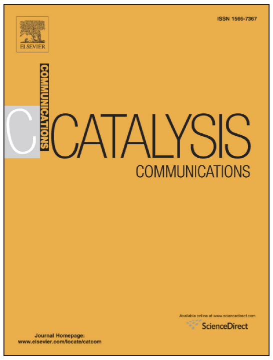

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Super-microporous silica-supported platinum catalyst for highly regioselective hydrosilylation

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Abstract: Super-microporous micelle-templated platinum on silica catalysts were successfully prepared by an improved one-pot procedure, using a water/acetonitrile/*n*-dodecylamine mixture. The catalyst showed high surface area and narrow pore size and was further characterized by powder X-ray diffraction and inductively coupled plasma mass spectrometry. The unique super-microporous materials were proven to be highly active for the microwave-assisted hydrosilylation reaction of terminal alkenes or alkynes using dichloromethylsilane as silicon source. The super-microporous structure was beneficial for the control of hydrosilylation regioselectivity, as the selectivity to the β-adduct reached 99%. Moreover, the catalyst could be easily recovered by simple filtration and re-used seven times without appreciable loss of activity and selectivity.

Keywords: Catalyst; Hydrosilylation; Super-microporous; Silica-supported platinum; Microwave-assisted

1. INTRODUCTION

Hydrosilylation is one of the most extensively studied reactions for the fabrication of functional silicone polymer materials [1]. Highly different polymer properties can be obtainedin function of the spatial addition of silyl groups to (unsaturated) C-H bonds. Hydrosilylation of terminal alkenes or alkynes is the most straightforward derivatization, producing 1-alkanesilanes in an efficient way, which were widely used for organic synthesis [2,3]. Generally, hydrosilylation of alkenes is catalyzed by various transition metal complexes, most of which are homogeneous platinum species such as Speier's catalyst (H_2PtCl_6 in isopropanol) and Karstedt's catalyst [4,5]. Early studies on Pt-based catalysts supported on both inorganic and on polymer supports were reviewed[6-10]. Recently, these catalysts were modified to obtain novel highly active catalysts and some excellent results were reported by Lin [11], Li [12] and Bai [13]. Most of these catalysts are silica based, primarily because silica displays many advantageous properties, e.g. excellent stability (chemical and thermal), high surface area, good accessibility and high robustness to anchor organic groups which provide catalytic centers [14]. Since the addition of homogeneous metal containing catalysts mostly reacts in a solvent system, they are often difficult to recover, which has a big impact on the process sustainability, especially when scarce transition metals are involved. Efficient re-utilization and high regioselectivity are key parameters for the catalyst to be successfully applied. Therefore, solvent-free heterogeneous reaction systems for hydrosilylation have recently been reported [15]. The regioselectivity largely depends on the pore size distribution where the active centers are present. Super-microporous materials bridge the gap existing between conventional microporous materials (< 2 nm) and mesoporous materials (2-50 nm). Since many organic compounds have molecular sizes of 1–2 nm which surpass the limit of various microporous materials (e.g. zeolites), super-microporous materials have important impacts on pore size- and pore shape-specific applications related to these bulky molecules, such as adsorption and catalysis [16-20].

In the present study, we report the synthesis of a super-microporous silica-supported Pt catalyst by a simple one-pot procedure using defined micelle-template mixtures (water/acetonitrile/*n*-dodecylamine) and its application in the regioselective hydrosilylation of terminal alkenes or alkynes with dichloromethylsilane under microwave activation.

2. EXPERIMENTAL

2.1. Reagents

Hexachloroplatinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$), dichloromethylsilane (DCMS), acetonitrile, *n*-octane, styrene, ethyne, octyne, phenylacetylene and *n*-dodecylamine were obtained from Sigma Aldrich. Triphenylphosphine ($P(C_6H_5)_3$), tetraethoxysilane ($Si(OC_2H_5)_4$) and mercaptopropyltrimethoxysilane ($Si(OMe)_3(C_3H_7S)$) were obtained from Lancaster. Other chemicals were purchased from local commercial suppliers. All chemicals were analytical grades and used without further purification.

