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# Platinum nanoparticles in suspension are as efficient as Karstedt's complex for alkene hydrosilylation<sup>†</sup>

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Colloidal suspensions of monodispersed platinum nanoparticles of 2 nm diameter have been used to catalyze the hydrosilylation of 1-octene with a polymethylhydrosiloxane. The nanoparticles were found to be as efficient as Karstedt's complex, showing that colloid formation from homogeneous species during hydrosilylation reactions is not necessarily a deactivation pathway. These results also reactivated the debate on whether Karstedt's complex was truly homogeneous or colloidal during catalysis.

Alkene hydrosilylation is a crucial reaction for the production of functional silanes and silicones, and for the crosslinking of silicones.<sup>1</sup> This reaction is most of the time catalysed by homogeneous platinum complexes, the most widely used in the industry being Speier's catalyst ( $\text{H}_2\text{PtCl}_6$  in isopropanol) and Karstedt's complex ( $\text{Pt}_2[(\text{Me}_2\text{SiCH}=\text{CH}_2)_2\text{O}]_3$ ). Given the very high and unstable price of platinum, it is crucial to improve the performances of the platinum-based catalysts to reduce the quantities of platinum used.<sup>2</sup>

For that purpose, important efforts have been directed to the better understanding of the reaction mechanism and to the determination of the structure of the active species—homogeneous or colloidal—, a subject which has been controversial for almost thirty years and also concerns other catalytic reactions.<sup>3</sup>

Several examples of platinum colloids have been reported to be catalytically active for alkene hydrosilylation,<sup>4–6</sup> thus

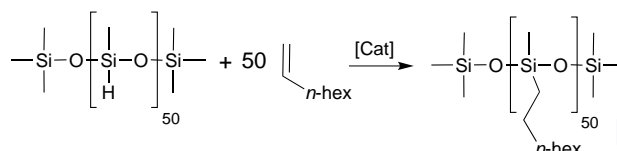


Fig. 1 Hydrosilylation of 1-octene by a PMHS

showing that their formation is not responsible for the deactivation of homogeneous catalysts, as it had been thought for a long time. At the reverse, several truly homogeneous platinum catalysts were also described,<sup>7–10</sup> meaning that colloid formation does not happen for all catalysts, contrary to the conclusions of several authors.<sup>11–14</sup> Thus, it seems that both can catalyze hydrosilylation.

For Karstedt's complex, the benchmark in the silicone industry, the exact nature of the active species is still unknown. Lewis and co-workers have suspected for a long time that platinum colloids could be the actual active species of hydrosilylation reactions in general, and that their formation was the origin of the induction period observed.<sup>11,12,14</sup> These results however lacked *in situ* data. More recently, they challenged their own conclusions by using *in situ* Extended X-Ray Absorption Fine Structure (EXAFS) to show that in the case of Karstedt's complex, the active Pt species presented Pt-C and Pt-Si bonds, but no Pt-Pt bonds, thus demonstrating that the catalyst was truly homogeneous.<sup>8</sup> Their turnover numbers (TONs, expressed in mol of transformed SiH per mol of platinum) were about 1000, because their set up only allowed to work with low substrate/catalyst ratios. In contrast, industrial TONs for this reaction are about  $10^5$ , so there is still a need to further examine what is occurring at TONs higher than 1000.

Besides providing mechanistic insights, studying platinum colloids as a catalyst for alkene hydrosilylation opens the way for reusable platinum catalysts. Up to now, none of the published colloidal platinum catalysts for alkene hydrosilylation could compete with Karstedt's complex in terms of TON.<sup>4–6</sup>

In the present work, we prepared three kinds of platinum nanoparticle suspensions and used them to catalyze the

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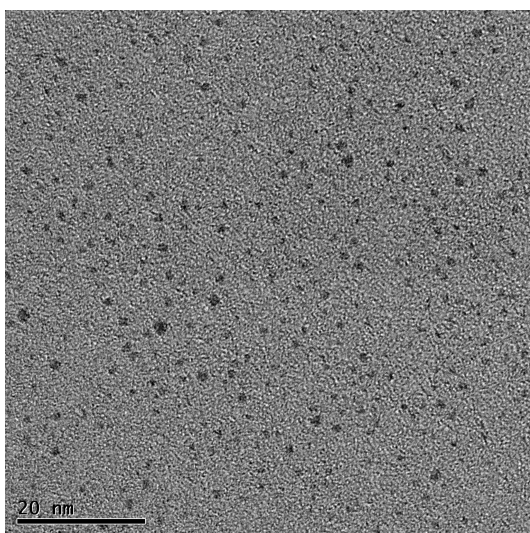
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**Table 1** Characteristics of the colloids and results of catalytic tests with the colloids and their platinum precursors. The SiH conversions were measured 30 minutes after the end of PMHS addition.

