

Platinum Catalysts Used in the Silicones Industry

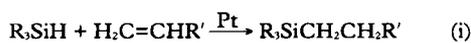
THEIR SYNTHESIS AND ACTIVITY IN HYDROSILYLATION

By Larry N. Lewis, Judith Stein, Yan Gao, Robert E. Colborn and Gudrun Hutchins

GE Corporate Research & Development Center, General Electric Company, Schenectady, New York

Hydrosilylation is a reaction widely used in the silicones industry for the preparation of monomers, containing silicon-carbon bonds, and for crosslinking polymers, and results in a variety of products. Hydrosilylation reactions are catalysed by highly active platinum catalysts, such as the silicone-soluble Karstedt's catalyst, which is prepared by the reaction of chloroplatinic acid, H_2PtCl_6 , with vinyl-silicon containing compounds, such as divinyltetramethyldisiloxane, M^mM^n . Inhibitors are widely used during hydrosilylation reactions to prevent premature crosslinking of polymers at ambient temperature, but permit rapid platinum-mediated crosslinking reactions at higher temperatures. Platinum colloids are formed at the end of the reaction and were identified by analysis. This paper discusses the mechanism of the hydrosilylation reaction, catalyst formation, characterisation, the effects of inhibitors and the range and complexity of the end products.

The silicones industry extensively uses the platinum-catalysed hydrosilylation reaction, in which a silicon-hydrogen (Si-H) bond is added across the unsaturated carbon-carbon double bond (C=C) of an olefin, Equation (i), resulting in the formation of a silicon-carbon (Si-C) bond (1-8).

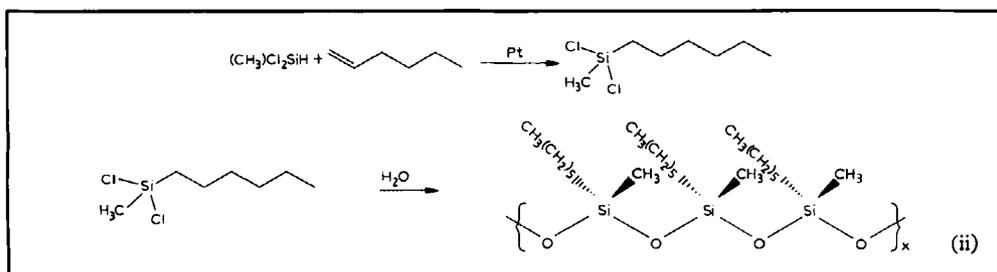


Hydrosilylation can be used for the synthesis of monomers; for example, in Equation (ii) the addition of a methyl dichlorosilane to an alkene gives a monomer, a methylchlorosilyl-

substituted compound, which upon hydrolysis gives a polymer, a polysiloxane with hydrocarbon functional groups.

Hydrosilylation is used to a much greater extent in industry to produce crosslinking reactions (9-11). The crosslinked network shown in Equation (iii), for example, is created by the addition of platinum to a mixture composed of a difunctional vinyl-containing polydimethylsiloxane and the multifunctional Si-H-containing copolymer of polydimethylsiloxane and methylhydrogen siloxane.

Here, to show the crosslinking in the polymer



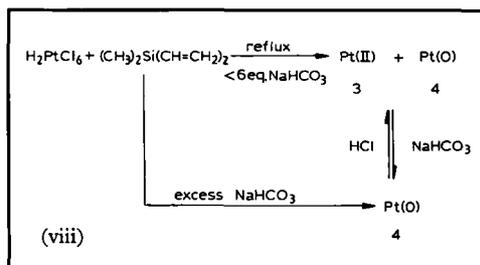
analysis of "solution A" by field desorption mass spectroscopy (FDMS) showed the presence of 2 and vinyl-stopped oligomers, as shown in Equation (iv).

The reduction of Pt(IV) to Pt(0) by a silicon-vinyl group, in Equation (iv), appeared to be a new reaction. When $M^{VI}M^{VI}$ was the reducing agent, some of the silicon vinyl functionality was converted to a silicon-oxygen group. The net result was the conversion of an M^{VI} group into a D (dimethylsiloxane) group. The vinyl group was changed primarily into either butadiene or ethylene. Water was the source of the new oxygen bond to silicon. Similarly, when D^{VI} is the source of reducing agent, as in the reaction of Equation (vii), a D^{VI} group is converted into a T group.

