

Platinum-Based Heterogeneously Catalyzed Hydrosilylation

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Efficient and recyclable solid catalysts for the hydrosilylation of olefins are highly desirable, both to reduce the economic and environmental costs of traditional homogeneous processes and to improve the health properties of products that find a number of uses in daily life. In this account we criti-

cally review selected examples amongst the numerous platinum-based materials developed in the last decade, with the goal of identifying important challenges in this relevant domain of synthetic organic chemistry.

Introduction

Hydrosilylation (or hydrosilation) is a reaction widely used in the chemical industry for the preparation of organosilicon compounds that are the building blocks of silic-

ones^[1] and of sol-gel silicates;^[2] that is, of organic and organic-inorganic Si polymers of enormous industrial relevance. Vinylsilanes obtained by the hydrosilylation of alkynes are, furthermore, versatile, nontoxic, and stable organometallic reagents for transition-metal-catalyzed cross-coupling with vinyl and aryl halides, replacing toxic or expensive organotin, organoboron, and organozinc counterparts.^[3]

The high-temperature direct process for preparing Si-C bonds – the copper-catalyzed reaction of alkyl halides with elemental silicon at 300 °C and under 2–5 bar – is currently

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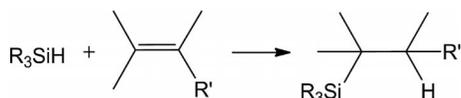


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only employed on a very large scale to synthesize dimethyl-dichlorosilane from silicon and methyl chloride.^[4] Hydrosilylation, in contrast, is a mild general method for the preparation of Si–C bonds. It generally consists of the addition of Si–H bonds to unsaturated bonds of alkenes or alkynes, promoted by a homogeneous or heterogeneous platinum group metal catalyst (Scheme 1).^[5]

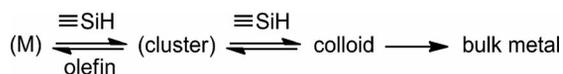


Scheme 1. Hydrosilylation (or hydrosilation) is the addition of an H–Si bond across a double bond.

In 1957 Speier reported^[6] that chloroplatinic acid (H_2PtCl_6) is a selective and efficient alkene hydrosilylation catalyst, even at room temperature and with readily available chlorosilanes, affording high yields of hydrosilylated products in short reaction time and with negligible side products.

Under ideal conditions, an ultralow amount of 10 ppm of catalyst per mol hydrosilane is sufficient for complete reaction. Platinum-based hydrosilylation hence almost immediately became one of the most important reactions for preparing organosilicon materials both in industry and in academia. The manufacture of silicone breast implants, for example, uses platinum catalysis to accelerate the transformation of silicone oil into silicone gel (catalytic crosslinking of polysiloxanes) for making the elastomer silicone shells, and also for making other medical silicone devices. Chloroplatinic acid, however, is a potent sensitizer and carcinogenic compound posing serious health hazards.^[7] Moreover, its use as hydrosilylation catalyst involves a variable induction period, due to the necessity for reduction of platinum in oxidation state IV into catalytically active Pt^0 .

During the reaction, platinum colloids are formed with accompanying color changes (yellow \rightarrow brown \rightarrow black). This is a relevant issue in the silicone industry, in which colorless products are desired. It is generally agreed that the reaction mechanism involves colloidal Pt^0 as the active catalyst precursor, whereas catalyst deactivation occurs with formation of catalytically inactive large colloidal particles (Scheme 2).^[8]



Scheme 2. Catalyst deactivation through formation of colloidal particles (adapted from ref.^[16] with kind permission).

In 1973 Karstedt reported that the platinum(0) and divinyltetramethyldisiloxane complex $[\text{Pt}_n(\text{H}_2\text{C}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)_m]$ (Figure 1) was active without an induction period. Today this compound, which is soluble in silicone oil, is the main catalyst employed by industry for the homogeneously catalyzed synthesis of organosilicon compounds.^[5]

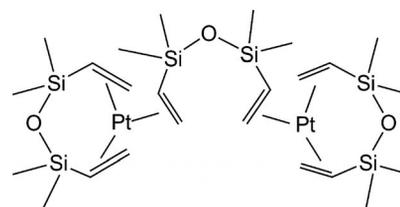


Figure 1. Structure of Karstedt's catalyst. Pt is in the Pt^0 oxidation state.

