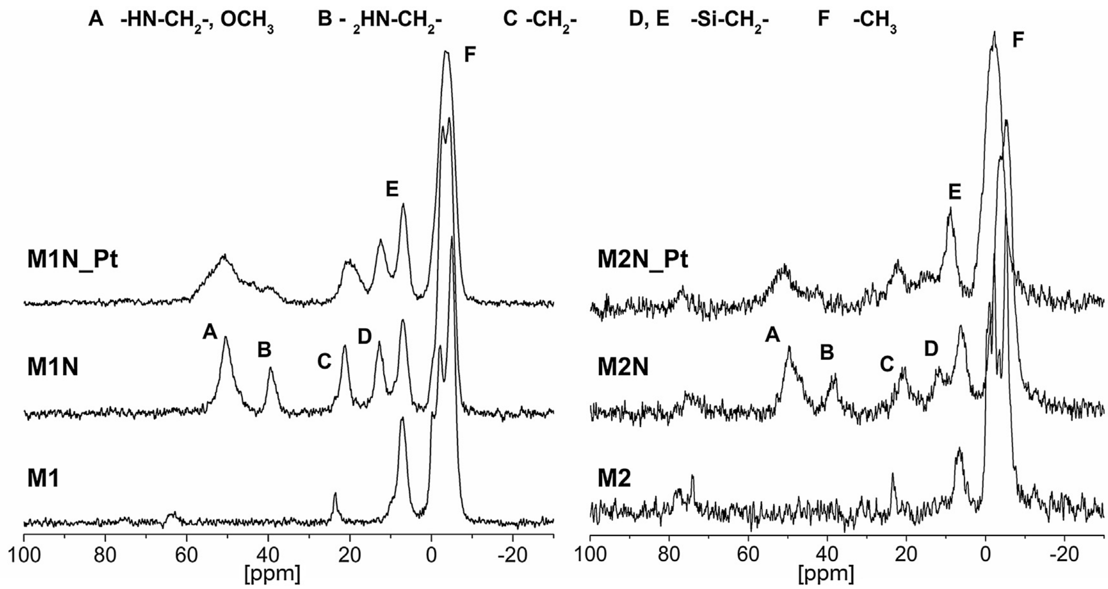
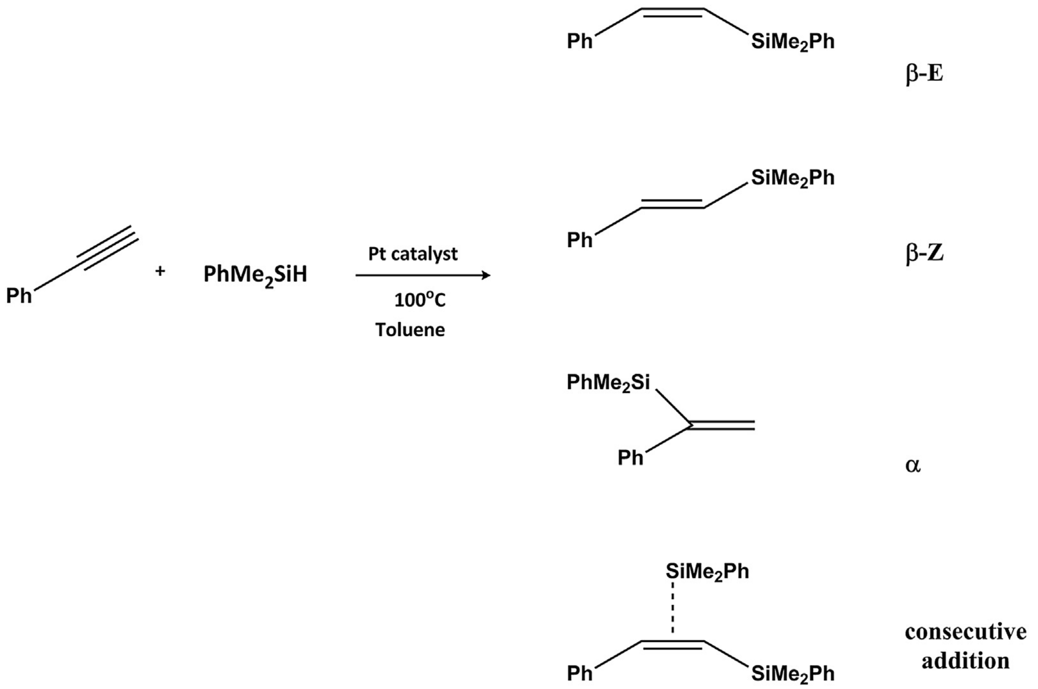


Fig. 3. ^{13}C MAS NMR spectra of microspheres.



