

Silicone waxes—synthesis via hydrosilylation in homo- and heterogeneous systems

Hieronim Maciejewski^{a,b,*}, Agata Wawrzyńczak^a,
Michał Dutkiewicz^a, Ryszard Fiedorow^{a,*}

^a Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

^b Poznań Science and Technology Park, AMU Foundation, Rubież 46, 61-612 Poznań, Poland

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Dedicated to our dear friend Professor Bogdan Marciniec on the occasion of his 65th birthday in appreciation of his outstanding contributions to organometallic chemistry and catalysis.

Abstract

Silicone waxes, i.e. polysiloxanes with a long alkyl chain (>C₈) as a pendant group make one of the most important classes of modified polysiloxanes widely applied to many branches of industry. Main methods of synthesis of silicone waxes are based on catalytic processes of hydrosilylation of alkenes with poly(hydro, methyl)siloxanes. Results of studies on syntheses of silicone waxes in homo- and heterogeneous catalytic systems are presented. The most effective catalyst for the reactions studied appeared to be siloxide rhodium complex [$\{\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})\}_2$]. The immobilisation of this complex in ionic liquids resulted in a highly selective and very active catalytic biphasic system that enabled easy product separation and repeated use of the catalytic system. Excellent selectivity was observed also in the case of hydrosilylation of the above alkenes in a typical heterogeneous system in the presence of supported metallic catalysts. In this group of catalysts particularly active was platinum supported on a highly hydrophobic styrene–divinylbenzene resin which enabled to obtain product yield of about 90% in reactions with 1-octene and well over 90% in reactions with 1-hexadecene. When platinum was accompanied by copper on supports such as activated carbon and carbon black, product yields were clearly higher than those obtained on monometallic catalysts. Supported rhodium was either inactive or poorly active in reactions studied.

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Keywords: Hydrosilylation; Silicone waxes; TM complexes; Ionic liquids; Supported platinum catalysts

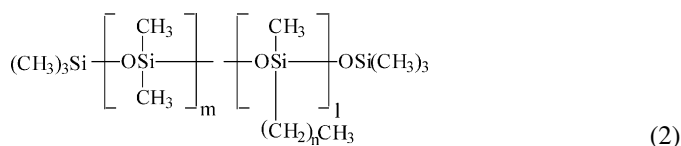
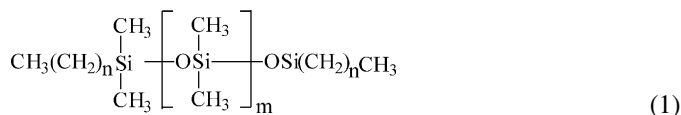
1. Introduction

Polydimethylsiloxanes are a basic component of one of the most popular and widely applied synthetic polymer materials—silicones. Their unique properties, such as wide-range thermal stability, resistance to oxidation, low surface tension, gas permeability, excellent dielectric properties, physiological inertness and moisture resistance [1–3] are the reason for a wide application of silicones to many branches of industry [4,5].

Typical silicones contain methyl (seldom ethyl) groups at silicon atom which results in their characteristic hydrophobic properties. Although alkyls can be hardly regarded as functional groups, it is worth of mentioning that longer alkyl chains (from

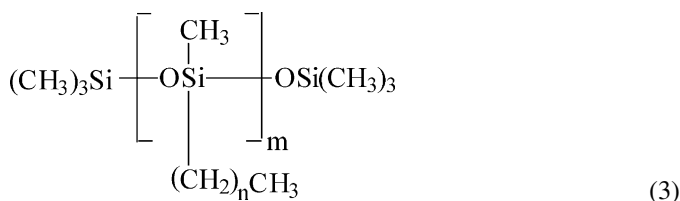
C₈ to C₄₀), linked to silicon atom of polysiloxane chain, can considerably modify physical and chemical properties of initial silicones due to the capability of penetrating organic systems, both monomeric and polymeric ones. Such modified polysiloxanes have significantly higher affinity to organic compounds than unmodified ones.

Silicones modified by terminal alkyl groups of siloxane chain (1) or by alkyl groups located at its side chain (2, 3) in many respects resemble hydrocarbons.



