



Functionalization of spherosilicates via hydrosilylation catalyzed by well-defined rhodium siloxide complexes immobilized on silica



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ABSTRACT

Well-defined rhodium siloxide complexes immobilized on silica ($[(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\text{cod})](\text{Aerosil 200})$ 1 and $[(\equiv\text{SiO})\text{Rh}(\text{cod})(\text{PCy}_3)](\text{Aerosil 200})$ 2) synthesized via direct condensation of respective molecular precursors appeared to be very effective catalysts for quantitative synthesis of functionalized spherosilicates via direct hydrosilylation of olefins with octahydridospherosilicate. Catalyst 1 was also very active in subsequent hydrosilylation of two different olefins, which permitted efficient syntheses of spherosilicates with mixed functional groups of desired stoichiometric ratios. The catalysts were recycled at least 10 times without loss of efficiency in all the hydrosilylation processes performed.

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1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) make a class of organosilicon compounds which can be efficiently used as building blocks for production of inorganic-organic hybrid materials [1–5]. The most important POSS derivatives are substituted cubic-like T_8 derivatives containing a nanosized inorganic core $(\text{RSiO}_{1.5})_8$ which can produce hybrid materials because the vertices of the cube can be easily functionalized [2]. Although the cubic T_8 arrangement is achieved by the hydrolysis/condensation reaction of many simple silicon compounds such as RSiCl_3 or $\text{R}^1\text{Si}(\text{OR}^2)_3$, only a few of the known T_8R_8 derivatives can be prepared directly in this manner. Functionalized POSS can be obtained in high yields by the three essential catalytic methods: (a) hydrosilylation [2,6,7], (b) nucleophilic substitution [8,9], and (c) metathesis/silylative coupling [10,11].

Functionalization of cubic silsesquioxane occurs by Pt-complexes catalyzed (mostly by Karstedt' catalyst) hydrosilylation

of olefins by either octahydridosilsesquioxanes, $\text{H}_8(\text{SiO}_{1.5})_8$, T_8H and/or octahydridospherosilicate $((\text{HSiMe}_2\text{O})_8(\text{SiO}_{1.5})_8)$ ($\text{H}_8\text{M}_8\text{Q}_8$) [6]. The latter has been recently regarded as very attractive thanks to the easier (compared with that of T_8H) and more effective synthesis. Besides, it is also more reactive and soluble in a large number of solvents. Although olefin hydrosilylation homogeneously catalyzed by Pt as well as Rh complexes is a well-recognized reaction leading to effective synthesis of functionalized POSS, the presence of metals in the reaction products, even in trace quantities, is often unacceptable, but the separation of the catalyst from the reaction mixture, particularly in the polymer systems of high viscosity, is a serious problem. Therefore, an attempt has been made to apply heterogeneous catalysts or immobilized metal complexes in order to obtain high catalytic activity in many recycled runs and with easy product isolation at the same time. We have previously reported the synthesis and characterization of well-defined rhodium siloxide complexes, prepared directly by the reaction of molecular rhodium siloxide precursors with Aerosil 200 silica, their structures have been characterized by ^{13}C , ^{29}Si , and ^{31}P magic-angle spinning (CP/MAS) NMR spectroscopy also [12–14]. The catalytic activity of these immobilized complexes has been tested in the hydrosilylation of olefins with siloxanes and polysiloxanes (for review see [15]). This investigation has also resulted in proposing a mechanism of hydrosilylation catalysis by single-site rhodium siloxide

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complexes based on the results of CP/MAS NMR measurements [12–14].

In this paper we report the synthesis of a functional spherosilicates obtained via hydrosilylation with octakis(hydriddimethylsiloxy)octasilsesquioxane in the presence of well-defined rhodium siloxide complexes immobilized on silica. A synthesis of octafunctional spherosilicates containing mixed functional groups at different stoichiometric ratios via successive hydrosilylation of two respective olefins is also presented. The synthesis of spherosilicates with exemplified mixed fluoropentyloxypropyl and glycidoxypropyl functional groups via hydrosilylation reaction catalyzed homogeneously by molecular rhodium complex $[\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})]_2$ we have published recently [16].

2. Experimental

2.1. General methods and chemicals

Tetraethoxysilane $\text{Si}(\text{OEt})_4$, tetramethylammonium hydroxide $(\text{CH}_3)_4\text{NOH}$, dimethylchlorosilane $\text{SiH}(\text{CH}_3)_2\text{Cl}$, olefins (allyl glycidyl ether, 1-octene, 4-allyl-1,2-dimethoxybenzene) were purchased from Aldrich and used without further purification. Aerosil 200 was obtained from Degussa AG. The catalysts **1** and **2** ($[(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\text{cod})]$ (Aerosil 200) and $[(\equiv\text{SiO})\text{Rh}(\text{cod})(\text{PCy}_3)]$ (Aerosil 200)) were synthesized according to the procedure described previously (the catalyst **1**–[12] in benzene; the catalyst **2**–[14]). Octa[hydriddimethylsiloxy]octasilsesquioxane $[\text{HMe}_2\text{SiOSiO}_{1.5}]_8$ was synthesized following the published procedures [17]. Allyl 1,1,2,2,3,3,4,4-octafluoropentyl ether was synthesized by the Williamson reaction [18].

