Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

to

Polymeric Monolith Supported Pt-Nanoparticles as Ligand-Free Catalysts for Olefin Hydrosilylation under Batch and Continuous Conditions

by

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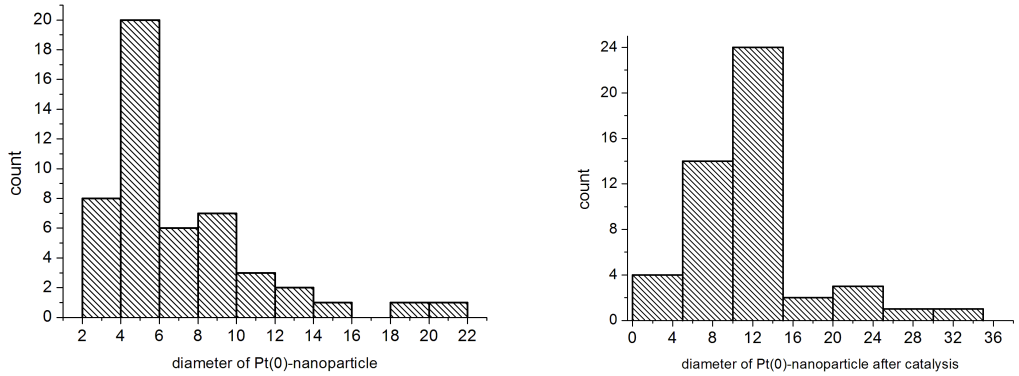


(a) **(b)**

Figure S1. Histogram of Pt(0) nanoparticles immobilized on a ROMP-derived monolith (**a**) before catalysis, mean particle diameter of the Pt nanoparticles=6.9 nm and (**b**) after catalysis, mean particle diameter of Pt nanoparticles=12.5 nm.

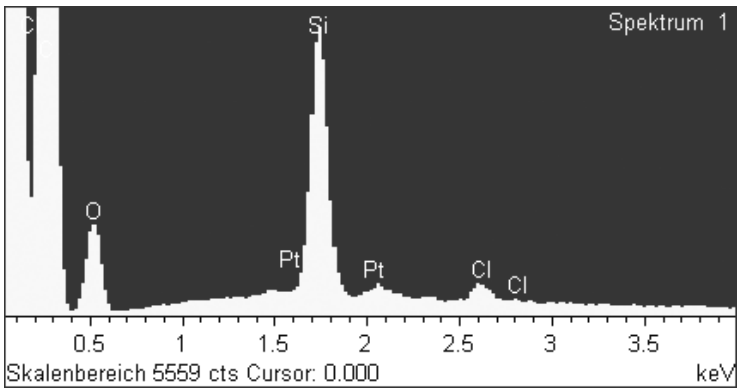


Figure S2. EDX spectrum of Pt-nanoparticles formed within the pores of a ROMP-derived monolith.

Table S1. Physical data for Pt(0)-nanoparticles immobilized on a ROMP-derived monoliths.

average Pt-nanoparticle diameter	6.939 nm
density of Pt	66 atoms·nm^{-3} (21.45g·cm^{-3})
no of Pt-atoms in a nanoparticle	ca. 11540
no of Pt-atoms on surface of a nanoparticle	632
weight of a Pt-nanoparticle	$3.76 \cdot 10^{-15}$ mg
total number of Pt-nanoparticles	$4.48 \cdot 10^{14}$ Pt-particles/g of monolith
total number of Pt-nanoparticles on the surface of the monolith	$2.45 \cdot 10^{13}$ Pt-particles/g of monolith

Calculations [1-3]

Assumption: The density of bulk face-centered cubic platinum is 21.45 gcm^{-3}. Assuming the same density for Pt nanoparticles, we calculate the density of the metal nanoparticles as 66 atomsnm^{-3}.