2.2 Characterization methods

The Pt content in the catalyst was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Perkin-Elmer P40 instrument. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was carried out on a Bruker Equinox 55 instrument. Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2010 instrument. The porosity and surface area were determined by the Brunauer-Emmett-Teller method and the pore size distribution was analyzed using Barrett-Joyner-Halenda (desorption branch) method or the Horvath-Kawazoe method. Before sorption measurements, the samples were degassed at 120 °C for 7h. Powder X-ray diffraction (XRD) patterns were acquired using a Siemens D5000 diffractometer with Cu-Kαirradiationat 40 kV and 20 mA. Solid UV spectra were analyzed using a Shimadzu UV-240 spectrophotometer using MgO as the reference sample in the 200-900 nm wavelength range.The product yields and conversions of various substrates were determined by ^{1}HNMR spectroscopy on a Bruker EX-Delta 270 instrument, and were also confirmed by gas chromatography-mass spectrometry (GC-MS) on a Agilent 6890N instrument, equipped with a HP-5MS capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness; Agilent). An auto-injector (Agilent 7683) was employed to inject the samples at 250 °C and was set to a 10:1 split ratio. Helium was used as carrier gas with flow rate of 1 mL min^{-1}. The temperature program was set as follows: the oven initially started at 50 °C, held for 2 min, raised to 280 °C at a rate of 15 °C min^{-1} and held for 10 min at 280 °C. The ionisation mode was EI (70 eV, 300 μA) and the ion source of the mass spectrometer was set at 230 °C.

The peaks were analyzed on the basis of retentiom time and using the NIST database (2005) and retention index. The structure and morphology of the catalyst samples were examined by scanning electron microscopy (SEM, SU8020). A mixture of the sample and ethanol after ultrasonic dispersion was dropped on a metallic disk and dried at room temperature. Then, a thin layer of gold was sprayed on the dried surface.

2.3 Catalyst preparation

The microporous silica was synthesized as described previously by our group in the literature [21]. Briefly, a suspension was prepared from *n*-dodecylamine, distilled water, acetonitrile, with $Si(OC_2H_5)_4$ and $Si(OMe)_3(C_3H_7S)$as the silica-hydride donors and then stirred for 18 h at 60 °C. Hereafter, the mixture was cooled, filtered and extracted with absolute ethanol to remove the template. Finally, the solid was air-dried at 80 °C. The silica-supported Pt catalyst was prepared by dissolving 5.08 g *n*-dodecylamine in 53 mL distilled water, followed by addition of 46 mL aqueous acetonitrile, which were placed in a 250 mL three-necked flask equipped with a mechanical stirrer and a dropping funnel. Then the solution was stirred vigorously for 30 min. at 40°C. Finally, 0.70 g $P(C_6H_5)_3$, 0.0905 g $H_2PtCl_6 \cdot xH_2O$, 18.8 g $Si(OC_2H_5)_4$ and 0.98 g $Si(OMe)_3(C_3H_7S)$ were slowly added to the mixture (slightly exotherm process). The yellow suspension was stirred for 18 h at 60 °C, followed by filtration and washing with water until neutral pH in the wash filtrate. The solid particles were obtained by drying overnight in air at 80°C. Then the particles were extracted with absolute ethanol in a Soxhlet apparatus for 16 h to remove the organic template, followed by oven-drying. The obtained white solid particles were denominated as silica-supported Pt catalyst.