The NMR spectra (^1H , ^{13}C , and ^{29}Si) were recorded on Varian Gemini 300 VT and Varian Mercury 300 VT spectrometers. CDCl_3 was used as the solvent. The solid-state cross-polarization magic angle spinning (CP/MAS) experiments were performed on a Bruker 600 MHz Avance III spectrometer at frequency of 150.90 MHz for ^{13}C and 119.23 MHz for ^{29}Si , equipped with a MAS probe head using 4-mm and 1.3 mm ZrO_2 rotors. FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrophotometer equipped with a SPECAC Golden Gate diamond ATR unit. In all experiments 16 scans at a resolution of 2 cm^{-1} were used to record the spectra. In situ FT-IR measurements were performed on a Mettler Toledo ReactIR 15 equipped with a DS 9.5 mm AgX DiComp Fiber Probe (1.5 m) with a diamond sensor, and a Mercury Cadmium Telluride (MCT) detector. For all the spectra 256 scans were recorded with the resolution of 1 cm^{-1} . The spectra were recorded for 1 h in 15 and 30 s intervals. Initial turnover frequency (TOF) values were expressed as mole of spherosilicate product, containing eight functional groups produced, per mole of Rh per minute.

2.2. Procedure for catalytic test

2.2.1. Octafunctionalized spherosilicates (with single olefin)

The appropriate amount of a catalyst (in the ratio of 5×10^{-5} mol per 1 mol Si–H) and the mixture of octakis(hydriddimethylsiloxy)octasilsesquioxane, 1.2 equiv of olefin (calculated per each Si–H group) in toluene (in the amount indispensable for dissolving spherosilicate) were placed under argon into the reaction vessel and heated up to 100°C for 1 h (for allyl octafluoropentyl ether –4 h). After 1 h, the reaction vessel was cooled to room temperature and then the reaction mixture was separated from the catalytic system by decantation. The mixture was analyzed by FT-IR spectroscopy and then, after the evaporation of toluene, the formation of desired products was

verified by NMR analysis. The recovered catalyst was reused in the next reaction run.

Additionally, hydrosilylation of 1-octene processes were monitored with in situ FT-IR spectroscopy. Due to the presence of spectral gap in the range from 2000 to 2300 cm^{-1} , characteristic for used in the experiment ATR probe with diamond window, a band at about 2100 cm^{-1} was not visible so the intensity change of the band at 903 cm^{-1} , also characteristic for Si–H bond, was analyzed for quantitative description of substrate conversion.

2.2.2. Spherosilicates containing mixed functional groups

The appropriate amount of the catalyst (in the ratio of 5×10^{-5} mol per 1 mol Si–H) and the mixture of octakis(hydriddimethylsiloxy)octasilsesquioxane, the olefin in the appropriate stoichiometric ratio (calculated per each Si–H group) in toluene (in the amount indispensable for dissolving spherosilicate) were placed under argon into the reaction vessel and heated up to 100°C for 1 h. After 1 h, an appropriate amount of allyl 1,1,2,2,3,3,4,4-octafluoropentyl ether (or 1-octene) in 10% excess was added and the reaction was carried out for another hour. Then the reaction vessel was cooled to room temperature and the reaction mixture was separated from the catalytic system by decantation. The mixture was analyzed by FT-IR spectroscopy and then, after the evaporation of toluene, the formation of desired products was verified by NMR analysis. The recovered catalyst was reused in the next reaction run.

2.3. Procedure for split test

The appropriate amount of the catalyst (in the ratio of 5×10^{-5} mol per 1 mol Si–H) and the mixture of octakis(hydriddimethylsiloxy)octasilsesquioxane, 1.2 equiv of the olefin (calculated per each Si–H group) in toluene (in the amount indispensable for dissolving spherosilicate) were placed under argon into the reaction vessel and heated up to 100°C for 15 min. Then the conversion of Si–H bond was measured by FT-IR spectroscopy and half of the volume of the upper liquid phase was transferred under argon to another reaction vessel. Both vessels were placed in the same oil bath and heating was continued for 45 min. Conversions of the Si–H bond were determined by FT-IR spectroscopy in both samples.

2.4. Spectroscopic characterization of hydrosilylation products

2.4.1.

Octakis(3-glycidyloxypropyldimethylsiloxy)octasilsesquioxane

^1H NMR (CDCl_3 , 298 K, 300 MHz) δ [ppm] = 0.05 (OSiCH_3); 0.51 (SiCH_2); 1.51 (CH_2); 2.47, 2.65 (CH_2O); 3.00 (CHO); 3.25 (CH_2O); 3.33, 3.56 (OCH_2).

^{13}C NMR (CDCl_3 , 298 K, 75.5 MHz) δ [ppm] = -0.66 (SiCH_3); 13.39 (SiCH_2); 22.89 (CH_2); 43.98 (CH_2O); 50.29 (CHO); 71.75 (OCH_2); 73.61 (CH_2O).

^{29}Si NMR (CDCl_3 , 298 K, 59.6 MHz) δ [ppm] = 12.87 ($\text{OSi}(\text{CH}_3)_2$); -109.13 (SiOSi).

2.4.2. Octakis(*n*-octyldimethylsiloxy)octasilsesquioxane

^1H NMR (CDCl_3 , 298 K, 300 MHz) δ [ppm] = 0.14 (OSiCH_3); 0.57 (CH_3); 0.87 (SiCH_2); 1.21 (CH_2).

^{13}C NMR (CDCl_3 , 298 K, 75.5 MHz) δ [ppm] = -0.50 (OSiCH_3); 13.62 (CH_3); 17.5–33.62 (CH_2).

^{29}Si NMR (CDCl_3 , 298 K, 59.6 MHz) δ [ppm] = 12.57 ($\text{OSi}(\text{CH}_3)_2$); -108.98 (SiOSi).

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