The approximate number of Pt atoms in a nanoparticle (volume) (N_{Pt}) = (66 nm^{-3}) 4/3 πr^3 = (66 nm^{-3}) (π /6) (D)^3

The mean particle diameter (D) obtained from the histogram (Figure **S1(a)**) was 6.939 nm

N_{Pt} = (66 nm^{-3}) (π /6) (6.939 nm)^3 = 11540 (1)

The weight of the Pt-nanoparticle (W_{Pt}) = 11540 x 195.084 (Atomic mass of Pt) = 2251306.06 Daltons. (1 Dalton equals the mass of a single hydrogen atom, or 1.67 x 10^{-24} g)

W_{Pt} = 2251306.06 x 1.67 x 10^{-24} g = $3.76 \cdot 10^{-18}$ g = $3.76 \cdot 10^{-15}$ mg (2)

Total number of Pt-nanoparticles = 1.67 mg·g^{-1}(from ICP)/ $3.76 \cdot 10^{-15}$ mg = $4.48 \cdot 10^{14}$ (3)

Surface area of the Pt-nanoparticles is = $4\pi r^2$ = 4x3.14x$(3.469)^2$ = 151.19 nm^2 (4)

Surface area of the Pt-atom = $4\pi r^2 = 4x3.14x(138 \cdot 10^{-3}\ nm)^2 = 0.23919\ nm^2$ (Pt atomic radius = 138 pm) (5)

From eq. (4) and (5) total number of Pt-atoms on the surface of one nanoparticle is = $41.78\ nm^2 / 0.23919\ nm^2 = 632$ (6)

From eq. (1), (3) and (6) total number of Pt- nanoparticles on the surface = $4.48 \cdot 10^{14}$ x 632/11540 = $2.45 \cdot 10^{13}$ (7)

From eq. (2) and (7) weight of the Pt participated in reaction = $2.4 \cdot 10^{13}$x $3.76 \cdot 10^{-15}$ mg = 0:0921 mg/g, $0.472 \cdot 10^{-3}$ mmol /g (8)

Triethoxyoctylsilane (1): Isolated yield 695 mg (90%). ^{1}H NMR ($CDCl_3$): δ = 3.76-3.84 (dd, 6H), 1.18-1.31 (m, 21H), 0.83-0.88 (t, 3H), 0.58-0.65 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 58.7, 33.6, 32.3, 31.7, 29.6, 23.1, 18.7, 14.5, 10.7. GC-MS: t_R = 8.345 min; calcd. for $C_{14}H_{32}O_3Si$, (*m/z*) = 276.21; found 276.1 ($M^{\cdot+}$).

1,1,1,3,5,5,5-Heptamethyl-3-octyltrisiloxane (2): Isolated yield 1.38 g (93%). ^{1}H NMR ($CDCl_3$): δ = 1.30-1.36 (m, 12H), 0.89-0.94 (t, 3H), 0.45-0.51 (t, 2H), 0.11-0.13 (t, 18H), 0.02 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 33.6, 32.3, 29.7, 29.6, 23.4, 23.1, 18.0, 14.5, 2.2. GC-MS: t_R = 8.242 min; calcd. for $C_{15}H_{38}O_2Si_3$, (*m/z*) = 334.22; found 319.2 ($M^{\cdot+}$-CH_3).

Triethoxy(3-phenylpropyl)silane (3): Isolated yield 730 mg (85%). ^{1}H NMR ($CDCl_3$): δ = 7.21-7.37 (m, 5H), 3.81-3.91 (m, 6H), 2.69-2.72 (m, 2H), 1.73-1.93 (m, 2H), 1.25-1.31 (m, 9H), 0.63-0.81 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 142.8, 128.9, 128.6, 126.1, 58.7, 39.6, 25.2, 18.7, 10.5. GC-MS: t_R = 9.181 min; calcd. for $C_{15}H_{26}O_3Si$, (*m/z*) = 282.17; found 282.1 ($M^{\cdot+}$).

1,1,1,3,5,5,5-Heptamethyl-3-(3-phenylpropyl)trisiloxane (4): Isolated yield 1.48 g (98%). ^{1}H NMR ($CDCl_3$): δ = 7.22-7.47 (m, 5H), 2.64-2.70 (t, 2H), 1.6-1.76 (m, 2H), 0.53-0.59 (t, 2H), 0.13-0.17 (bs, 18H), 0.05 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 143.1, 128.9, 128.6, 126.0, 39.8, 31.7, 25.6, 17.8, 2.3, 0.17. GC-MS: t_R = 9.020 min; calcd. for $C_{16}H_{32}O_2Si_3$, (*m/z*) = 340.17; found 340.1 ($M^{\cdot+}$).