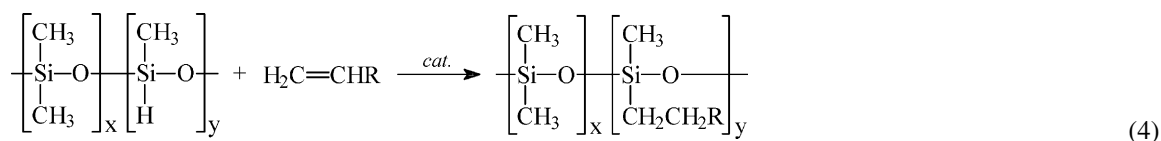
* Corresponding authors. Tel.: +48 61 829 14 93; fax: +48 61 865 80 08.

E-mail addresses: maciejm@amu.edu.pl (H. Maciejewski),
fiedorow@amu.edu.pl (R. Fiedorow).



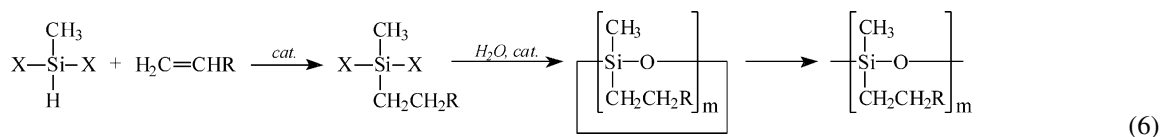
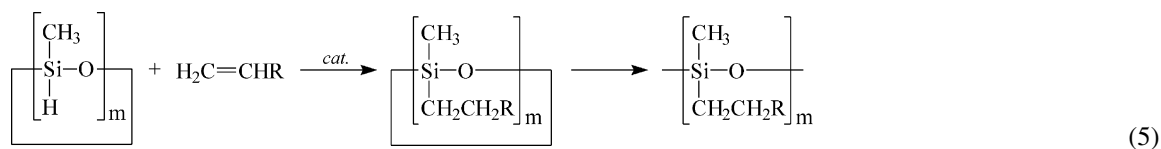
We deal either with homopolymers (3) or with copolymers (2) of different controlled content of methylalkylsilicone fragments.

Under standard conditions, alkyl-modified silicones are colourless liquids (C_8 – C_{14}) of various viscosities or colourless



solids (C_{18} and higher), melting points of which increase with growing alkyl chain from room temperature to about 70°C . The above compounds are called silicone waxes as the term is popularly understood.

Alkylpolymethylsiloxanes are characterised by moistening and softening activities as well as by biological inertness,



excellent lubricating and spreading abilities which predispose them to the application to cosmetic industry as components of many products [6–16]. The main application have found alkyl derivatives of silicones with chains longer than C_{12} , which are capable of excellent mixing with cosmetic raw materials (oils, waxes, alcohols and fatty acids) and, when present in final products, they do not leave greasy or sticky sensation on the skin. Their adhesive properties are similar to those of petroleum jelly. Other examples of alkylpolysiloxane applications include their use as hydrophobising and softening agents for fibres [17,18], lubricants and oils [19–21], fuels and motor oils for two-stroke engines [22], brake fluids [23], foam inhibitors for diesel oil [24], surfactants for paints and varnishes [25], agents for masonry protection against moisture, preparations for surface maintenance in the household, car cosmetics, preparations for surface maintenance in the household [26], leak stoppers for toners [27], coatings of heated shafts (Xerox machines and laser printers) [28], abrasive compounds [29,30], agents for assembly of printing plates [31],

agents modifying surfaces of fillers for polyamide resins [32] and detergents for washing machines [33]. More and more frequently reports appear in the literature on polysiloxanes that contain, in addition to alkyl groups, siloxane fragments with other chains. They can be applied as emulsifiers, alkyl and polyether chain-containing frothing agents [25,34], additives to herbicides that contain alkyl and amino group-containing monomers [35].

The most important, efficient and widely applied method of functional group introduction into polysiloxane chain is the addition of Si–H bond to unsaturated compounds that contain a functional group, i.e. the process of hydrosilylation, as shown in Eq. (4):

As starting materials that contain a hydrosilyl group can serve a siloxane polymer, a cyclic siloxane oligomer as well as a monomeric silane with Si–H function and two hydrolysable substituents at silicon atom. Substituted cyclic siloxanes and monomeric silanes (after the addition to a functional olefin) can further undergo polymerisation either by ring-opening polymerisation (5) or polycondensation (6).