Catalyst	Pt precursor	Stabilizer	Average diameter (nm)	SiH conv. (TON) 0.5 ppm Pt	SiH conv. (TON) 7 ppm Pt	1-octene isomerization
Karstedt	-	-	-	87% ( $1.5 \times 10^6$ )	96% ( $1.0 \times 10^5$ )	12%
Pt(dba) <sub>2</sub>	-	-	-	86% ( $1.5 \times 10^6$ )	98% ( $1.1 \times 10^5$ )	12%
Colloid1	Pt(dba) <sub>2</sub>	<i>n</i> -octylsilane	1.6	77% ( $1.3 \times 10^6$ )	98% ( $1.1 \times 10^5$ )	11%
Colloid2	Karstedt	PMHS	1.7	84% ( $1.5 \times 10^6$ )	97% ( $1.0 \times 10^5$ )	11%
Colloid3	Karstedt	<i>n</i> -octylsilane	1.7	81% ( $1.4 \times 10^6$ )	99% ( $1.1 \times 10^5$ )	11%



**Fig. 2** Transmission Electron Micrograph of Colloid1.

hydrosilylation of 1-octene with a polymethylhydrosiloxane (PMHS) containing approximately 50 SiH units (see Fig. 1). TONs higher than  $10^5$  were rapidly reached without significant deactivation, demonstrating that platinum nanoparticles could be as efficient as Karstedt's complex. We also reactivated the debate on whether Karstedt's complex is truly homogeneous or colloidal during catalysis.

Three kinds of platinum nanoparticles (Pt NPs) were synthesized using an experimental procedure developed in our laboratory for the synthesis of platinum and nickel nanoparticles.<sup>15,16</sup> A typical procedure comprises dissolution of 0.015 mmol of Pt(dba)<sub>2</sub> (dba = dibenzylideneacetone) or Karstedt's complex in 43 mL of toluene, adding a quantity of *n*-octylsilane or PMHS corresponding to 1 equivalent of SiH<sub>3</sub> (or SiH, respectively) and stirring overnight at room temperature under 4 bars of hydrogen. Full details about the synthesis, characterization and catalytic tests of the colloids are provided in ESI†. It should be noted that only one example of platinum nanoparticles stabilized by polymethylhydrosiloxanes was reported in the literature.<sup>5</sup>

The colloids were characterized by Transmission Electron

Microscopy (TEM, see Fig. 2 for an example). The nanoparticles were found to be small, isolated and crystalline. Their mean diameter was calculated by averaging the size of at least 200 particles per colloid, measured from the TEM images. It was of 1.6 nm for Colloid1, and 1.7 nm for Colloid2 and Colloid3 (see Table 1).

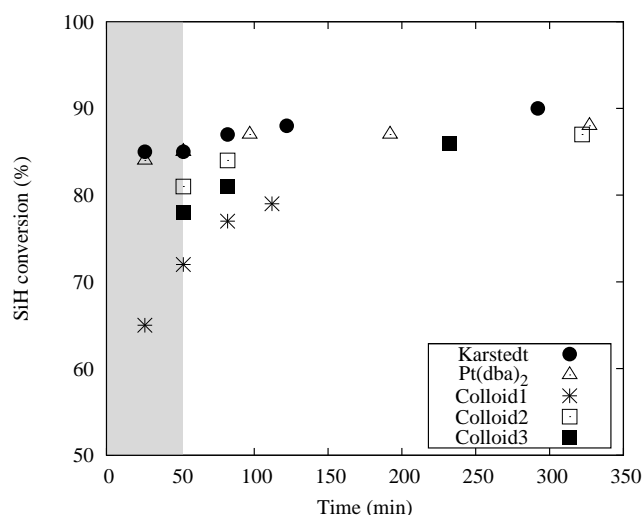
Catalytic tests were performed to compare the activities of platinum nanoparticles and their homogeneous precursors at 0.5 ppm and 7 ppm of platinum in the reaction mixture (see Table 1). A typical procedure involves preheating a mixture of 1-octene and colloidal suspension at 75°C and then adding a quantity of PMHS corresponding to 0.7 equivalent of SiH over 52 minutes. The SiH conversions were determined by <sup>1</sup>H NMR at regular intervals after the end of the addition of PMHS. Blank experiments were performed at various points of the project and showed that the catalytic test setup was not contaminated by any trace of catalyst.