2.4 Hydrosilylation reaction of terminal alkenes withdichloromethylsilane

Hydrosilylation reactions were carried out in a microwave reactor using 20.50 g DCMS mixed with a certain amount of alkene and 0.3 g silica-supported Pt catalyst. The reaction was carried out at 40-70 °C using a computer controlled CEM-Discover focused microwave synthesis device operating at 200 W. The product was separated by centrifugation (2200 rpm, 15 min., 25 °C) and further characterized by ^{1}H-NMR and GC-MS.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The Pt content of the silica-supported Pt catalyst as determined by ICP-MS was 0.7 wt%. The porosity of the supported catalyst was characterized by nitrogen adsorption analysis (see **Table S1** and **Fig. S1** in the Supporting Information). Nitrogen adsorption-desorption isotherms were classified as reversible Type I or Langmuir isotherm, typical for microporous materials [22]. The Pt supported catalyst had lower specific surface (970 m^2 g^{-1}) than pure super-microporous silica (1140 m^2 g^{-1}) due to the deposition of a metallic layer. The fitted pore distributions showed pore diameters below 2 nm and pore volumes between 0.7 and 0.9 $cm^3 \cdot g^{-1}$, with the silica-supported Pt catalyst exhibiting slightly lower sizes. The Pt/MCM-41 catalyst showed larger pore diameters (3.1 nm) and lower pore volume (0.6 cm^3 g^{-1}). Microporous materials with pores ranging between 0.7 and 2.0 nm are classified as super-microporous [23,24], a similar feature found in this study. The isotherms showed no hysteresis neither pore collapsing events, suggesting that the architecture of the individual pores was uniform, without significant blocking phenomena [25] and with stable pore integrity, even in the case of the supported catalyst which showed smaller pore sizes. Compared to previously prepared materials using a template system, the pore sizes of the present home-made super-microporous silica were smaller, probably due to the stronger interaction of triphenylphosphine in the synthesis mixture with the surfactant head groups.

Powder X-ray diffractions of the pure silica and the silica-supported catalyst are shown in **Fig. S2**. In the low angle range, exist only one strong diffraction peak existed, which was the typical characteristic of HMS silicate (mesoporous silicate prepared in the presence of a long-chain alkyl amine surfactant having pore diameters in the 2-5 nm range [26,27,28]). Moreover, the intensity of this peak was relatively weaker in the silica supported with Pt, which resulted in a decreasing order of degree of the silica nano-channels. The lattice parameters of the pure silica and the silica-supported Pt catalyst are 3.75 and 3.40 nm, and pore wall thickness of 2.42 and 2.23 nm, respectively. These wall thicknesses are significant higher compared to mesoporous silica (0.5-1.5 nm) [29], which support its stable pore integrity. In the high-angle range, four diffraction peaks existed for 2θ at 39.8°, 46.1°, 67.4° and 81.4°

corresponding to the (111), (200), (220) and (311) crystal planes, respectively. **Fig. S3** shows the corresponding IR and UV-Vis absoprtion spectra of these solid samples. In the spectrum of the silica-supported Pt catalyst an absorption was noticed at 260 nm due to bonding interaction between the Pt d-orbitals and the electron from 2p-orbitals of oxygen atoms. The IR absorption band at 960 cm^{-1} is associated with the conformational change of the Si-O tetrahedron frame due to the incorporation of Pt particles, consistent with previously reports [24,30,31]. It is also similar to the spectrum of super-microporous silica-pillared layered niobic acid [32,33]. The strong absorption at 1086 cm^{-1} originates from the transversal asymmetric stretching vibration of Si–O–Si linkages. **Fig. S4** shows the SEM micrographs of the pure silica and silica-supported Pt catalyst. The morphology of pure silica was regular and globular [22], while the silica-supported Pt catalyst displayed a much smoother surface (granular structure more difficult to be appreciable), which suggests that Pt particles were deposited uniformely on the super-microporous silica.

3.2 Catalytic performances and regioselectivity

Two reaction pathways in the hydrosilylation of terminal olefins exist: α-addition and β-addition (**Scheme 1**) [30]. The microwave-induced hydrosilylation reactions were performed using octene as the substrate (**Table 1**). Surprisingly, the super-microporous silica-supported Pt catalyst (entry 1) exhibited both better catalytic activity and more importantly, better regioselectivity than the Speier´s catalyst (entry 2) and the ´in-house´ prepared Pt/MCM-41 catalyst (entry 3). This might be related to the supermicroporous nature of the catalyst, having lower pore sizes. Still, good access to the super-microporous silica pores was observed based on the high DCMS conversion after already 2 h. More interestingly, the super-microporous structure seems to play an important role in the control of the selectivity to the β-adduct.

((Scheme 1))

((Table 1))

3.3 Optimization of reaction conditions

The catalyst activity was further analyzed at different temperatures using the hydrosilylation of DCMS with octene as a model reaction (**Fig. 2**). The reaction temperature was critical for the conversion of DCMS. The conversion reached to its maximal (98 %) when the reaction was carried out at 60 °C. When the temperature increased to 70 ^{o}C, however, the conversion decreased to 92 %. As we observed that the catalyst showed high activity at higher temperatures (120 °C), the drop in conversion was probably related to DCMS volatilization loss in the reflux system (boiling point DCMS 70 °C). The effect of the reaction time on the DCMS conversion up to 70 °C is shown in **Fig. 3**. The conversion increased substantially with reaction until levelling off after 3 h.