The overall platinum conversion occurring in Equation (iv), is from Pt(IV) to Pt(0); the platinum in "solution A" being in the zero oxidation state. We attempted to observe the imputed Pt(II) intermediate from this vinyl-silicon-mediated reduction in Equation (iv). Typically, in this reaction, chloroplatinic acid is reacted with $M^{VI}M^{VI}$ in the presence of some ethanol, which aids in the dissolution of H_2PtCl_6 . Sodium bicarbonate was added to remove chloride. Both ethanol and $NaHCO_3$ may aid the reduction. A ^{195}Pt NMR spectrum of "solution A" showed the previously mentioned resonances at -6200 ppm.

However, when the reduction was carried out without ethanol or $NaHCO_3$, a broad ^{195}Pt resonance was observed at -3470 ppm, which may be due to a Pt(II) intermediate. In order to characterise further the potential Pt(II) intermediates and to improve understanding of the mech-

anism of the reduction process, H_2PtCl_6 was reacted with several silicon-vinyl-containing species. The product of the reaction of H_2PtCl_6 and dimethyldivinylsilane, $(CH_3)_2Si(CH=CH_2)_2$, gave two products, see Equation (viii), a Pt(II) complex, 3, and a Pt(0) structure, 4. Complex 3 was isolated and a single crystal X-ray



anism of the reduction process, H_2PtCl_6 was reacted with several silicon-vinyl-containing species. The product of the reaction of H_2PtCl_6 and dimethyldivinylsilane, $(CH_3)_2Si(CH=CH_2)_2$, gave two products, see Equation (viii), a Pt(II) complex, 3, and a Pt(0) structure, 4. Complex 3 was isolated and a single crystal X-ray structure, see Figure 1, showed it to be a dinuclear complex with two bridging chlorine atoms and a bridging $(CH_3)_2Si(CH=CH_2)_2$ ligand. Additionally each platinum atom in 3 contained a $\eta^1:\eta^2-(CH_3)_2Si(CH=CH_2)(CH_2CH_3)$ ligand. Compound 3 had a ^{195}Pt NMR resonance at -3603 ppm, while the Pt(0) product, 4, had a ^{195}Pt NMR resonance at -6152 ppm. Although the structure of 4 was not determined directly, addition of PPh_3 to solutions containing 4 produced $(M^{VI}M^{VI})Pt(PPh_3)$ suggesting that 4 was $Pt_2(M^{VI}M^{VI})_x((CH_3)_2Si(CH=CH_2)_2)_y$ (20).

Inhibitors

Another important aspect of industrial hydrosilylation is the use of inhibitors (21-23). The crosslinking reaction of Equation (iii) will usually occur with as little as 10 ppm platinum, at ambient temperature in a matter of minutes. The rapidity of this reaction leads to the need

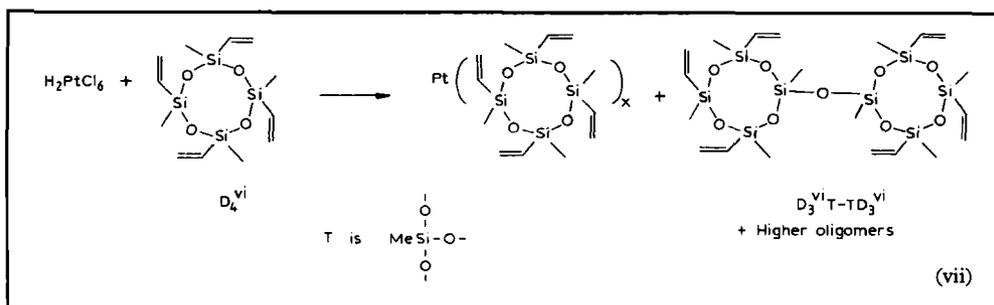
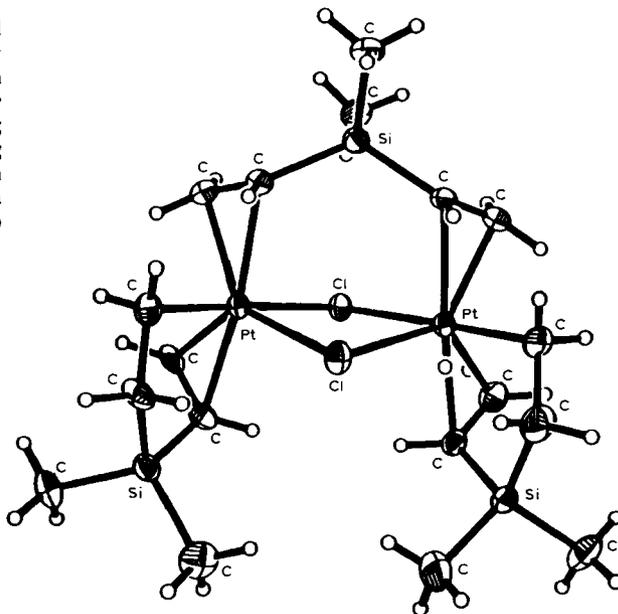