The homogeneous Speier and Karstedt catalysts, being highly active and showing good solubility in the silicone products, are both still widely employed in industry. However, separation and recycling of the homogeneous catalysts from solution after the reaction is generally not possible because light-scattering platinum colloids are formed at the end of the reaction;^[9] in the case of silicone synthesis these can render the silicone yellow.

As a result, these catalysts can be used only once, and the expensive platinum species cannot be recovered and recycled. On the other hand, the presence of platinum in the reaction products, even in trace quantities, is unacceptable for many applications. Trace quantities of platinum leaking from a silicone breast implant, for example, might contaminate the surrounding pectoral tissues^[10] with leached metal species including platinum in dangerous oxidized states.^[11]

Research into the topic continues, with recent advances having included homogeneous catalysis by “self-dosing” PtO_2 (releasing the soluble active species)^[12] or biphasic hydrosilylation with $\text{Pt}(\text{PPh}_3)_4$ in ionic liquids.^[13]

Another approach, more desirable from a practical viewpoint, involves heterogeneous catalysis. Attempts to heterogenize platinum nanoparticles or platinum complexes supported on polymers or inorganic materials – on silica, for example – go back to the early 1970s.^[14] Conventional heterogeneous catalysts such as $\text{Pt}/\text{Al}_2\text{O}_3$ or Pt/C , however, are not effective because their typical large agglomerates of metal particles show much lower levels of catalytic activity than homogeneous catalysts.

In the last decade, therefore, great research efforts have been devoted to identifying efficient and recyclable solid catalysts, because industry was (and remains) highly interested in such efficient solid hydrosilylation catalysts.^[15] In 2009 Marciniak concluded, in a comprehensive survey of the hydrosilylation of alkenes and their derivatives, that immobilized hydrosilylation catalysts offer many convenient synthetic routes to molecular organosilicon reagents.^[16]

Today, a variety of alternative metal catalysts – including representatives based on Rh ^[17] and Ru ^[18] – mediate the hydrosilylation of alkenes and alkynes. Hydrosilylation of a large variety of unsaturated compounds over Au nanoparticles (NPs), for example, will likely emerge as one of the first practical uses of gold nanocatalysis, thanks to the high chemo- and regioselectivities shown by Au NPs.^[19] This review, however, focuses on Pt-based catalysts, the selectivity and tolerance of which towards a wide range of functionalities makes catalytic hydrosilylation the most important application of platinum in catalysis.^[20]

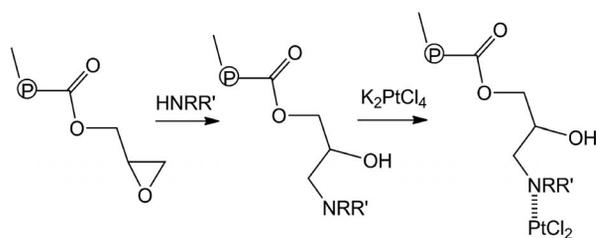
The first survey of catalysts for hydrosilylation in heterogeneous systems was published in 2006,^[21] followed in 2011 by a review in Chinese of the numerous methods for preparation of heterogeneous catalysts for hydrosilylation developed in the last decade.^[22] Going through these recent review articles, one may notice how a number of new supported platinum catalysts for hydrosilylation of olefins and alkynes have been identified. Some of them are truly heterogeneous; others act as reservoirs of the valuable metal, which is leached into solution during the reaction.

Few solid catalysts have been found to be recyclable, and most of them have been found to give rise to metal particle sintering. The heterogeneous platinum-catalyzed hydrosilylation of alkynes, for example, in the presence of Pt/C,^[23] silica-entrapped Pt,^[24] or unsupported platinum oxide,^[25] generally affords good yields and selectivities, but the catalysts cannot be reused. A selection of methods and materials are therefore critically reviewed below, to show how researchers are tackling the stability and selectivity issues, with the goal of developing catalytic materials suitable for practical application.

Supported Pt Complexes

In 2000 Sherrington, in cooperation with co-workers from industry, reported that Pt²⁺ species coordinated to the surface functionalities of aminated polystyrene and polymethacrylate resins display higher conversion, improved selectivity, and good recyclability relative to Speier's catalyst in the room temperature hydrosilylation of oct-1-ene with trichlorosilane in the absence of solvent.^[26] In detail, resins based on vinylbenzyl chloride (VBC) were prepared with use of a high level of divinylbenzene (DVB) with toluene as a porogen to produce high surface areas (>600 m² g⁻¹) in the resins. These were subsequently aminated with *N,N,N'*-trimethylethylenediamine, and Pt was loaded onto each.