Hydrosilylation is a catalytic process that proceeds in the presence of precursors of free radicals or various catalysts, e.g. amines, Lewis acids (salts of metals), supported metals and transition metal complexes [36–39]. In most cases, the role of hydrosilylation catalysts is played by transition metal complexes, those of platinum in particular [40–43].

A major problem, particularly in the case of polymer systems of high viscosity, is the separation of catalyst from a reaction mixture. The presence of metals in the reaction products, even in trace quantities, is unacceptable for many applications, therefore efforts are made to apply heterogeneous catalysts or immobilised metal complexes in order to attain high catalytic activity and easy product isolation at the same time. For the above reason our work was aimed at studying synthesis of silicone waxes (which make one of the most important groups of modified silicones) by using different catalysts, both homo- and heterogeneous ones, as well as at comparing the ease of their separation from the post-reaction mixture and possibilities of multiple use of a given catalyst.

2. Experimental

2.1. Materials employed for experiments carried out in the homogenous system

All reagents were dried and purified before being used by the usual procedures. Rhodium complexes [$\{\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})_2\}$], [$\{\text{Rh}(\mu\text{-Cl})(\text{cod})_2\}$] and platinum complex H_2PtCl_6 in cyclohexanone were prepared as described in refs. [44,45], Karstedt's and Wilkinson's catalysts as well as ionic liquids: 1,2,3-trimethylimidazolium methylsulphate [TriMIM]MeSO₄, 1-methylimidazolium tetrafluoroborate [MIM]BF₄ and 1-methylimidazolium trifluoromethylsulphate [MIM]SO₃CF₃ were purchased from Aldrich. All ionic liquids were dried under vacuum at 60 °C for 8 h prior to their use. Heptamethyltrisiloxane ($\text{Me}_3\text{SiOSi}(\text{Me})(\text{H})\text{OSiMe}_3$) and poly(hydromethyl, dimethyl)siloxane ($\text{Me}_3\text{SiO}[\text{Si}(\text{Me})_2\text{O}]_{50}[\text{Si}(\text{Me})(\text{H})\text{O}]_{25}\text{SiMe}_3$) random polymer were purchased from Gelest, whereas reagents were obtained from Aldrich.

2.2. Preparation of supported metal catalysts

Monometallic catalysts with platinum or rhodium loading of 1 wt.% and bimetallic catalysts with platinum and copper loading of 1 and 0.1 wt.%, respectively, were prepared by the incipient wetness method using a highly crosslinked styrene–divinylbenzene (SDB) copolymer (Aldrich), a polymeric support prepared from divinylbenzene (DVB), activated carbon RX3 Extra (Norit) and carbon black XC72 (Cabot). Textural properties of the supports were determined on the ground of low-temperature nitrogen adsorption isotherms measured on an ASAP 2010 sorptometer (Micromeritics). The preparation of the DVB support consisted in the block polymerisation of divinylbenzene (55%, Aldrich) carried out in sealed vessels at 80 °C for 24 h in the presence of isooctane as a porogen. 1%Pt/SDB and 1%Pt/DVB catalysts were prepared from platinum(II) acetylacetonate using chloroform as a solvent, 1%Pt/RX3 and 1%Pt/XC72 catalysts from aqueous solutions of hexachloroplatinic acid, whereas bimetallic catalysts (1%Pt+0.1%Cu/RX3 and 1%Pt+0.1%Cu/XC72) from aqueous solution of H_2PtCl_6 and CuCl_2 . In the case of rhodium catalysts, ethanolic solution of rhodium(III) chloride was used. Supports impregnated with metal precursors were dried at 60 °C and then reduced in hydrogen flow (50 cm³/min). In the case of SDB- and DVB-supported platinum catalysts, reduction temperature and time were 160 °C and 3 h, respectively. The SDB-supported rhodium catalyst was prepared by 5 h reduction at 150 °C followed by 2 h at 200 °C, whereas 1%Pt/RX3, 1%Pt/XC72, 1%Pt+0.1%Cu/RX3 and 1%Pt+0.1%Cu/XC72 catalysts were obtained by subjecting relevant metal precursor/support systems to a three-stage reduction: 160 °C (3 h), 250 °C (2 h) and 500 °C (1 h). Then hydrogen flow was replaced with helium flow (50 cm³/min) and catalysts were cooled to room temperature in flowing helium.