Triethoxy(2-phenylethyl)silane (5) and triethoxy(1-phenylethyl)silane (6): Isolated yield 748mg (92%). ^{1}H NMR ($CDCl_3$): δ = 7.22-7.36 (m, 5H), 3.76-3.89 (m, 6H), 2.76-2.83 (m, 2H), 2.36 (m, 3H), 1.318-1.49 (m, 9H), 1.5 (d, 1H), 1.02 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 145.0, 144.4, 128.7, 128.4, 128.3, 128.2, 126.0, 125.8, 125.6, 125.2, 59.2, 58.8, 31.7, 29.3, 26.5, 18.7, 18.6, 16.0, 12.9. GC-MS: t_R = 8.271 and 8.774 min; calcd. for $C_{14}H_{24}O_3Si$, (*m/z*) = 268.15; found 268.1 ($M^{\cdot+}$).

1,1,1,3,5,5,5-Heptamethyl-3-phenylethyltrisiloxane (7) and 1,1,1,3,5,5,5-heptamethyl-3-(1-phenylethyl)trisiloxane (8): Isolated yield 1.17 g (80%). ^{1}H NMR ($CDCl_3$): δ = 7.13-7.34 (m, 5H), 2.69-2.76 (m, 2H), 1.39-1.44 (d, 1H), 0.89-0.96 (m, 2H). 0.18-0.23 (m, 18H), 0.10-0.12 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 145.2, 145.5, 128.7, 128.3, 128.2, 128.0, 125.9, 31.2, 29.7, 20.2, 14.9, 2.8, 0.14. GC-MS: t_R = 8.403 and 8.700 min; calcd. for $C_{15}H_{30}O_2Si_3$, (*m/z*) = 326.16; found 326.1 ($M^{\cdot+}$).

Bicyclo[2.2.1]hept-2-yltriethoxysilane (9): 26% of yield from GC-MS, t_R= 8.002 min; calcd. for $C_{13}H_{26}O_3Si$, (*m/z*) = 258.17; found 258.1 ($M^{\cdot+}$).

Bicyclo[2.2.1]hept-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (10): Isolated yield 1.016 g (50%). ^{1}H NMR ($CDCl_3$): δ = 2.24 (s, 2H), 1.12-1.54 (m, 8H), 0.50 (s, 1H), 0.11-0.12 (bs, 18H), 0.005 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 38.0, 37.1, 37.0, 34.2, 31.9, 31.7, 30.6, 29.4, 2.27, 1.04. GC-MS: t_R = 7.979 min; calcd. for $C_{14}H_{32}O_2Si_3$, (*m/z*) = 316.17; found 316.2 ($M^{\cdot+}$).

Bicyclo[2.2.1]hept-5-en-2-yltriethoxysilane (*exo/endo*, 13): Isolated yield 778 mg (96%). ^{1}H NMR ($CDCl_3$): δ = 5.88-6.12 (m, 2H), 3.74-3.89 (m, 6H), 2.88-3.03 (m, 2H), 1.81-1.92 (m, 1H), 1.33-1.39 (m, 1H), 1.14-128 (m, 9H), 1.03-1.12 (m, 2H), 0.44 8 (m, 1H). ^{13}C NMR ($CDCl_3$): δ = 138.1, 135.6, 135.0, 134.1, 128.4, 125.7, 125.6, 58.9, 58.7, 58.6, 51.2, 47.3, 44.5, 43.1, 42.8, 36.1, 31.9, 31.8, 31.7, 29.0, 27.3, 26.6, 21.1, 20.6, 18.6, 12.3, 10.6. GC-MS: t_R = 7.853 and 7.996 min; calcd. for $C_{13}H_{24}O_3Si$, (*m/z*) = 256.15; found 256.1 ($M^{\cdot+}$).

Hydrosilylation Kinetics of 1-Octene using Pt-nanoparticles immobilized on ROMP-derived monoliths

t-Butylbenzene (50 mg, 0.373 mmol), 1-octene (0.504 g, 4.4 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.0 g, 4.4 mmol) were dissolved in 5 mL of n-hexane in a 8-mL of vial, then the monolithic material (15 mg, $1.3 \cdot 10^{-4}$ mmol of platinum) was added. The reaction mixture was then stirred at the 45°C for 4 h. At certain intervals, aliquots were taken from the reaction mixture analyzed by GC-MS (Figure S3).