Shortly afterwards, the same authors identified a supported ligand derived from ethylene diamine as providing the most active and stable Pt catalyst (Scheme 3). They ascribed the enhanced activity of styrene-based resins, relative to methacrylate-based ones, to the more hydrophobic nature of the former^[27] and concluded that these materials have good prospects for exploitation as recyclable laboratory-scale alkene hydrosilylation catalysts. However, no quantitative evaluation of residual Pt loading on extensively

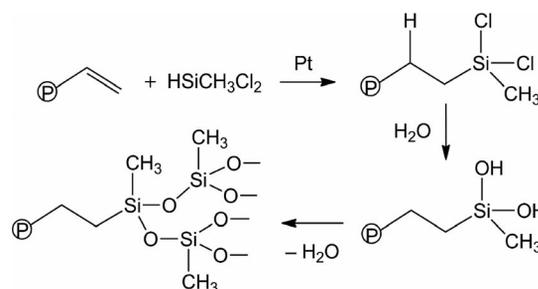


Scheme 3. Typical synthesis of functionalized catalysts based on GMA (glycidyl methacrylate) resin (adapted from ref.,^[27] with kind permission).

recycled resins was possible because it proved experimentally to be very difficult to purify and extract supernatant solutions.

In 2004, the same team reported the results of extensive recycling and Pt leaching studies directed towards identifying the most active, selective, and stable catalyst for the hydrosilylation of oct-1-ene with methylchlorosilane at room temperature.^[28] Remarkably, they found that hydrosilylation is catalyzed by immobilized Pt complexes, whereas concurrent alkene isomerization is due to leached soluble Pt species.

Analysis of spent resin catalyst from multiple recycling experiments showed fouling of the catalyst by chemically bonded oligosiloxanes arising from hydrosilylation of pendent unreacted vinyl groups in the resin followed by hydrolysis and condensation of resin-bound chlorosilane groups when exposed to atmospheric moisture. Hydrolysis is followed by condensation and the fouling of the resin with oligosiloxanes (Scheme 4).



Scheme 4. Hydrosilylation of pendent vinyl groups on resins and hydrolysis/condensation to form grafted oligosiloxanes (adapted from ref.,^[28] with kind permission).

Another Pt complex catalyst heterogenized over silica was described in 2002 by Okamoto and co-workers.^[29] The obtained catalyst was based on supporting tetraammineplatinum(II) chloride dissolved in polyethylene glycol (PEG) in the porosity of silica gel. The resulting material was active and markedly stable in the hydrosilylation of acetylene with trichlorosilane or trimethoxysilane in a vapor-phase flow reactor, as well as in hydrosilylation of ethylene and propylene with trichlorosilane only. The optimal metal content was 0.5 wt.-%, whereas when the amount (volume) of PEG was 40 vol.-% of the pore volume of silica gel, PEG was coated on the pore walls of the silica gel without blocking the pores. The use of PEG with an average molecular weight of 1000 g mol⁻¹ minimized the loss of PEG through evaporation under the relatively harsh reaction conditions (150 °C).

Subsequently, the same authors reported that, as well as Pt(NH₃)₄Cl₂-PEG/SiO₂, K₂PtCl₆-PEG/SiO₂ also shows high and stable activity,^[30] and double hydrosilylation proceeding to form bis(trichlorosilyl)ethane was also observed.

A thorough EXAFS analysis of the material (Figure 2) showed the active species to be a platinum complex with six coordinating chloride ions, originating from trichlorosilane, as the coordination number of the chloride ion increases with time on stream.