2.3. Catalytic measurements in heterogeneous system

Reactions studied were hydrosilylation of 1-octene and 1-hexadecene with 1,1,1,3,5,5,5-heptamethyltrisiloxane (further abbreviated to trisiloxane) or poly(hydromethyl, dimethyl)siloxane (further abbreviated to polysiloxane). Reaction substrates and catalyst were placed in vials of 10 cm³ in capacity in such a proportion that mole ratio of alkene:trisiloxane (or polysiloxane):metal = 1:1:2 × 10⁻⁴. Vials were sealed using aluminium seals with Teflon-coated septa and placed in a thermostated bath at 100 °C with shaking. After 1 and 3 h, vials were removed from the bath and the post-reaction mixture was analysed by using either a gas chromatograph Varian 3300 (in the case of reactions with trisiloxane) or Fourier transform IR Bruker IFS 113v spectrometer (in the case of reactions with polysiloxane). Moreover, in the case of 1%Pt/SDB catalyst, experiments on catalyst recycling were performed. In these experiments, the catalyst was separated from the post-reaction mixture after 1 h at 100 °C and reused in the next 1 h reaction cycle.

2.4. Catalytic measurements in homogeneous system

All manipulations were carried out under argon using standard Schlenk techniques. The Si–H functional siloxane (or polysiloxane) and alkene (1-octene or 1-hexadecene) were placed into the reaction vessel in the mole ratio of 1:1 (related to Si–H group) and heated to 90 °C. Then, a catalyst was added in such an amount to meet the ratio of 10⁻⁵ mol per 1 mol Si–H. If the reaction proceeded in the presence of ionic liquids, the catalyst (5 × 10⁻⁵ mol per 1 mol Si–H) was dissolved in an appropriate ionic liquid (1 wt.% based on total weight of combined substrates) and such an obtained mixture was added to substrates. After 2 h, the reaction mixture was separated from the catalytic system phase by decantation. The mixture was analysed by GC (or FTIR) techniques and the formation of desired products was verified by GC–MS technique. The recovered catalytic system (catalyst in ionic liquid) was reused in a subsequent reaction run.

3. Results and discussion

A straight majority of polysiloxane syntheses, reported both in open and patent literature, are catalysed by platinum complexes [6–8,19,23,46,47]. Modifications, mentioned in the introduction, are usually carried out in the temperature range of 60–120 °C for 6–18 h, using about 5–50 ppm of the catalyst. Platinum complexes show a high catalytic activity for hydrosilylation of olefins with different functional groups, however, some impurities present in reagents lead to catalyst deactivation. That is why other metal complexes of comparably high catalytic hydrosilylation activity are searched for. The catalysts that are characterised by a higher resistance to poisoning are rhodium complexes. The contribution of Marciniak group to this field was synthesis, isolation and full characterisation of several new rhodium and iridium siloxide complexes, both dimeric [44,48,49] and monomeric [50] ones. Catalytic activity of the Rh(I) siloxide complexes has been demonstrated for some reac-

Table 1
Catalytic activity of platinum and rhodium complexes for hydrosilylation of alkenes (CH₂=CHCH₂Z) with heptamethyltrisiloxane and poly(hydromethyl, dimethyl)siloxane

Z	Catalyst	Reaction temperature [°C]	Yield of product [%]	
			With trisiloxane ^a	With polysiloxane ^b
C ₅ H ₁₁	Pt-Karstedt	100	93	85
	H ₂ PtCl ₆ in cyclohexanone	100	91	86
	{Rh(μ-OSiMe ₃)(cod)} ₂	25	90	95
		60	99	100
	{Rh(μ-Cl)(cod)} ₂	100	60	51
	[RhCl(PPh ₃) ₃]	100	21	12
C ₁₃ H ₂₇	Pt-Karstedt	100	98	92
	H ₂ PtCl ₆ in cyclohexanone	100	96	90
	{Rh(μ-OSiMe ₃)(cod)} ₂	25	95	98
		60	100	100
	{Rh(μ-Cl)(cod)} ₂	100	87	75
	[RhCl(PPh ₃) ₃]	100	32	15