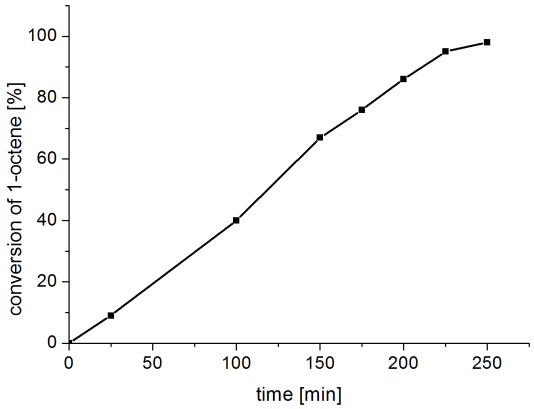


Figure S3. Hydrosilylation of 1-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane using Pt nanoparticle-loaded on a ROMP-derived monoliths.

Recycling of the Monolith-Supported Pt-catalyst (ROMP-derived monolith)

The hydrosilylation experiment consisted of t-butylbenzene (50 mg, 0.373 mmol), 1-octene (0.504 g, 4.4 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (1 .0g, 4.4 mmol) and 5 mL of n-hexane in a 8-mL of vial, then the monolithic material (15 mg, $1.3 \cdot 10^{-4}$ mmol of platinum) was added. The reaction mixture was then stirred at the 45°C for 4 h and the conversion was checked by the GC-MS. After 4 h the mixture was cooled to room temperature and filtered through filter paper and the monolithic material was washed with n-hexane. The monolithic material was transferred into a fresh portion of reaction mixture and performed again under similar conditions. Up to two successive runs were performed giving conversions of 97.5% and 94% respectively.

Leaching of Pt-nanoparticles (ROMP-derived monolith)

A hydrosilylation experiment was carried out using 5 mL of n-hexane, t-butylbenzene (50 mg, 0.373 mmol), 1-octene (0.504 g, 4.4 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.0 g, 4.4

mmol) in a 8-mL of vial, then the monolithic material (15 mg, $1.3 \cdot 10^{-4}$ mmol of platinum) was added. The reaction mixture was stirred at 45°C for 4 h. After reactions had been completed, the mixture was filtered through the Whatman filter paper at 45°C. Then the fresh reaction mixture was added to the filtrate and checked the GC-MS shown the 45% of product, then the reaction mixture stirred for another 16 h at 45°C, but no further conversion was observed.

Synthesis GMA-Based Monoliths: GMA-based monoliths were prepared according to published procedure[S1]. Briefly, stainless steel columns (100 x 4.6 mm i.d.) were cleaned, rinsed and sonicated in a 1:1 mixture of ethanol and acetone. The columns were closed at one end with frits and end fittings, respectively. Then the columns were filled with the polymerization mixture consisting of of GMA: TMPTA:1-dodecanol:2-ProH:toluene:AIBN=15:15:30:30:10:1.0 (all wt.%), sealed at either side and kept at 60°C for 16 h. After polymerization, the columns were directly connected to a HPLC pump and flushed with CH_2Cl_2 for 4 h at a flow rate of 0.2 mL/min, then with THF for 30 min at a flow rate of 0.3 mL/min and finally with water for 30 min at a flow rate of 0.3 mL/min.

Hydrolysis of the Epoxy Groups Within Pores >7 nm

The epoxide groups of porous polymer rods were hydrolyzed by flushing the monolithic column with a solution of poly(styrenesulfonic acid), M_w=69400 g/mol, 4.5 wt.-% in water) for 15 min at a flow rate 0.3 mL/min. Then the monolith was kept for 15 h at 65°C. The hydrolyzed column was then washed with water, methanol and THF for 2 h at a flow rate of 0.3 mL/min, respectively.