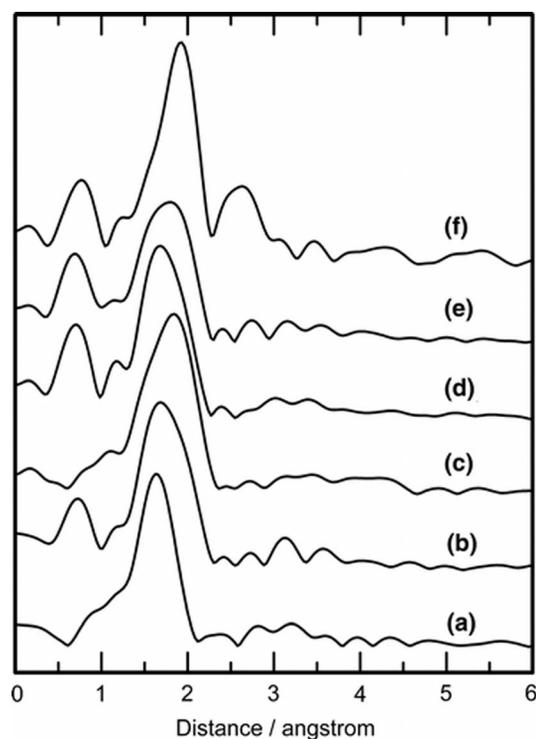


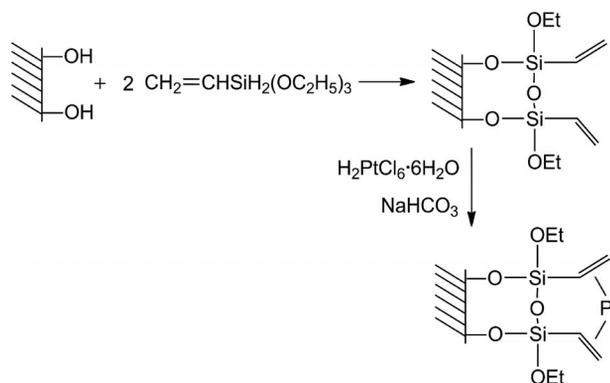
Figure 2. Pt LIII-edge EXAFS Fourier transforms of tetraammineplatinum(II) chloride dissolved in a PEG supported on silica gel. Curves from (a) through (f) are after prolonged material treatment first with HSiCl_3 and then with C_2H_2 (reproduced from ref.^[30] with kind permission).

In these hexacoordinate platinum complexes, the chlorine ligands can readily be eliminated and unsaturated reactants such as acetylene can coordinate to platinum to form active intermediates for hydrosilylation. Both trichlorosilane and acetylene, however, are indispensable for the formation of such active species. Indeed, hydrosilylation of alkenes (ethylene and propylene) with trimethoxysilane mediated by $\text{Pt}(\text{NH}_3)_4\text{Cl}_2\text{-PEG/SiO}_2$ affords only modest yields of hydrosilylated products.

In 2003, a silica-supported Karstedt-type (Pt) catalyst showing good catalytic activity at room temperature under atmospheric pressure was reported.^[31] Vinylsiloxane groups are bound to the silica surface by derivatization of the Si-OH groups with vinyltriethoxysilane. Further treatment of this material with an aqueous solution of chloroplatinic acid leads to formation of the heterogeneous Karstedt-like catalyst (Scheme 5).

Screening of the catalyst activity with various olefins condensed with Me_2PhSiH showed yields of up to 90% with styrene, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, and vinyl dimethylphenylsilane (90%, 87%, and 83% conversion, respectively, after 70 min at 20 °C).

A maximum of 70% conversion was reached in the hydrosilylation of allyl epoxypropyl ether, whereas the maximum 49% conversion obtained in the hydrosilylation of methyl methacrylate with Me_2PhSiH required 85 min at 70 °C (Figure 3). When employed in the hydrosilylation of styrene with dimethylphenylsilane at 20 °C, the catalyst was



Scheme 5. Preparation of the heterogeneous Karstedt-like silica catalyst (adapted from ref.^[31] with kind permission).

reported to be reusable for five consecutive times, although no analysis of leached Pt or of the catalyst prior to and after the reaction was included.

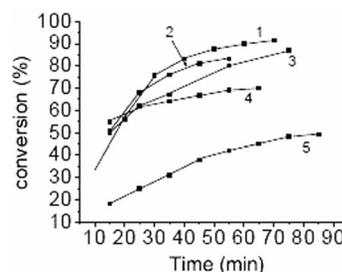


Figure 3. The results for hydrosilylation of various olefins with Me_2PhSiH : 1) styrene, 2) vinyl dimethylphenylsilane, 3) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 4) allyl epoxypropyl ether, 5) MMA. Reaction temperature for methyl methacrylate is 70 °C; others are 20 °C (reproduced from ref.^[31] with kind permission).

When analysis of leaching is reported, one often finds that supported metal complexes suffer from poor chemical stability. Figure 4, for example, shows results for the hydrosilylation of hex-1-ene with dimethylphenylsilane mediated by a hybrid GOA/Pt catalyst during the fourth, sixth, and eighth use.