((Figure 2))

((Figure 3))

The effect of the molar ratio of the reactants on the DCMS conversation was also studied (**Fig. 3**). The difference in conversion with increasing molar ratio of DCMS over octene was most noticeable after 2 h, especially when increasing to 1:1 molar ratio (90 % conversion). After 3 h, 97 % conversion was achieved. The differences with ratios higher than 1:1 were minimal (98 and 97 % conversion for 1.1:1 and 1.2:1, respectively). Overall, the optimum reaction conditions were set at 60 °C, 3 h and DCMS:octene molar ratio of 1.1:1, using 0.3 g silica-supported Pt catalyst (2 mg Pt).

((Figure 3))

3.4 Catalyst recyclability and versatility

Even when using cheaper Fe-based homogenous catalysts for selective hydrosylilation [34], the bis(imino)pyridine ligands do raise the catalyst cost considerably. When using a heterogeneous Pt catalyst for this conversion, it is important to evaluate the recyclability of the supported catalyst. Therefore, a serie of 7 consecutive hydrosilylation reactions were carried out under optimum reaction conditions with 200 W microwave power (**Fig. 4)**. The supported Pt catalyst showed outstanding recyclability for the hydrosilylation of DCMS. The catalyst could be easily separated from the reaction medium after filtration and washing with acetone and ethanol.

To explore the versatility of this catalyst, microwave assisted hydrosilylation reactions were carried out under the aforementioned optimal conditions using various terminal alkenes or alkynes (**Table 2**). Promising results were obtained, as styrene, phenylacetylene and other terminal alkynes were efficiently converted by the silica-supported Pt catalyst, with selectivities to the β-adduct over 97 %.

((Figure 4))

((Table 2))

4. CONCLUSIONS

The super-microporous silica-supported platinum catalyst prepared by using *n*-dodecylamine as a surfactant template was applied for the hydrosilylation of octene with dichloromethylsilane. Platinum particles were successfully supported on diatomite silica forming Si-Pt bonds as characterized by a decrease of surface area and pore volume of the super-microporous silica. The conversion of dichloromethylsilane reached 98 % under optimal reaction conditions (60°C, 3 h and DCMS:octene molar ratio of 1.1:1). This silica-supported catalyst shows better catalytic activity and higher regioselectivity (over 97 % to the β-adduct) for the hydrosylilation of octene as compared to other platinum based catalysts. The catalyst could be recycled and re-used seven times without significant activity loss.

ACKNOWLEDGEMENTS

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Table 1. DCMS conversion and selectivity to α- and β-adduct for hydrosilylation of octane using different Pt catalysts.

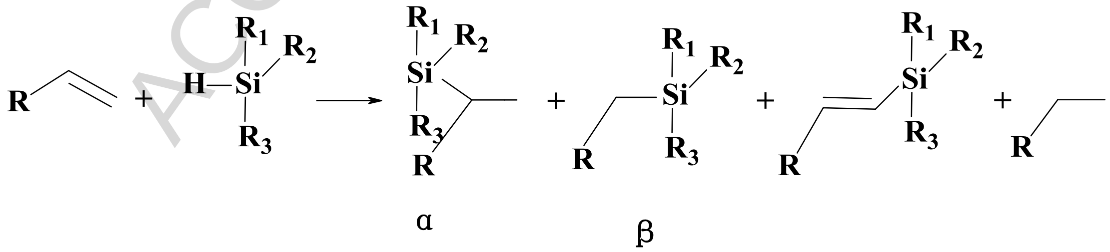
Entry	Catalyst	Selectivity (%)		DCMS conversion (%)
		α-adduct	β-adduct	
1	Super-microporous Pt *	1	99	97
2	Speier´s catalyst	30	70	83
3	Pt/MCM-41	37	63	72

[*] 0.3 g catalyst (2.03 mg Pt), 60 °C, 2 h, DCMS:octane molar ratio 1:1.