Scheme 2. Hydrosilylation reaction.

2.8. *Studies of hydrosilylation*

Phenylacetylene (0.16 mL, 1.5 mmol), dimethylphenylsilane (0.23 mL, 1.5 mmol), toluene (0.5 mL) and undecane (0.07 mL) were placed in a screw cap vial and then Pt complex containing ca. 0.02 mmol Pt was added. The reaction mixture was heated to 100 °C with a mild shaking. Samples were withdrawn at certain time intervals and analyzed by gas chromatography using undecane as the internal standard. The conversion was determined based on the amount of consumed phenylacetylene. After the reaction the mixture was cooled down and the catalyst was separated by sedimentation, washed by acetone, dried and used for the next reaction cycle. The products were isolated by distillation under reduced pressure and characterized by ^{1}H, ^{13}C and ^{29}Si NMR.

2.8.1. *Dimethylphenylstyrylsilane*

^{1}H (500 MHz, $CDCl_3$): δ 0.69 (s, $-C\underline{H}_3$), 6.85, 6.88 (d, $=C\underline{H}$-Si), 7.21, 7.25 (d, =CH-Ph), 7.48-7.85 (m, phenyl); ^{13}C (500 MHz, $CDCl_3$, δ in ppm at maximum): −2.46 (-$\underline{C}H_3$), 126.38, 126.57, 127.93, 128.38, 128.61 ($\underline{C}_{arom}$), 133.84 (=$\underline{C}$H-Si) 133.94 (Si-C_{arom}),138.13 (Si-$\underline{C}_{arom}$), 138.45 ($\underline{C}_{arom}$—C), 145.39 (=C$\underline{H}$-Ph); ^{29}Si (500 MHz, $CDCl_3$, δ in ppm at maximum): −10.0

2.8.2. *Dimethylphenyl(1-phenylvinyl)silane*

^{1}H (500 MHz, $CDCl_3$): δ 0.62 (s, $C\underline{H}_3$), 5.88 (s,=$C\underline{H}_2$), 6.20 (s, =$C\underline{H}_2$), 7.34-7.77 (m, phenyl); ^{13}C (500 MHz, $CDCl_3$, δ in ppm at maximum): −2.08 (-$\underline{C}H_3$), 126.68, 127.10, 128.09, 128.32 (C_{arom}), 129.04 (=CH_2), 134.14 (Si-C_{arom}), 138.44 (Si-$\underline{C}_{arom}$), 144.33 (C-$\underline{C}_{arom}$), 151.17 (=$\underline{C}$(Si)-C); ^{29}Si (500 MHz, $CDCl_3$, δ in ppm at maximum): −7.9

2.8.3. *Bis-(1,2-dimethylphenylsilyl)ethylbenzene*

^{1}H (500 MHz, $CDCl_3$): δ 0.29 (s, $C\underline{H}_3$), 0.41 (s, $-C\underline{H}$-), 0.51 (s, $-C\underline{H}_2$-), 6.87–7.74 (m, phenyl); ^{13}C (500 MHz, $CDCl_3$, δ in ppm at maximum): 0.38 (-$\underline{C}H_3$), 125.87, 126.70, 127.80, 128.92 (C_{arom}), 134.05, 134.49 (Si-C_{arom}), 139.16, 139.85 (Si-$\underline{C}_{arom}$), 149.08 (C-$\underline{C}_{arom}$); ^{29}Si (500 MHz, $CDCl_3$, δ in ppm at maximum): −10.5 $Ph(CH_3)_2Si$-CHPh-, 14.6 $Ph(CH_3)_2Si$-CH_2-