The hybrid catalyst is obtained by grafting onto silica vinyl-functionalized linear polysiloxane {poly[vinylmethylsiloxane-co-(grad)-dimethylsiloxane]} and by further immobilizing the complex $\text{Pt}(\text{PPh}_3)_4$ on the grafted material (Scheme 6).^[32]

The decrease in the initial reaction rates after each catalytic cycle due to metal leaching from the support is self-evident. Indeed, chemical analysis of the eight-times-recycled catalyst showed a 50% loss of Pt loading.

Examples of supported Pt complexes far outnumber those reviewed above. The reader is referred to the mentioned reviews^[16,21,22] for comprehensive surveys of methods and materials. In general, however, the practical application of supported platinum complexes for large-scale manufacture of organosilicon compounds is hampered by limited stability, high cost of the ligands, and the multi-step synthetic procedures needed to afford the functionalized materials.

The yields were generally unsatisfactory in comparison with homogeneous catalysis, and selectivity was poor, with similar product distributions with either catalyst. The catalyst obtained in the basic medium lost its catalytic activity after each reaction, so further activation was needed, pointing to formation of active small colloidal particles and consequent loss of catalyst in each reaction step.

Minimizing platinum leaching and aggregation is crucial to maintaining catalytic activity and avoiding the formation of colored materials during reaction. In this sense, a remarkable previous finding based on silica functionalized with Pt⁰ had been reported by Brook and co-workers in 1997.^[37]

The team modified colloidal silica particles with triethoxysilane [HSi(OEt)₃] and further treated the resulting modified Stöber particles with Karstedt's catalyst (Figure 5).

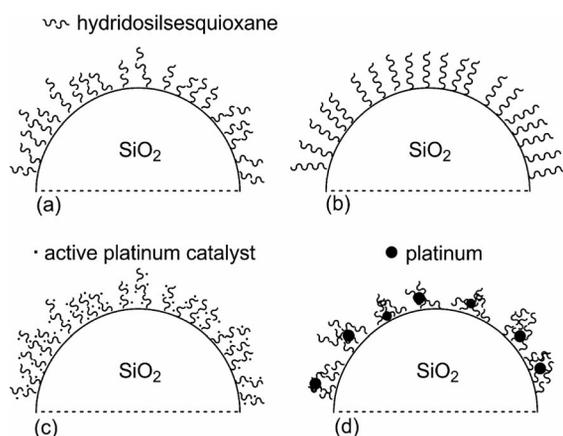


Figure 5. A schematic of the hydrosilsesquioxane: (a) on the surface in a good solvent, (b) after addition of a better solvent, or at high pH, (c) after addition of Karstedt's catalyst to (a) to give a supported active catalyst, and (d) after drying of (c) to give clusters of Pt of 2 nm in diameter (adapted from ref.^[37] with kind permission).

A mobile hydrosilsesquioxane layer 13 nm thick and consisting of a collection of highly mobile chains forms on the surfaces of the silica particles, preventing aggregation of platinum into active colloidal species, so the hydrosilylation of different silanes with phenylacetylene or with allylbenzene could be performed heterogeneously for at least three consecutive cycles. If the yellow catalytic particles were dried, the color changed from yellow to grey, a clear sign of nanoparticle aggregation, with complete loss of their catalytic activity.

Brook subsequently also developed a polydimethylsiloxane-supported (PDMS-supported) Pt catalyst^[38] that exhibited good catalytic activity for hydrosilylation of vinylsilanes without undergoing decomplexation to form colloidal metal particles, but was soluble and stable both in organic solvents and in polysiloxanes.

This approach, however, was not further explored until 2012, when Zhang and co-workers reported a similar methodology, this time making use of a carboxyl-ended hyper-

branched polymer (HTD-2) functionalized with Pt⁰ nanoparticles.^[39]

In the solventless hydrosilylation of styrene with 1,1,3,3-tetramethyldisiloxane (TMDS) at 50 °C, the hyperbranched polymer/Pt⁰ catalysts obtained by varying the Pt content and the polymer/solvent mass ratio in each case showed markedly enhanced catalytic activity relative to the traditional homogeneous reaction mediated by Speier and Karstedt catalysts (Figure 6).