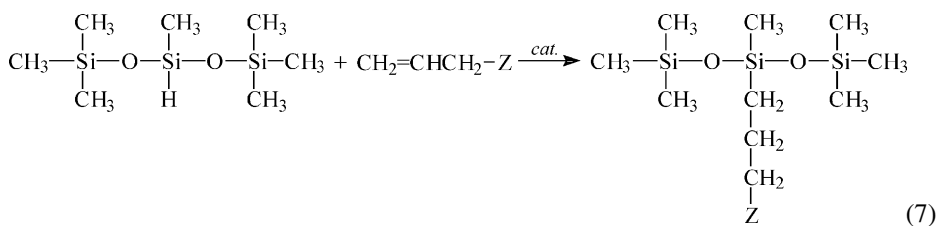
[HSi]:[CH₂=CH]:[cat] = 1:1:10⁻⁵; reaction time: 2 h.

^a Trisiloxane: Me₃SiOSi(Me)(H)OSiMe₃.

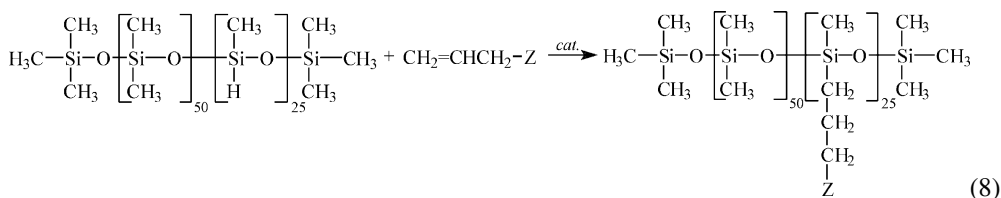
^b Polysiloxane: Me₃SiO[Si(Me)₂O]₅₀[Si(Me)(H)O]₂₅SiMe₃.

tions, e.g. hydrosilylation of alkenes [51] and allyl alkyl ethers [50,52–55] as well as for silylative coupling of vinylsilanes with alkenes [56,57].

Some of the above rhodium siloxide complexes have found application to hydrosilylation of 1-octene and 1-hexadecene with 1,1,1,3,5,5,5-heptamethyltrisiloxane. The mentioned reaction, which is a model one for the polymeric system (i.e. polysiloxane), proceeds according to the following Eq. (7):



Contrary to the polymeric system, the above system provided a possibility of analysing the reaction progress with the use of gas chromatography. Selected active catalysts have been applied to hydrosilylation of the same alkenes with the use of poly(hydromethyl, dimethyl)siloxane according to Eq. (8):



For the sake of comparing catalytic performance, the most common platinum catalysts such as Karstedt's catalyst [Pt₂{(CH₂=CHSiMe₂)₂O}₃] and H₂PtCl₆ in cyclohexanone as well as rhodium Wilkinson's complex [RhCl(PPh₃)₃] were applied (Table 1).

The formation of one product has been established for the reactions studied. In the case of hydrosilylation with trisiloxane, 100% selectivity was proved by GC-MS and ¹H NMR tech-

niques, whereas in that of hydrosilylation with polysiloxane—by FTIR and ¹H NMR methods. Moreover, it was found by using GPC technique that the reaction with polysiloxane resulted in a considerable increase in molecular weight corresponding to the addition of 25 alkene molecules to one polysiloxane molecule. In the case of reactions with heptamethyltrisiloxane, the conversion of parent substances and yield of reaction product were determined by means of gas chromatography, whereas in that

of reactions in the polymeric system, the determination was carried out with the use FTIR analysis by calculating the decrease in ratios of absorbance of Si–H band (2157 cm⁻¹) as well as that of C=C bands (at 1642 and 910 cm⁻¹) to absorbance of the band originated from –Si(CH₃)₂ (1261 cm⁻¹). The results given in

Table 1 show that hydrosilylation of hexadecene proceeds easier than that of octene which is reflected by the fact that yields of hexadecene reaction product are higher than those of octene reaction product for all catalysts investigated. The most effective catalysts, both for the reaction with trisiloxane and polysiloxane, are platinum complexes and rhodium siloxide complexes. It should be emphasised that [{Rh(μ-OSiMe₃)(cod)}₂] is highly

Table 2

Catalytic activity of platinum and rhodium complexes, immobilised in various ionic liquids, for hydrosilylation of alkenes ($\text{CH}_2=\text{CHCH}_2\text{Z}$) with heptamethyltrisiloxane and poly(hydromethyl, dimethyl)siloxane