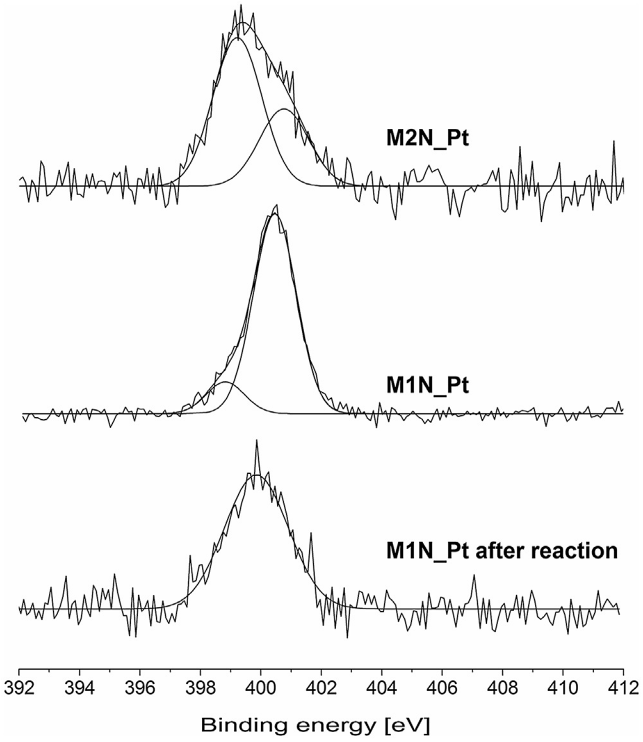


Fig. 5. XPS spectra N 1s of **M1N_Pt** before and after 5 cycles of the hydrosilylation reaction and for **M2N_Pt** before the reaction.

2.9. *Studies of cinnamaldehyde hydrogenation*

The hydrogenation reactions were carried out in Autoclave Engineers B030SS using the procedure similar to that described in Ref. [29]. The exact description of the synthesis was placed in Supporting information.

Table 1
Conversion of dimethylphenylsilane and selectivity in catalytic runs in the hydrosilylation reaction.

catalyst	Cycle	Complex [g] (mol of Pt)	Conversion [%]	TON	Dimethylphenyl (1-phenylvinyl)silane [%]	*trans* dimethylphenyl-styrylsilane [%]	consecutive addition [%]
M1N_Pt	1	0.0501 (2.12×10^{-5})	39.8[a]	28	35.1	64.9	0.0
	3		94.6	66	33.8	66.2	0.0
	5		99.4	69	30.4	64.3	0.0
M1N_Pt after reduction	1	0.05 (2.14×10^{-5})	85.0[b]	58.0	29.3	64.8	5.9
	3		97.1	66.2	31.4	68.6	3.5
	5		100.0	68.2	28.8	64.6	6.6
M2N_Pt	1	0.0507 (2.15×10^{-5})	23.9[a]	16.2	33.4	66.6	0.0
	3		95.8	65.0	33.7	66.3	0.0
	5		100.0	67.9	30.6	63.7	5.7
	7		100.0	67.9	28.6	65.1	6.3
	10		100.0	67.9	29.3	64.0	6.8
K_2PtCl_2	1	0.008 (1.93×10^{-5})	100.0[a]	67.9	51.5	46.9	1.6
Karstedt	1	0.0017 (1.8×10^{-6})	97.2[c]	787.4	27.6	66.4	6.0

[a] After 22 h.
[b] After 360 min.
[c] After 5 min.

3. Results and discussion

3.1. Synthesis of magnetic microspheres

We developed a method of synthesis of all-polysiloxane microspheres having magnetic properties and containing an easy to modification SiOH groups. The method is based on cross-linking of polyhydromethylsiloxane in aqueous emulsion [30]. Magnetic properties of these microspheres were gained by the introduction of iron oxide nanoparticles produced according to a published method [28]. They were added to the PHMS/DVTMDS mixture before its emulsification using the previously described procedure [30]. We observed that the incorporation of magnetite into microspheres slightly influenced the SiH/SiOH ratio. The analysis of the ^{29}Si MAS NMR spectrum (Fig. 1) indicated that in the standard method of the preparation of non-magnetic microspheres a large number of SiOH was produced (5.1 mmol/g) whereas the addition of Fe_3O_4 caused a moderate decrease of SiOH (3.8 mmol/g).

The TEM investigations, of the microsphere cross-section showed that the iron in the microspheres appeared in the form of particle clusters (Fig. 2). The SEM photograms indicated that the shape and surface structure of the microspheres were not changed after the introduction of magnetite (Fig. 4).

3.2. Modification of microspheres

The presence of reactive silanol groups on the microspheres gives a broad possibility of the functionalization of these particles by organofunctional chloro- or alkoxysilanes. The microspheres with N-chelating ligands were obtained by the condensation of silanol groups on the spheres with N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (Scheme 1). The reaction was carried out in the suspension of microspheres in toluene with an excess of the silane reagent.

The analysis of the ^{29}Si MAS NMR spectrum indicated that most of hydroxyl functions on polysiloxane were consumed. During the reaction we observed a disappearance of remaining SiH groups by their dehydrogenative condensation with the silanol groups (Fig. 1). The structure of the obtained product was also confirmed by ^{13}C MAS NMR spectrum (Fig. 3). The amount of the ligands bonded to microspheres, determined by elemental analysis, was 2.56 mmol per gram for native microspheres and 1.74 mmol per gram for their magnetic form.