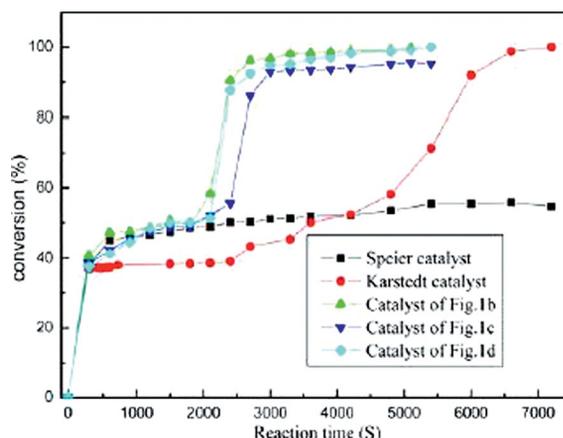


Figure 6. Levels of conversion and reaction times in hydrosilylation of styrene with 1,1,3,3-tetramethyldisiloxane at 100 °C mediated by Speier or Karstedt catalysts and by hyperbranched polymer/Pt⁰ catalysts (reproduced from ref.^[39] with kind permission; see the reference for explanation of the legend).

The authors ascribed such higher hydrosilylation activity to: *i*) the even dispersion of Pt⁰ nanoparticles or clusters in the snail-shaped polymer nanocavities forming after reduction with propan-2-ol the complex polymer/Pt⁺⁴, and *ii*) the action of molecular chains of the hyperbranched polymer HTD-2 on the surfaces of the snail-shaped micelles, inhibiting aggregation of the active Pt⁰ nanoparticles.

Towards Leach-Proof Catalysts of Broad Scope

Supported metal nanoparticles (MNPs), with their ability to catalyze a range of chemical reactions, are finding increasing application in synthetic organic chemistry.^[40] In general, the atomic structures of the exposed surfaces of the active “naked” nanoparticles are made up of plentiful unsaturated sites capable of adsorbing the reactants and catalyzing their conversion.^[41]

As Marciniec put it,^[16] supported MNPs often show catalytic activity in the hydrosilylation of olefins similar to that of metal colloids formed in situ by the reduction of metal salts. They do not, however, require expensive separation techniques for recovery, and might circumvent the known sinterization issue. Hence, for example, high-yielding and selective production of 3-glycidoxypropyltrialkoxysilanes from allyl glycidyl ether (the functionalized olefin) and trialkoxysilanes on Pt/C (Pt nanoparticles over microporous active carbon) was claimed by Evonik (Degussa–Huls) as early as in 2000,^[42] almost simultaneously with the hydro-

silylation of cyclopentene and cyclohexene mediated by platinum nanoparticles (0.5%) supported on porous Al_2O_3 claimed by Dow Corning.^[43]

In principle, heterogenization of MNPs should prevent the tendency of atoms of “naked” MNPs to aggregate into bulk materials as a result of their high surface energies, which gives rise to rapid decreases in their intrinsic catalytic activities and selectivities over time.^[44] Unfortunately, however, most heterogeneous catalysts reported in the literature act as reservoirs for MNPs that are leached into solution where they catalyze reactions, but also rapidly aggregate, resulting in spent catalysts of poor residual activity.

In brief, industry will replace traditional homogeneous processes if a newly proposed process based on solid catalysts is capable of:

1. *High activity*: to reduce reaction time and to increase throughput,
2. *High selectivity*: reducing costs for product purification and byproduct disposal, and
3. *Recyclability and recovery*: to allow multiple use of the catalyst and recovery of precious metal.

Traditional surface-modified organic resins and oxides, even if frequently found to be active and selective in the first reaction run, all too often fail to meet the stability requirement, due both to metal leaching and to deactivation.

Examples in the literature abound. As one example, a highly active 1%Pt/SDB catalyst (SDB is a crosslinked styrene–divinylbenzene copolymer) repeatedly employed in the hydrosilylation of alkenes with polyhydrosiloxanes to produce long-chain (> C8) silicone waxes showed pronounced catalytic activity only for three cycles, after which product yields dramatically decreased (Figure 7).^[45]

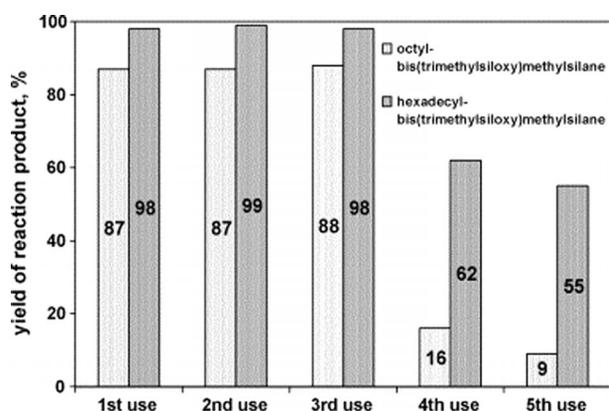


Figure 7. Repeated use of 1%Pt/SDB catalyst in hydrosilylation of oct-1-ene and hexadec-1-ene with heptamethyltrisiloxane (100 °C, 1 h; reproduced from ref.^[45] with kind permission).