Z	Ionic liquid	Catalyst	Yield of product [%]	
			With trisiloxane ^a	With polysiloxane ^b
C ₅ H ₁₁	[MIM]BF ₄	H ₂ PtCl ₆ in cyclohexanone	0	0
	[MIM]SO ₃ CF ₃	[{Rh(μ -OSiMe ₃)(cod)} ₂]	85 (48, 29)	81 (32, 12)
		H ₂ PtCl ₆ in cyclohexanone	91 (55, 9)	87 (41, 35)
	[TriMIM]MeSO ₄	[{Rh(μ -OSiMe ₃)(cod)} ₂]	91 (82, 20)	87 (55, 49)
C ₁₃ H ₂₇	[MIM]BF ₄	H ₂ PtCl ₆ in cyclohexanone	96 (93, 85, 64)	95
		[{Rh(μ -OSiMe ₃)(cod)} ₂]	93 (92, 90, 88, 81)	94 (92, 91, 89, 84)
	[MIM]SO ₃ CF ₃	H ₂ PtCl ₆ in cyclohexanone	0	0
		[{Rh(μ -OSiMe ₃)(cod)} ₂]	93 (69, 43)	98 (71, 50)
[TriMIM]MeSO ₄	H ₂ PtCl ₆ in cyclohexanone	95 (77, 55)	93 (68, 50)	
	[{Rh(μ -OSiMe ₃)(cod)} ₂]	94 (69, 23)	90 (50, 12)	
[TriMIM]MeSO ₄	H ₂ PtCl ₆ in cyclohexanone	95 (90, 82, 70)	90 (88, 82, 76)	
	[{Rh(μ -OSiMe ₃)(cod)} ₂]	100 (99, 99, 97, 95)	96 (95, 92, 90, 89)	

[HSi]:[CH₂=CH]:[cat] = 1:1:5 × 10⁻⁵; ionic liquid content: 1 wt.% based on total weight of combined substrates; reaction temperature and time: 90 °C and 2 h, respectively; the values given in parentheses represent the yields obtained in subsequent catalytic runs with the use of the same recovered catalytic system.

^a Trisiloxane: Me₃SiOSi(Me)(H)OSiMe₃.

^b Polysiloxane: Me₃SiO[Si(Me)₂O]₅₀[Si(Me)(H)O]₂₅SiMe₃.

active for the above reactions even at room temperature. Moreover, rhodium siloxide complex is more catalytically active than its chloro-rhodium analogue [{Rh(μ -Cl)(cod)}₂] and Wilkinson's complex [RhCl(PPh₃)₃], which is a well-known hydrosilylation catalyst. Unfortunately, this complex, similarly to other catalysts used in the homogeneous system, decomposes after one catalytic run, therefore there is no possibility of reusing such catalysts.

Two-phase catalysis in a liquid–liquid system seems to be an ideal approach that enables to take advantage of both homogeneous and heterogeneous catalysis [58]. Nowadays, many reactions are known to proceed in biphasic systems using ionic liquids as immobilising agents for metal complexes, e.g. processes of hydroformylation, hydrogenation, oxidation, dimerisation, coupling [58–60], whereas only a few examples of catalytic hydrosilylation in the presence of ionic liquids were reported as yet [61–64].

On the ground of results of experiments with hydrosilylation in the homogeneous system, the most effective rhodium and platinum catalysts have been selected for studies in the presence of ionic liquids. One of our objectives was to find suitable ionic liquids, which via immobilisation of the metal complex, would permit easy separation of the catalyst from the reaction product. Ionic liquids with weakly coordinating inert anions and inert cations can activate homogeneously dissolved transition metal complexes. They can at the same time play the role of ordinary solvents [60]. Ionic liquids employed in our studies were based on imidazolium derivatives. Results of these studies are presented in Table 2.

Post-reaction mixtures consisted of two phases, one of which was the catalyst system (a catalyst in an ionic liquid), while reactants were the other one. After the separation of products, the catalytic system was reused. Yields of products obtained in repeated runs are given in Table 2 in parentheses. The results confirmed high catalytic activity of the rhodium siloxide complex for reactions carried out in the presence of various ionic liquids.