Functionalization of Pores <7 nm

The epoxide groups remaining within the small pores of the monolith were reacted with bicyclo[2.2.1]hept-5-en-2-ylmethylamine. For these purposes, a 10 wt.-% solution of bicyclo[2.2.1]hept-5-en-2-yl-methylamine in 1,4-dioxane was introduced into the monolith, which was then kept at 60°C for 16 h. The thus modified column was then washed with 55 mL of CH_2Cl_2 (flow rate 0.3 mL/min for 3 h). After this procedure, the monoliths were ready for the ROMP-based grafting.

Functionalization of Pores <7 nm via ROMP-based Grafting

The Grubbs`1st generation catalyst $[RuCl_2((PCy)_3)_2(CHPh]$ (4.0 mg, 4.86 μmol) was dissolved in 1.5 mL of CH_2Cl_2 and introduced into the monolith. The monolith was sealed and kept at room temperature for overnight. Then the monolith was flushed with CH_2Cl_2 for 30 min at a flow rate of 0.3 mL/min to remove any unattached catalyst, then with argon to remove all solvent. A 100 mg sample of N,N-di(pyridin-2-yl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide was dissolved in 1.5 mL of CH_2Cl_2 and introduced into the monolith. The monolith was sealed and kept at the 40°C overnight. The following day, the monolith was flushed with a 20 vol.-% solution of ethyl vinyl ether (EVE) in a 1:1 mixture of DMSO and THF. Finally, the monolith was washed with THF and kept *in vacuo* for overnight. The amount of grafted monomer (194 μmol/g) was determined by elemental analysis.

Preparation of Pt-loaded GMA-based Monoliths

A solution of $PtCl_4$ (15 mg, 0.077 mmol) in 1.5 mL of THF was introduced into the monolith modified with N,N-di(pyridin-2-yl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide. Then the

monolith was washed with 30 mL of THF. Finally, the support was dried *in vacuo* for 4 h. The Pt-content (4.17 mg/g) was determined by ICP-OES.

Characterization of Monoliths

Before and after functionalization of the GMA-based monoliths were characterized by inverse size-exclusion chromatography (ISEC) in terms of inter-microglobule porosity (ε_z), pore porosity (ε_p), total porosity (ε_t), pore volume (V_p) and the mean pore diameter (Φ_m). Results are summarized in Table S2 and Figure S4. Furthermore, Pt-loaded GMA-based monoliths were characterized by transmission electron microscopy (TEM), the results are shown in Table S2, Figure S5 and Figure S6.

Table S2. Composition and structural data of GMA-based monoliths.

Composition (wt.-%)				
GMA	**TMPTA**	**1-dodecanol/2-propanol (1:1)**	**toluene**	**AIBN**
15	15	60	10	1.0
Structural data (before functionalization)				
ε_p **(vol.-%)**	ε_z **(vol.-%)**	ε_t **(vol.-%)**	V_p **(µL/g)**	Φ_m **(Å)**
7	71	78	243	1180
Structural data (after functionalization)				
7	69	76	255	1113