Table 2. Effect of the substrate on the conversion of DCMS and selectivity to the β-product.

substrate	DCMS conversion (%)	Selectivity toβ-adduct (%)	TON
octene*	98	99	48.1
styrene	98	98	44.9
ethyne	97	99	45.6
octyne	99	97	45.2
phenylacetylene	98	99	46.5

* 0.3 g catalyst (2.03 mg Pt), 60 °C, 3 h, DCMS:olefin mola ratio 1.1:1.



Scheme 1. Hydrosilylation pathways of alkenes to α- and β-adducts.

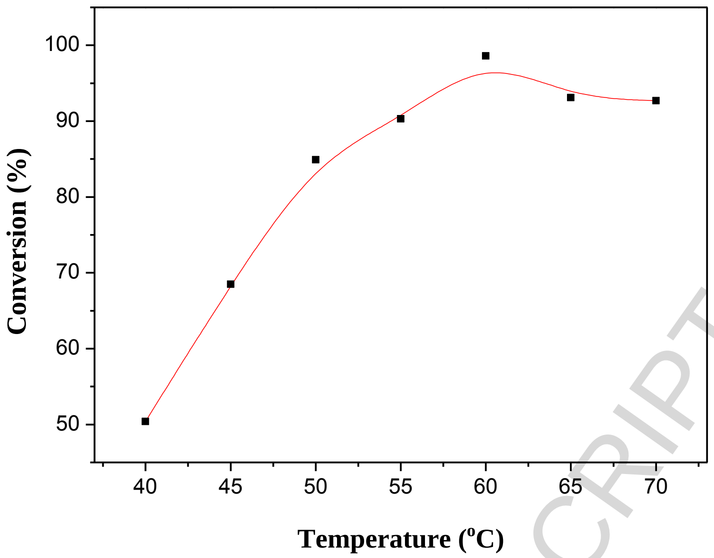


Figure 1. Effect of reaction temperature on the DCMS conversion after 3 h with 0.3 g silica-supported Pt catalyst.

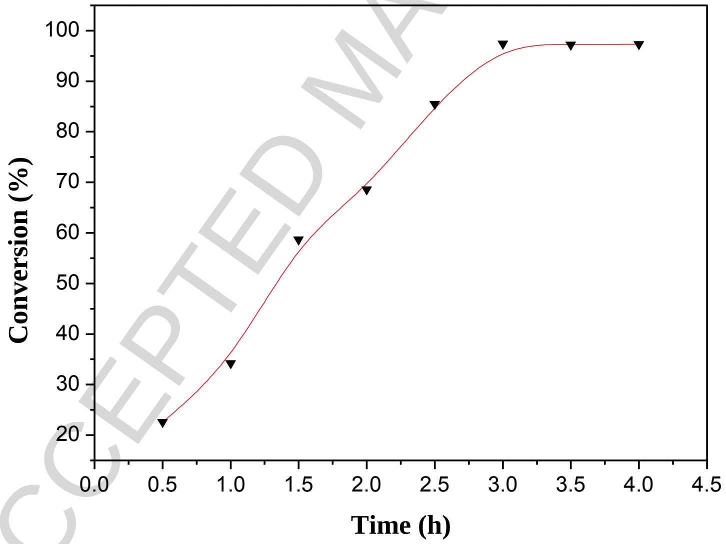


Figure 2. Effect of the reaction time on the DCMS conversion using 0.3 g silica-supported Pt catalyst at 60°C.

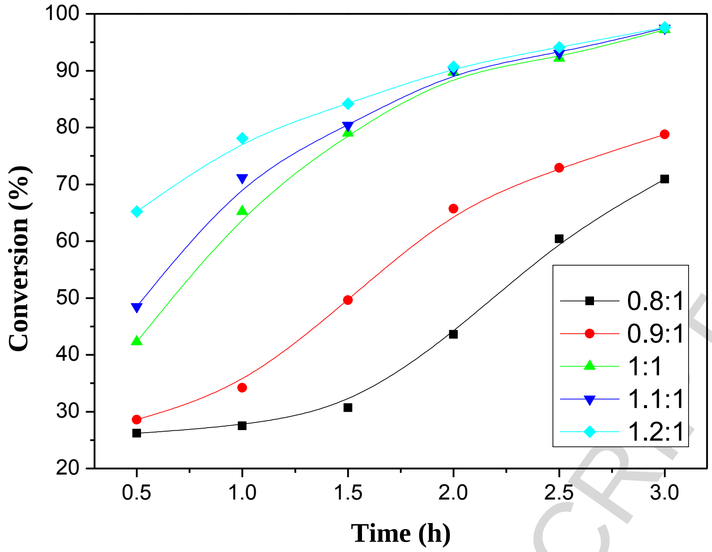


Figure 3. Effect of the molar ratio of the reactants on DCMS conversion using 0.3 g silica-supported Pt catalyst at 60°C.