3.3. Structural studies of platinum immobilized on microspheres

Platinum complex immobilized on the microspheres using bidentate nitrogen ligands was very conveniently synthesized by reacting the previously modified microspheres (**M1N**, **M2N**) with potassium chloroplatinate (Scheme 1). The obtained complexes were characterized by standard analytical techniques.

The ^{29}Si MAS NMR spectrum was not changed after the immobilization of platinum but widening of carbon signals neighbouring with N atoms was observed in ^{13}C MAS NMR spectrum (Figs. 1 and 3), which was an effect of platinum bonding to the nitrogen ligand. SEM photographs (Fig. 4) gave us information that the surface of microspheres was not changed after the modification and immobilization of platinum. We suppose that platinum is distributed in the whole microsphere volume.

The detailed information about **M1N_Pt** and **M2N_Pt** complex structure was provided by XPS and FIR analysis. In both cases the analysis of the XPS spectra (Table A in supp. inf.) confirmed that platinum occurred only in the form of Pt(II). Binding energies observed for Cl, C, O and Si were in accordance with earlier data [16,32] (Table A supp. inf.) In both complexes binding energies observed for N pointed to the presence of the NH_4^+ structure or hydrogen bonds [33,34] (Fig. 5). The analysis O1s XPS (signal BE 533.5, Table A, Fig. A in supp. inf.) indicates the presence of water which suggests the existence of hydrogen bonds. It is also confirmed by a simple simulation DFT (Scheme A supp. inf.), which proves that the structure in which platinum is coordinated to nitrogen by a hydrogen bonded molecule of water is more stable.

A far IR spectroscopy confirmed existence of Pt-N and Pt-Cl bonds. The characteristic bands with maxima around 330 cm^{-1} belonged to Pt-Cl and the bands at 208, 235, 260 cm^{-1} originated from Pt-N [35–37] (Fig. C supp. inf.).

3.4. Studies of the hydrosilylation reaction

The hydrosilylation is the most important reaction in silicone industry and the platinum catalysts are most commonly used. Hence the choice of model reaction was obvious. Hydrosilylation of dimethylphenylsilane with phenylacetylene can give a whole range of products and therefore may be used for the examining of the catalyst selectivity (Scheme 2).

Activity and selectivity of the reaction was determined by the GC analysis of samples withdrawn from the reaction system. After the reaction, the catalyst was separated from the mixture, washed with