New research efforts devoted to the development of sinter-proof catalysts in the last decade include, for example, the approach of Schüth and co-workers, who developed pre-prepared colloidal metal nanoparticles with tuned size, shape, and composition that are then “embedded” by porous support shells.^[46] Because sintering is caused by mo-

bility of the metal particles on the support surfaces, encapsulation of nanoparticles within the inner porosity of porous solids should minimize agglomeration and allow catalyst recyclability.

The validity of this approach was recently shown by a new halloysite-supported Pt catalyst obtained simply by wet impregnation from halloysite and chloroplatinic acid. The resulting material was successfully applied to the synthesis of a liquid allyl-ended hyperbranched organic silicone resin (AHSR) by hydrosilylation between phenyltriallylsilane (PTAS) and TMDS.^[47]

Halloysite is an economical double-layered aluminosilicate mineral with a predominantly hollow tubular structure and high surface area, showing good chemical and thermal stability. The nano-Pt–halloysite composite catalyst (c) in Figure 8 had a higher activity than the traditional Speier and Karstedt catalysts, and the degree of hydrosilylation could simply be controlled by the reaction time.

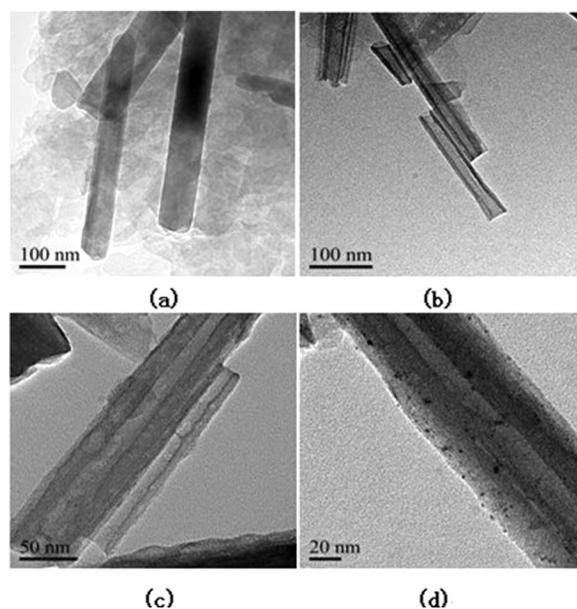


Figure 8. TEM micrographs of (a) crude halloysite, (b) purified halloysite, (c) Pt–halloysite composite, and (d) Pt–halloysite catalyst reduced by H_2 . The lengths and diameters of the regular nanotubes are 0.5–1.5 μm and 20–30 nm (reproduced from ref.^[47] with kind permission).

The high hydrosilylation activity of the Pt–halloysite catalyst was ascribed to good dispersion of the Pt^{4+} complex throughout the channels of the halloysite tubes, whereas the recyclability is due to the protective action of the oxide tubules surface against nanoparticle reaggregation.

The same catalyst and the AHSR resin were used to synthesize a hyperbranched epoxy resin with a silicone skeleton (HERSS) through hydrosilylation reaction between 1,1,3,3-tetramethyldisiloxane-propylglycidyl ether (TDPGE) and AHSR in THF at 65–70 °C.^[48] Again, not only was a hyperbranched silicone resin obtained in high yield (90%), but the catalyst and excess reactants and solvent were found to be recyclable, with the same sample of catalyst affording

98.4% conversion of the Si–H bond of TMDS in the seventh run. Considerably less solvent was needed than in the homogeneous process, suggesting future use of this heterogeneous syntheses on a large scale.

Most recently a new sol–gel entrapped Pt⁰ catalyst based on ultrasmall Pt nanoparticles (4–6 nm) encapsulated within a methyl-modified ORMOSIL porous matrix was reported to be a selective and recyclable hydrosilylation catalyst for different olefins under Ar at room temperature or at 65 °C, depending on the substrate.^[49] In these sol–gel entrapped catalysts, the porosity is due to the material's aggregated nature, which gives rise to interstitial porosity accessible to incoming substrate molecules.

Isolation of the nanosized active Pt⁰ particles within the inner porosity of a nanohybrid sol–gel ORMOSIL matrix results in an isolated metallic nanophase (Figure 9), ensuring two concomitant advantages.