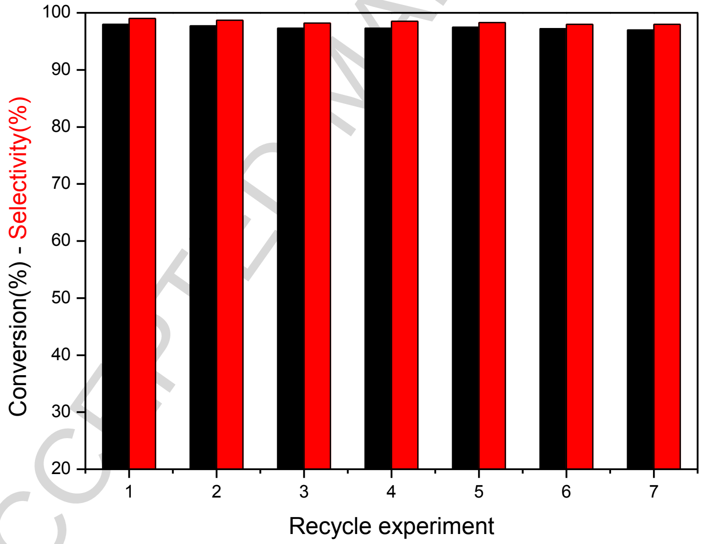
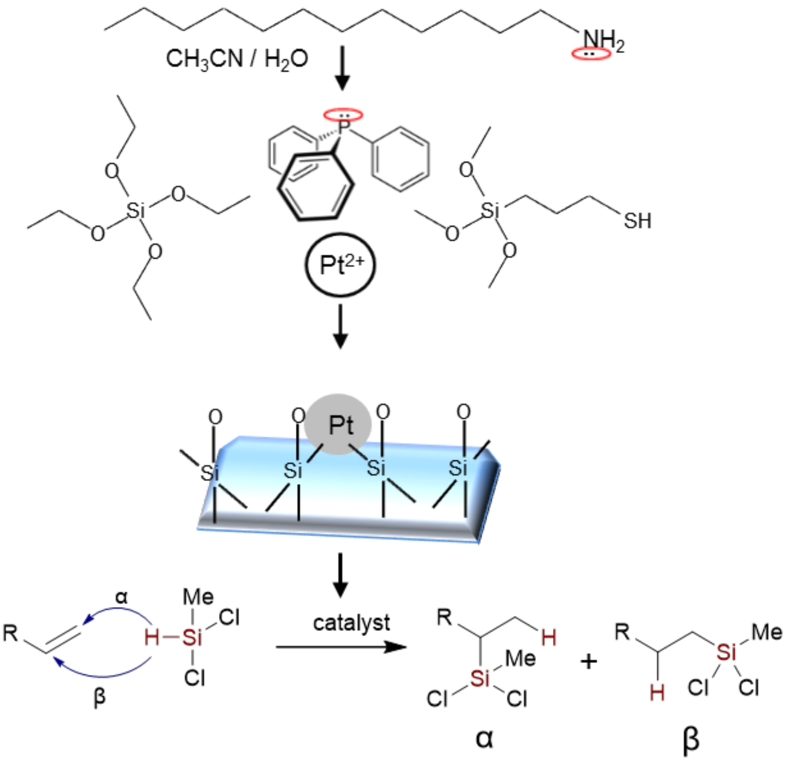


Figure 5. Catalyst recycle experiments for the hydrosilylation of octene with DCMS.



Graphical abstract

HIGHLIGHTS

- One-pot synthesis of Pt-containing microporous silica Materials
- Catalysts highly active in hydrosilylation reactions under microwave irradiation
- Selectivity of beta-adduct in hydrosilylation reaching 99%
- Catalyst highly stable and reusable under the investigated conditions