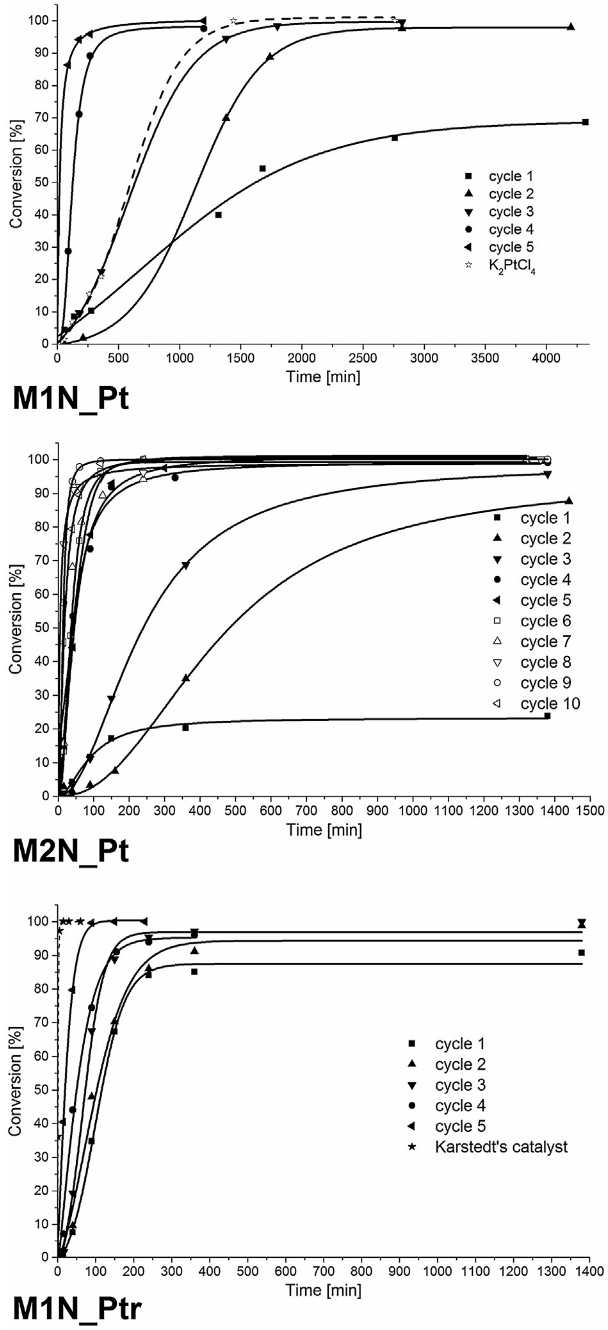


Fig. 6. Hydrosilylation runs.

acetone, dried and reused. Catalytic activities of **M1N_Pt**, **M2N_Pt** and **M1N_Pt** after reduction of platinum to Pt(0) (**M1N_PtR**) were compared to those of K_2PtCl_4 and Karstedt complexes.

The activity of **M1N_Pt** and **M2N_Pt** complexes significantly increased in consecutive cycles (Fig. 6, Table 1). Instead, **M1N_PtR** was active at a high level in all cycles (Fig. 6). These changes of activities were not related to the oxidation state of platinum which was confirmed by Pt XPS analysis of the catalysts before and after five cycles of the reaction (Table A supp. inf.). The reason for this strange behaviour was probably the formation of the hydrogen bonds between water and nitrogen as mentioned above (see also supp. inf., Scheme A). These structures can be created during the immobilization process and are less active. Additionally, annealing of the catalyst at a temperature above 100 °C under vacuum for a several hours also increases the activity of the hydrosilylation reaction (Fig. B supp. inf.), as this operation removes water from the complex. However, after the formation of the final structure of complex the activity remains constant (Fig. 6, Table 1 and Table B in supp. inf.). The SEM-EDX analysis determined a loss of platinum for subsequent cycles, and showed a gradual loss of platinum during subsequent cycles of the reaction (~20% after 5 cycles). The greatest loss was observed in the case of the catalyst **M2N_Ptr** (>40% after five cycles). The catalytic activity of the heterogenized platinum complex was comparable to that of K_2PtCl_4. On the other hand the homogeneous Karstedt catalyst was much more active than the others.

The use of phenylacetylene as the reactant in the hydrosilylation provides information about the selectivity of the adopted platinum complex. In this reaction at least four main products may be formed: dimethylphenylstyrylsilane (cis and trans form), dimethylphenyl(1-phenylvinyl)silane and a product of the consecutive addition to olefin bond. The ratio of *trans* dimethylphenylstyrylsilane to dimethylphenyl(1-phenylvinyl)silane was about 70:30 for all the three used catalysts. In the cases of **M2N_Ptr** catalyst we also observed the formation of the consecutive addition product (Scheme 2, Table 1) which is in accordance with the results obtained for Karstedt catalyst. We also observed the consecutive addition product using **M2N_Pt** catalyst but only in the last two cycles, which may indicate a gradual reduction of platinum in subsequent cycles. The selectivity of the studied heterogenized catalysts is different from that observed for K_2PtCl_4 and Karstedt catalysts where the ratio of the obtained α and β-(Z) products of the addition is about 50:50.