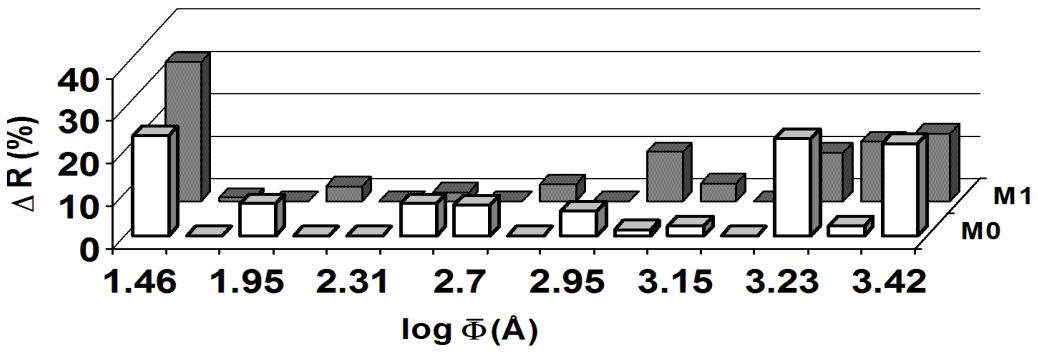
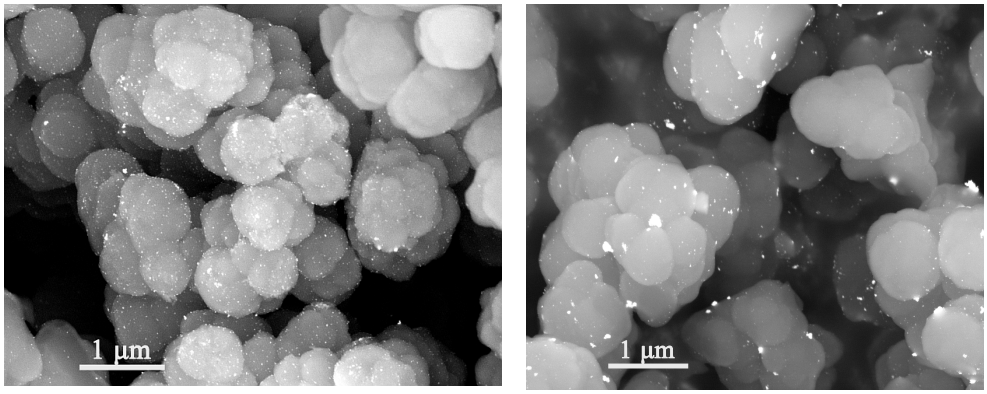
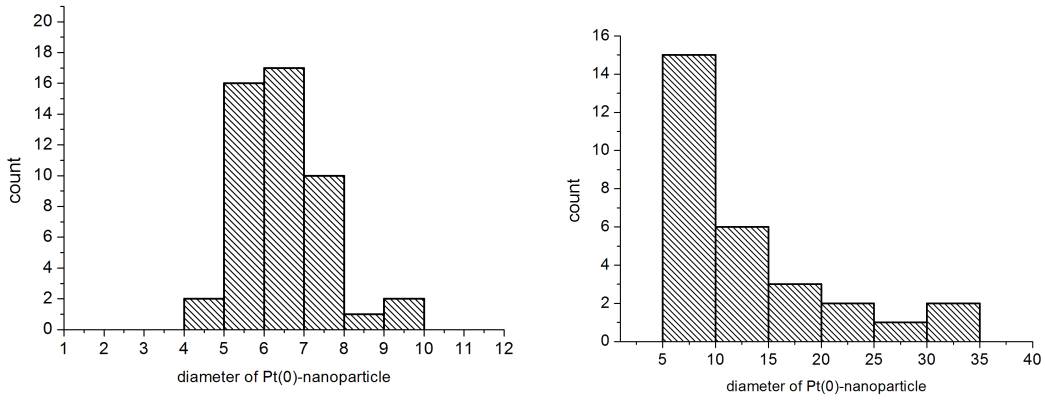


Figure S4. $\log \Phi_{average}$ (Å) *vs*. ΔR (%) for an unmodified GMA-based monolith (**M0**) and after pore-size-selective functionalization (**M1**).



(**a**) (**b**)

Figure S5. TEM graphs of Pt(0) immobilized on GMA-based monolithic materials. (**a**) Before, (**b**) after use in olefin hydrosilylation reactions.



(**a**) (**b**)

Figure S6. Histogram of Pt-nanoparticles immobilized on GMA-based monoliths (**a**) before catalysis; the mean particle diameter of the Pt nanoparticles was 6.4 nm. (**b**) After catalysis; the mean particle diameter of Pt nanoparticles was 12.6 nm.

Table S3. Physical data for Pt-nanoparticles immobilized on GMA-based monoliths.

average Pt-nanoparticle diameter	6.39 nm
density of Pt	66 atoms·nm^{-3}
no of Pt-atoms in a nanoparticle	ca. 9012
no of Pt-atoms on surface of a nanoparticle	536
weight of a Pt-nanoparticle	$2.94 \cdot 10^{-15}$ mg
total number of Pt-nanoparticles	$1.418 \cdot 10^{15}$ Pt-particles/g of monolith
total number of Pt-nanoparticles on the surface of the monolith	$8.43 \cdot 10^{13}$ Pt-particles/g of monolith

Calculations:

The approximate number of Pt atoms in a nanoparticle (volume) (N_{Pt}) = (66 nm^{-3}) 4/3 πr^3 = (66 nm^{-3}) (π /6) $(D)^3$

The mean particle diameter (D) obtained from the histogram (Figure **S6a**) was 6.39 nm

N_{Pt} = (66 nm^{-3}) (π /6) (6.39 nm) ^{3} = 9012 (1)

The weight of the Pt-nanoparticle (W_{Pt}) = 9012 x 195.084 (atomic mass of Pt) = 1758097.00 Daltons. (1 Dalton equals the mass of a single hydrogen atom, or 1.67 x 10^{-24} g)

W_{Pt} = 1758097.008 x $1.67 \cdot 10^{-24}$ g = $2.94 \cdot 10^{-18}$ g = $2.94 \cdot 10^{-15}$ mg (2)

Total number of Pt- nanoparticles = 4.17 mgg^{-1}(from ICP)/ $2.94 \cdot 10^{-15}$ mg = $1.418 \cdot 10^{15}$(3)

Surface area of the Pt-nanoparticles is = $4\pi r^2$ = 4x 3.14x $(3.195)^2$ = 128.21 nm^2 (4)

Surface area of the Pt-atom = $4\pi r^2$ = 4x 3.14x $(138 \cdot 10^{-3}$ nm$)^2$ = 0.23919 nm^2 (Pt atomic radius = 138 pm) (5)

From eq. (4) and (5) total number of Pt-atoms on the surface of one nanoparticle is = 41.78 nm^2 /0.23919 nm^2 = 536 (6)

From eq. (1), (3) and (6) total number of Pt-nanoparticles on the surface = $1.418 \cdot 10^{15}$ x 536/9012 = $8.43 \cdot 10^{13}$ (7)

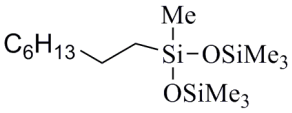
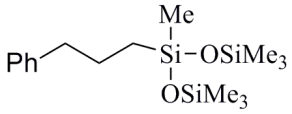
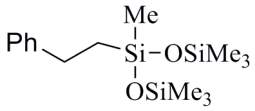
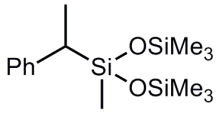
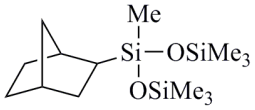
From eq. (2) and (7) weight of the Pt participated in reaction = $8.43 \cdot 10^{+13}$ x $2.94 \cdot 10^{-15}$ mg = 0.247 mg/g or 0.247/195.08 = $1.2 \cdot 10^{-3}$ mmol /g (8)

Hydrosilylation of Olefins using Pt-nanoparticles immobilized on GMA-based monoliths

Hydrosilylation experiments consisted of t-butylbenzene (50 mg, 0.373 mmol), the corresponding terminal alkene, norborn-2-ene or norbornadiene (4.4 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (4.4 mmol) and 5 mL of n-hexane in a 8-mL of vial, then the GMA-based

monolithic material (7 mg, $0.149 \cdot 10^{-3}$ mmol of platinum) was added. The reaction mixture was then stirred at the 45°C for 16 h; conversion was checked by the GC-MS. The results are summarized in Table S4.

Table S4. Data of Pt-nanoparticle catalyzed olefin hydrosilylation reactions using GMA-based monoliths. Yields were determined by GC-MS using t-butylbenzene as internal standard.

#	Olefin	Product	Conversion [%]	TON[a]	TON[b]
S4a	1-octene		98	29000	513000
S4b	allylbenzene		6	1800	31000
S4c	styrene		27	10000	183000
S4c´			8		
S4d	norborn-2-ene		10	3000	52000

[a]Assuming every Pt atom participates in the reaction; [b]assuming that only the surface Pt-atoms participate in the reaction.

References

[S1] R. Bandari, T. Höche, A. Prager, K. Dirnberger, M. R. Buchmeiser, *Chem. Eur. J.* **2010**, *16*, 4650.

[S2] K. R. Gopidas, J. K. Whitesell, M. A. Fox, *Nano Lett.* **2003**, *3*, 1757.

[S3] K. R. Gopidas, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2003**, *125*, 6491.