Although yields obtained after one catalytic run in the presence of [{Rh(μ -OSiMe₃)(cod)}₂] immobilised in every ionic liquids studied are high and so are yields in the case of H₂PtCl₆ in cyclohexanone in some of the above liquids, subsequent runs performed when using imidazolium salts containing BF₄⁻ or SO₃CF₃⁻ anions result in a decrease in catalytic activity. One of the reasons for this decrease could be the decomposition of anion of ionic liquid (caused by the contact with moisture) resulting in the release of fluoride ions that act as a catalyst poison. 1,2,3-Trimethylimidazolium methylsulphate [TriMIM]MeSO₄, which enables to reuse a catalyst for five times without a loss of activity, seems to be the most suitable for reactions catalysed by rhodium complexes.

Analogous reactions were carried out in the presence of supported metallic catalysts, both platinum and rhodium ones. Preliminary studies have shown that catalytic performance of platinum supported on hydrophilic surfaces (metal oxides) was poorer than that supported on surfaces having hydrophobic properties. Therefore further experiments were carried out using hydrophobic styrene–divinylbenzene copolymer (water contact angle, 109–117° [65]) and activated carbon as supports. In general, activated carbon surface is hydrophobic [66], however, hydrophobicity of this material decreases with increasing content of surface oxides. The supports employed considerably differ in their porosity (Table 3) ranging from microporous acti-

Table 3

Textural characterisation of supports employed for the preparation of metallic catalysts

Support	Surface area [m ² /g]	Pore volume [cm ³ /g]	Average pore diameter [nm]
SDB	1172	0.77	2.6
DVB	474	0.52	4.4
RX3	1124	0.57	2.0
XC72	214	0.33	6.2

Table 4
Hydrosilylation of olefins with siloxanes on supported metallic catalysts

Z	Catalyst	Time [h]	Yield of product [%]	
			With trisiloxane	With polysiloxane
C ₅ H ₁₁	1%Pt/SDB	1	87	88
		3	89	95
	1%Pt/DVB	3	73	78
	1%Pt/RX3	3	76	52
	1%Pt/XC72	3	63	60
	1%Pt + 0.1%Cu/RX3	3	81	58
	1%Pt + 0.1%Cu/XC72	3	71	69
	1% Rh/SDB	3	0	0
1%Rh/RX-3	3	0	0	
C ₁₃ H ₂₇	1%Pt/SDB	1	98	91
		3	99	93
	1%Pt/DVB	3	88	81
	1%Pt/RX3	3	81	69
	1%Pt/XC72	3	87	79
	1% Rh/SDB	3	48	0
	1%Rh/RX-3	3	0	0

vated carbon through SDB resin having both micropores and mesopores (*t*-plot has shown the predomination of the former ones) to clearly mesoporous DVB and XC72.

The greatest surface area was found for SDB resin (Table 3) and the SDB-supported platinum catalyst appeared to be the most active of all heterogeneous catalysts studied in hydrosilylation of 1-octene and 1-hexadecene (Table 4). High product yield was achieved on the above catalyst already after reaction time of 1 h and the extension of time to 3 h resulted only in a small rise in product yields.

The 1%Pt/SDB catalyst was also subjected to repeated use experiments (Fig. 1) which have shown that catalytic activity is maintained on a high, constant level for three cycles. When the catalyst was reused for the fourth and the fifth times, product yields decreased, the decrease being particularly sharp in the case of hydrosilylation of 1-octene (Fig. 1). The reduction in catalytic activity can be a result of platinum leaching or deactivation. The 1%Pt/SDB catalyst was characterised by low platinum dispersion (5.2% as determined by hydrogen chemisorption

at room temperature) which could suggest the occurrence of large platinum crystallites (21.7 nm). Such crystallites would be weakly bound to the support surface and vulnerable to leaching. On the other hand, the presence of bands at 989 and 903 cm⁻¹ in infrared spectra (rather weak ones) of our polymeric supports suggests that a certain number of vinyl groups have remained after polymerisation, and therefore a possibility of forming a surface complex as a result of the interaction between platinum and vinyl ligands cannot be ruled out. In the latter case, the small volume of chemisorbed hydrogen could be a result of unavailability of platinum, bound by vinyl groups, to hydrogen uptake rather than a result of the occurrence of the whole amount of platinum in the form of large crystallites. This could also explain why the decrease in catalytic activity occurs only after the fourth use of the catalyst, because a significant effect of rupture of links between metal complexes and solid supports, i.e. a considerable leaching, is usually observed in the case anchored complexes after several reaction cycles. However, the fact that some amount of hydrogen was chemisorbed testifies to the presence of metallic platinum species as well.