3.5. *Studies of the hydrogenation reaction*

3.5.1. *Substrate conversion*

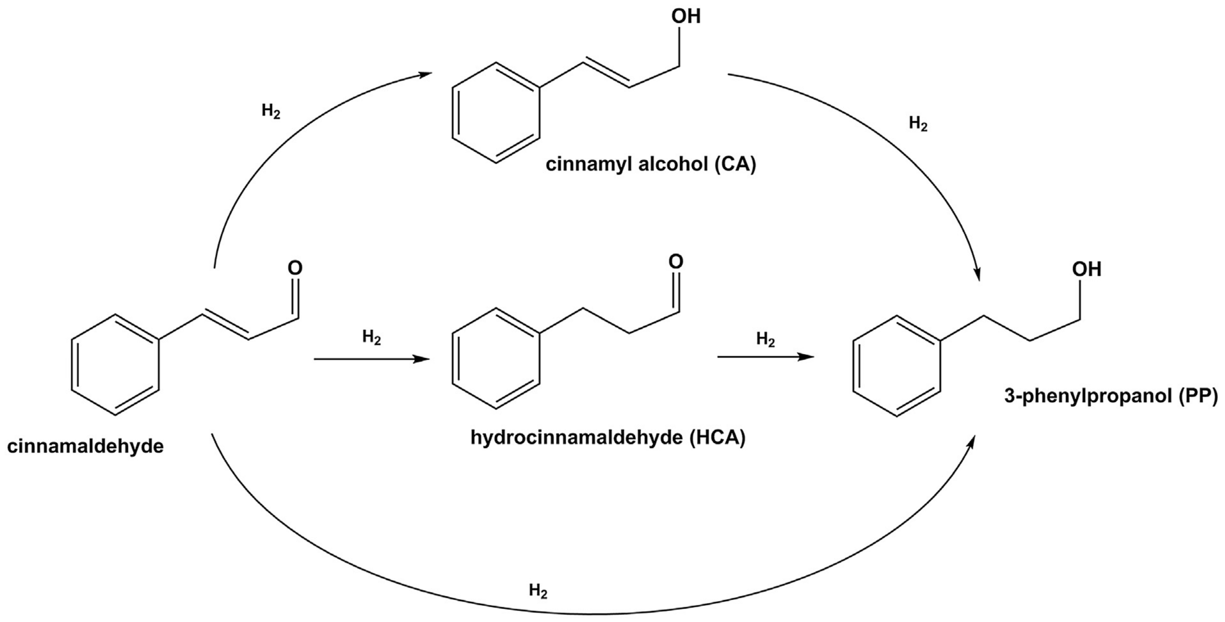
The commonly used hydrogenation reaction of cinnamaldehyde was chosen as the second model catalytic reaction for the testing of activity and selectivity of the platinum heterogenized on microspheres (Scheme 3). The catalyst activity was compared to that of K_2PtCl_4 and Karstedt catalyst. The reaction was performed under the fixed conditions and the conversion and ratio of the products was compared in five cycles of the reaction. In the case of **M1N_Pt** catalyst the full conversion of cinnamaldehyde in the experimental runs was achieved in 60–90 min (Fig. 7). The rate of substrate conversion in the subsequent cycles slowly decreased which could be caused by gradual leaching of the platinum from the complex. Moreover, the catalytic activity of heterogenized platinum complex was comparable to those operating in the presence of K_2PtCl_4 or Karstedt catalyst, see Table 2.

The opposite effect appeared when **M2N_Pt** catalyst was used. In any of the five cycles of reaction after 6 h the full conversion of cinnamaldehyde was not achieved. In all the five cycles after a 120 min conversion was only at the level of about 25–35%, although the rate of reaction gradually increased in subsequent cycles.

3.5.2. *Analysis of products*

Hydrogenation of cinnamaldehyde is a commonly used model for testing various catalysts, because it provides information about the regioselectivity in the hydrogenation of olefinic and carbonyl functional groups. In this reaction three main products may be formed: hydrocinnamaldehyde (HCA), cinnamyl alcohol (CA), and γ-phenylpropanol (PP). Yields of these products depend on the type of catalyst, catalyst support, co-catalyst and reaction conditions [38–41].

Using our platinum catalysts in the cinnamaldehyde hydrogenation reaction we observed two major products HCA and PP. The chemoselectivity of reactions was not changed with consecutive cycles (Table 2). The ratio of the HCA:PP was as 60:40 for the **M1N_Pt**



Scheme 3. hydrogenation reaction.

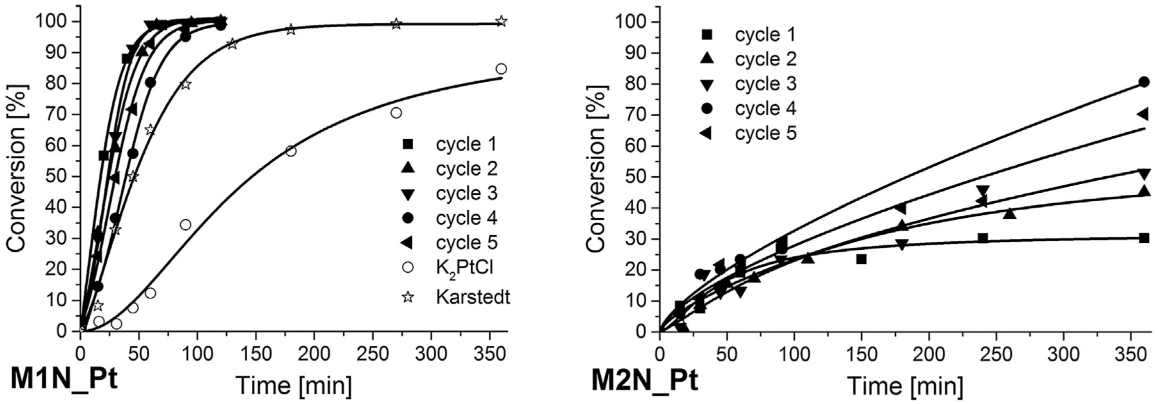


Fig. 7. Cinnamaldehyde hydrogenation runs.