SiH conversions are compared 30 minutes after the end of the addition of PMHS in the Table 1. At 7 ppm of platinum, conversions are almost quantitative (> 96%) for all catalysts. At 0.5 ppm of platinum, the colloidal catalyst gave 77%–84% conversion while Karstedt's complex gave 87% conversion. At 7 ppm platinum, full conversion of the PMHS could easily be reached with longer reaction times, but at 0.5 ppm, conversions never got higher than 90%. We suspected a deactivation of the catalysts due to traces of contaminant in the reactants, given the very small platinum concentrations used.

Colloids were found to be as selective as Karstedt's complex, and showed only anti-Markovnikov addition of the SiH on the C=C bond (like most platinum catalysts). The proportion of isomerization of 1-octene to 2-octene, a side reaction very common in hydrosilylation with platinum catalysts, was between 10% and 12% for all catalysts.

These results clearly show that well-stabilized nanoparticles are as efficient as Karstedt's complex, and not a deactivation form of homogeneous catalysts. Noteworthy, if colloids were not well-stabilized (for example because of a lack of stabilizer) and started to agglomerate, their catalytic performance dropped (see ESI†).

On Fig. 3 the SiH conversion is plotted vs. time at 0.5 ppm Pt for Pt colloids and Pt complexes. The tendency is that ho-



**Fig. 3** SiH conversion as a function of time, in batch tests (0.5 ppm Pt). The period in grey, from 0 to 52 minutes, is the addition of PMHS in the reactor.

homogeneous Pt(0) precatalysts such as Karstedt's complex or Pt(dba)<sub>2</sub> are more active than Pt nanoparticles in the first minutes of reaction, but that all catalyst tend to have similar activities in the late stage of the reaction. Pt complexes and colloids also give similar selectivities towards 1-octene isomerization in the late stages of the reaction.

Our group recently demonstrated using <sup>1</sup>H and <sup>29</sup>Si NMR that for high octene/SiH ratios and at low SiH conversions, the active species arising from Karstedt's complex and from the Pt NPs are different. At higher conversions, the behaviour of both catalysts is the same, highlighting the fact that Karstedt's complex was progressively transformed into a different active species at TONs of 10<sup>3</sup>–10<sup>4</sup>.<sup>17</sup> The higher activities of Pt complexes relatively to Pt colloids at the beginning of reaction are consistent with these conclusions. They are also in agreement with the results of the group of Lewis, who used *in situ* EXAFS experiments to prove that at very low TONs (< 1000) Karstedt's complex was truly homogeneous.<sup>8</sup>

In contrast, Lewis<sup>14</sup> and Fischer<sup>7</sup> gathered some evidence that when using Pt complexes as precatalysts, colloids were formed and catalytically active. This is in agreement with our experiments at very low Pt concentrations and very high TONs, in which Pt colloids and Pt complexes reached the same overall performances and same selectivities towards 1-octene isomerization, suggesting that Karstedt's complex is rapidly transformed into catalytically active Pt clusters/colloids.

We tried to gain further information about the active species using techniques such as <sup>195</sup>Pt NMR and Dynamic Light Scattering (DLS), but could not obtain significant results because

the Pt concentration was under the detection limits of these techniques. However, a Celite adsorption experiment during a catalytic test with Pt NPs (see ESI†) provided some evidence that in that case the catalytic activity arised mainly from the Pt NPs themselves and not some dissolved Pt species.

In conclusion, we showed that platinum nanoparticles used in same concentrations as Karstedt's complex, the benchmark in the silicone industry, gave equal to superior performances, and could reach full conversions even at concentrations as low as 7 ppm. We also reactivated the debate on whether Karstedt's complex was truly homogeneous or colloidal during catalysis. Albeit the exact nature of the catalytically active Pt species at high TONs could not be elucidated because of low Pt concentrations, our results suggest that dissolved Pt species (i.e. not colloidal) are not playing a significant role in the reaction.

The results also open the way towards the development of nanostructured heterogeneous platinum catalysts for alkene hydrosilylation.<sup>18,19</sup> Immobilizing the nanoparticles on solid supports would allow to reuse catalysts and to obtain platinum-free and colorless hydrosilylation products, two highly desirable qualities for the silicone industry.<sup>20</sup> One important challenge will be to develop a heterogeneous catalyst which is extremely stable towards deactivation and platinum leaching, in order to outperform homogeneous catalysts in terms of TONs. Since the nanoparticles presented herein have already reached TONs as high as Karstedt's complex, once immobilized they would be recyclable and could give even higher TONs. It would allow the development of hydrosilylation processes with reduced platinum consumption, thus more sustainable. Our group is currently working towards this objective.

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