Good catalytic performance was observed also in the case of platinum on activated carbon RX3, surface area of which was only slightly smaller than that of SDB. However, results of catalytic tests performed in the reactions of hydrosilylation of 1-hexadecene with trisiloxane and polysiloxane show that the activity of catalysts investigated does not depend on surface area only, since yields of relevant reaction products on 1%Pt/DVB and 1%Pt/XC72 are higher than those on 1%Pt/RX3, although surface areas of the former two catalysts are considerably lower than that of the latter one. (It is worth to add that surface areas of catalysts with 1 wt.% metal loading differed from those of relevant supports only to an insignificant extent.) If platinum is accompanied by copper on supports such as activated carbon and carbon black, the resulted bimetallic catalysts can be counted among the best for achieving high yields in the reactions studied, whereas the performance of rhodium catalysts appeared to be

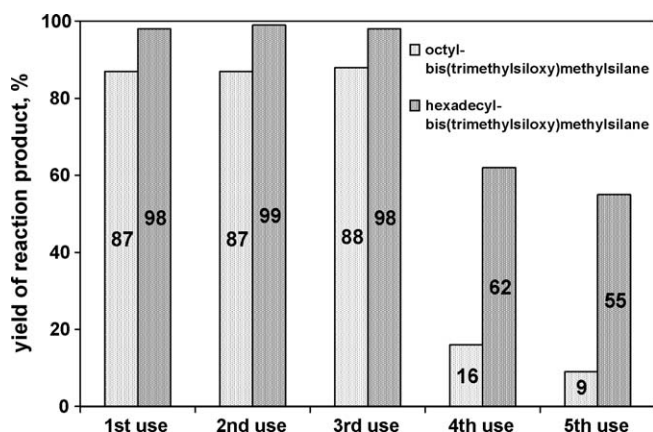


Fig. 1. Repeated use of 1%Pt/SDB catalyst in hydrosilylation of 1-octene and 1-hexadecene with heptamethyltrisiloxane (100 °C, 1 h).

highly disappointing (Table 4). This points to a considerable difference in the behaviour of the latter metal in hetero- and homogeneous catalytic systems.

4. Conclusions

Hydrosilylation of 1-octene and 1-hexadecene with heptamethyltrisiloxane or poly(hydro, dimethyl)siloxane catalysed by complexes of rhodium and platinum in homogeneous systems or the above complexes immobilised in ionic liquids (biphase systems) proceeds selectively with the formation of only one desired product. The above reactions proceed easier in the case of 1-hexadecene than in that of 1-octene.

The best catalyst is clearly the siloxide rhodium complex $[\{\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ that is characterised by a high catalytic activity even at room temperature. Immobilisation of the above complex in 1,2,3-trimethylimidazolium methylsulphate $[\text{TriMIM}]\text{MeSO}_4$ results in the formation of a biphase system made by reactants on the one side and the catalytic complex in ionic liquid on the other, which enables easy separation of the catalyst from reaction products. High catalytic activity of the biphase system was maintained even after five catalytic runs.

Hydrosilylation of alkenes in heterogeneous system also proceeds with excellent selectivity and can result in high product yield, particularly in the case of platinum supported on styrene–divinylbenzene resin. Suitable support material can be both microporous solids of high surface area like the above resin and activated carbon as well mesoporous ones of several times smaller surface area, e.g. carbon black. A certain advantage of the above catalysts is the fact that they can be reused three times without a change in their activity.

Bimetallic catalysts, obtained by supporting platinum and copper on activated carbon and carbon black, are characterised by higher activity compared to those containing platinum only.

Contrary to rhodium complexes used as catalysts in the homogeneous system, metallic rhodium, supported both on activated carbon or styrene–divinylbenzene resin, is not a good choice for catalysing alkene hydrosilylation.

A wide variety of applications of silicone waxes in many branches of industry explicitly points to a high demand for compounds of this type. Therefore, of a key importance to economic manufacturing of this group of modified silicones is a highly active and 100% selective catalyst. Siloxide rhodium complex, both in a homogeneous system and immobilised in $[\text{TriMIM}]\text{MeSO}_4$ as well as some supported platinum catalysts meet the above requirements.

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