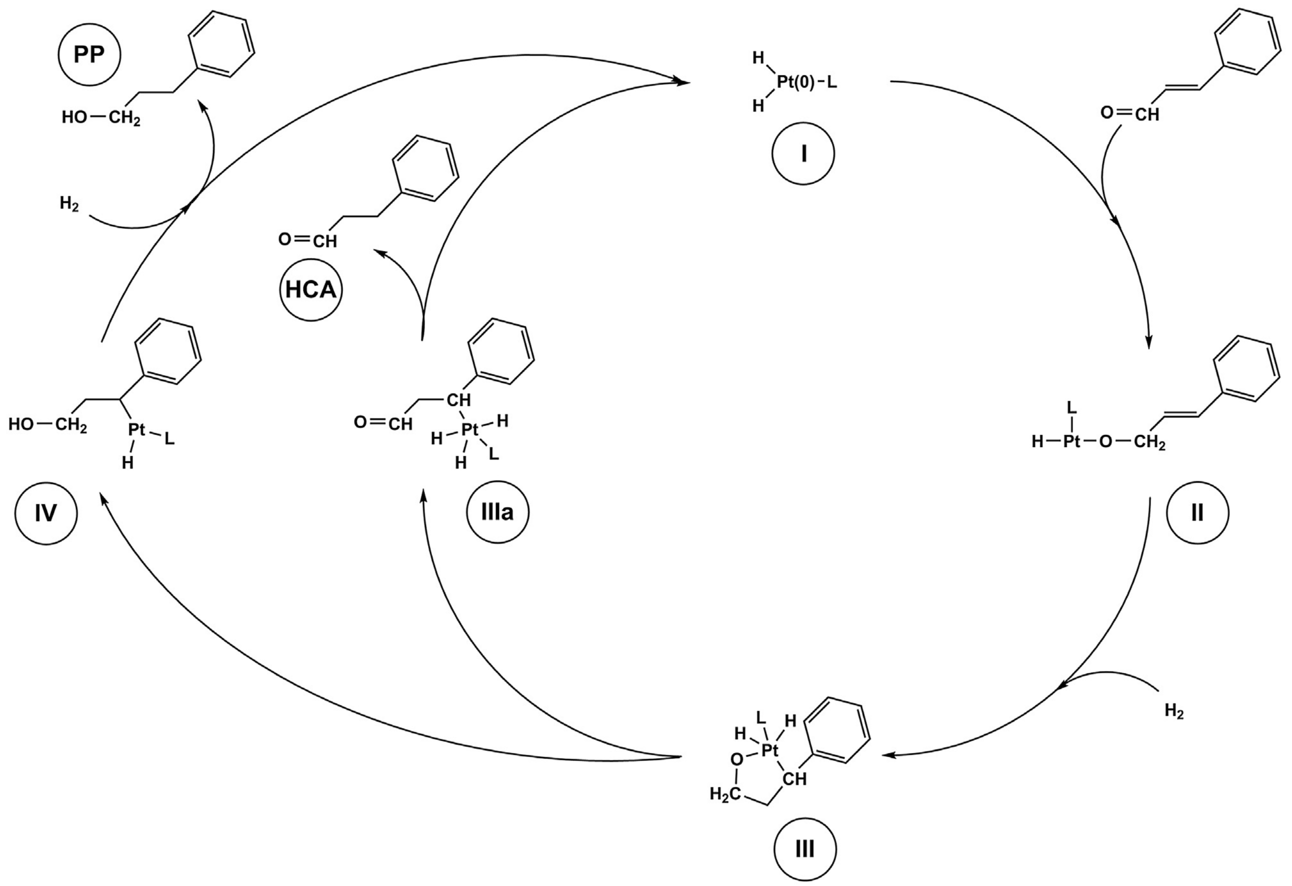
Table 2
Conversion of cinnamaldehyde and selectivity in catalytic runs in the hydrogenation reaction.