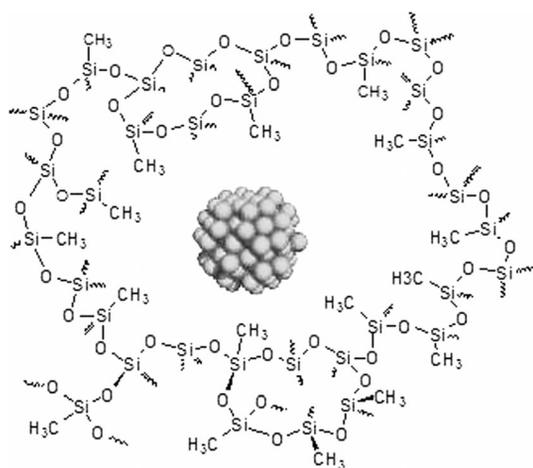


Figure 9. Schematic representation of a bare Pt nanoparticle entrapped in the methyl-modified cage of the SiliaCat Pt⁰ catalyst (adapted from ref.^[49] with kind permission).

On one hand, the strongly lipophilic nature of the ORMOSIL matrix dictates preferential access of the electron-rich double bond moiety to (and its adsorption on) the 2.9 nm ultrasmall Pt nanoparticles curved surface where hydrosilylation takes place, whereas interaction with other substituents of the alkene moiety (taking place on large metal particles and flat surfaces) is minimized. On the other hand, encapsulation of the nanoparticles within the sol–gel cages (Figure 9) ensures physical and chemical stabilization of the isolated Pt nanoensembles, and thus prolonged activity of the catalyst.

The results of Pt leaching tests in the crude reaction product showed very low levels of Pt (4–6 ppm), with higher leaching values found only for molecules bearing functional groups capable of coordinating the Pt nanoparticles. The catalyst was found to be reusable in three consecutive reaction runs with oct-1-ene as representative substrate.

It may also be noted how catalytic hydrosilylation over this ORMOSIL-entrapped catalyst closes a synthetic loop: namely, the catalyst is obtained by entrapment of Pt nano-

particles through sol–gel polycondensation of methyltriethoxysilane (MTES). This organosilane, and many others, can now be synthesized over the Pt⁰ organosilica catalyst obtained from MTES itself, expanding the use of unstable conventional Pt catalysts.

This approach complements that of Nagashima and co-workers in which polysiloxane gels doped with platinum species are prepared by treatment of polymethylhydrosiloxane with alkenes in the presence of Karstedt's catalyst, and these materials are used, for example, in truly heterogeneous hydrogenation.^[50]

Outlook and Conclusions

In relation to the well-known platinum homogeneous catalysts, examples of heterogeneous platinum-based catalysts actually used in large-scale hydrosilylation reactions are rare. This state of affairs, in neat contrast with the high cost and hazardous nature of homogeneous Pt catalysts, is due to the low activities and to the poor stabilities of the solid catalysts developed until recently, most of which suffer from significant leaching, sintering, or both.

Only in the last few years have efforts in nanochemistry resulted in the first examples of leach-proof and recyclable solid hydrosilylation catalysts, some of which are reviewed above. These materials not only transform traditional hydrosilylation into a method that is less expensive, greener, and safer, but open the route to more selective hydrosilylation processes affording organosilicon compounds and derived polymers free of platinum contaminants. Two main strategies, we argue, will in future be pursued to afford heterogeneously catalyzed processes suitable for practical application.

On one hand, alteration and improvement of the regioselectivity will be achieved by altering the chemical and textural properties of the cavities containing the metal nanoparticles to control the reactivities of encapsulated molecules, as elegantly shown with carbon nanotubes doped with PtRu nanoparticles employed in alkyne hydro-silylation.^[51]

On the other hand, solid nanocatalysts based on entrapped Pt nanoparticles will be used in continuous processes, which are known in the silicone industry to provide highly controllable reaction process and high product yields.^[52] Second-generation microreactors, capable of effectively handling solids,^[53] will be used for both small- and large-scale production of organosilicon compounds, avoiding purification steps with gains in yield, safety, and process simplification so significant as to justify the capital investment associated with the development of the new catalytic processes under flow.^[54] Almost six decades after the introduction of Speier's catalyst, the time is ripe to replace homogeneous hydrosilylation with high-yielding, high-throughput processes based on nanocatalysis. Hopefully, the arguments provided in this account will assist in the development of new catalysts and related processes to make this economically viable transition possible.

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