catalyst	Cycle	Complex [g] (mmol of Pt)	Conversion [%]	TON	Hydrocinnamaldehyde [%]	cinnamyl alcohol [%]	γ-Phenylpropanol [%]
M1N_Pt	1	0.0575 (0.0279)	100.0[*]	710.6	57.9	0.00	42.1
	2		100.0		55.6	0.00	44.4
	3		100.0		58.00	0.00	42.00
	4	0.0466 (0.0226)	98.7		59.4	0.00	40.6
	5		99.6	876.8	61.9	0.00	38.1
M2N_Pt	1	0.0992 (0.0421)	30.3[**]	354.3	89.0	0.00	11.0
	2		45.2		77.1	1.9	21.0
	3		51.4		77.0	2.1	20.9
	4	0.089 (0.0377)	80.6		77.7	1.8	20.5
	5		70.3	823.0	78.0	2.0	20.0
K_2PtCl_2	1	0.0103 (0.0248)	84.7[**]	678.0	52.2	13.7	34.1
Karstedt catalyst	1	0.0331 (0.017)	92.8[*]	1085.6	35.28	38.46	26.26

[*] After 120 min.
[**] After 360 min.

catalyst and 77:21 for the **M2N_Pt** catalyst. In the case of **M2N_Pt** catalyst the formation of a small amount of cinnamyl alcohol (c.a. 2%) was observed after 6 h. The reaction selectivity using K_2PtCl_4 or Karstedt catalyst was significantly different from that using platinum on microspheres.

The formation of products was followed together with the conversion of cinamaldehyde. PP was expected to arise as a consecutive product of the transformation of HCA and/or CA (Scheme 3). However, the kinetic runs displayed in Fig. 8 clearly showed that PP and HCA are formed in parallel. A very rapid transformation of CA into PP was excluded (see Fig. D in sup. inf.). Therefore the most of PP



Scheme 4. The proposed mechanism of cinnamaldehyde hydrogenation.

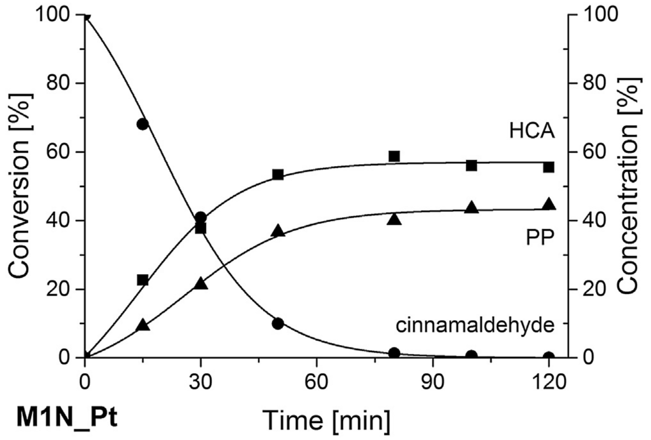


Fig. 8. Conversion of cinnamaldehyde and increase of products in time for **M1N_Pt** catalyst.

is formed directly from cinnamaldehyde without the intermediacy of CA and HCA according to the mechanistic pathway analogous to that found for the hydrogenation of cinnamaldehyde catalysed by palladium [29]. The key intermediate in this mechanism is complex III (Scheme 4), which may be transformed to PP or HCA.

4. Conclusions

Magnetic and non-magnetic polysiloxanes microspheres obtained by the emulsion process of PHMS and containing a large number of SiOH groups may be efficiently functionalized by reactions of N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane with the SiOH groups. The nitrogen chelating groups pendant to polysiloxanes chain on these microspheres may serve as ligands for the effective formation of platinum complexes. This new Platinum(II) catalyst, immobilized on the polysiloxane microspheres, shows a high catalytic activity in hydrosilylation and hydrogenation reactions. This complex is stable under the reaction conditions and may be reused. The Pt(0) form of this catalyst, which may be generated by reducing the Pt(II) complex with sodium borohydride, is also a stable and effective catalyst.

The Pt(II) and Pt(0) catalysts showed excellent conversion and recyclability in the hydrosilylation of dimethylphenylsilane and Pt(II) in the hydrogenation of cinnamaldehyde. The selectivity towards the formation of β(Z) substituted compound is achieved in the hydrosilylation process. A fairly high yield of hydrocinnamaldehyde may be obtained in the hydrogenation of cinnamaldehyde. The complex with Pt(0) form was more active but less selective than platinum (II). The influence of the presence of iron nanoparticles is observed. The magnetic complex is slightly less active in the hydrogenation process than the platinum on microspheres without iron.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.09.016.

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