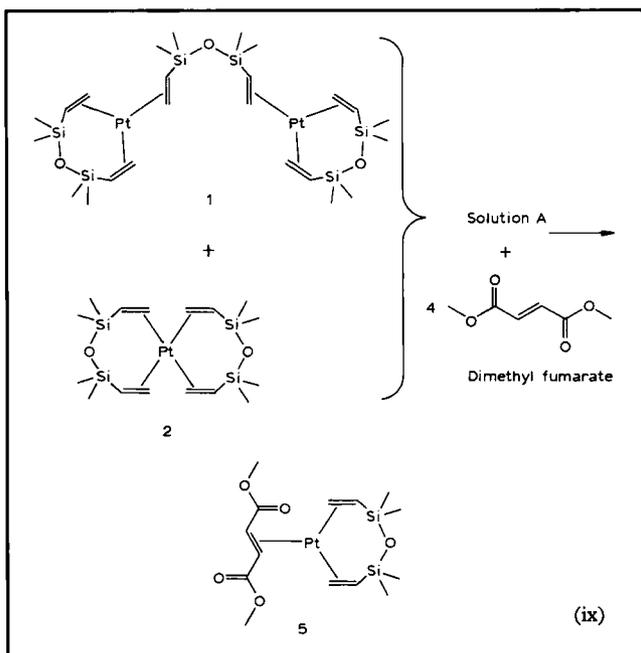
Fig. 1 The three dimensional structure of **3** produced by the reaction of H_2PtCl_6 with $(CH_3)_2Si(CH=CH_2)_2$. This dinuclear complex has two bridging chlorine atoms and a bridging $(CH_3)_2Si(CH=CH_2)_2$ ligand. Each platinum atom in **3** contains a $\eta^1:\eta^2-(CH_3)_2Si(CH=CH_2)(CH_2CH_3)$ ligand (**20**)

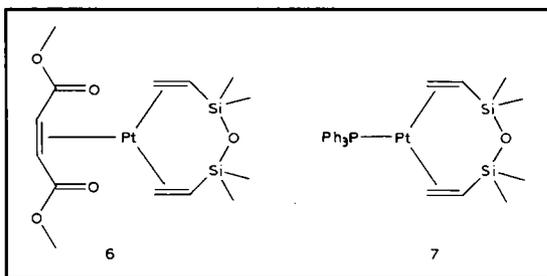


for inhibitors to give some control over the reaction. Typical industrial applications require long work times at low temperatures, followed by fast curing times at elevated temperature.

Two inhibitors, dimethyl fumarate and dimethyl maleate, are commonly added to platinum-catalysed crosslinkable silicone formulations to permit long work life by the end user at ambient temperature with a rapid cure at elevated temperature. The reaction of "solution A" with four equivalents of dimethyl fumarate, relative to platinum, resulted in formation of a platinum-fumarate complex, **5**, see Equation (ix). Complex **5** was characterised on the basis of its ^{13}C NMR spectrum and by comparison of its spectrum with those of the maleate analog, **6**, and the previously well characterised compound $PPh_3Pt(M^{VI}M^{VI})$, **7**. Compound **7** was prepared by

the reaction of "solution A" with one equivalent of PPh_3 , in the presence of 10 equivalents of $M^{VI}M^{VI}$. In effect the fumarate (or maleate) replaces the bridging, but not the chelating





ligand of **6**, while the methyne carbon was the triplet upfield at 71.94 ppm ($J_{\text{Pt-C}} = 42$ Hz). Both **5** and **6** showed peaks in the ^{13}C NMR due to the olefinic carbons of fumarate and maleate, respectively, with large coupling constants: $J_{\text{Pt-C}} = 89$ and 104 Hz, respectively. Compound **7**, where maleate or fumarate was replaced with PPh_3 had two resonances for those of the olefinic carbons of $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$, but shifted upfield relative to those in **6** due to the presence of the PPh_3 ligand.

$\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ ligand in Karstedt's catalyst.

A comparison of the ^{13}C NMR spectra for **5**, **6** and **7** in the olefin-platinum region is shown in Figure 2. All the ^{13}C olefin resonances had ^{195}Pt satellites. The spectrum of **5** showed four overlapping triplets from 68 to 72 ppm. These four resonances derived from the four different olefinic carbons present in the chelating $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ ligand.

By contrast, the ^{13}C NMR spectrum for **6** had two resonances for the olefinic carbons of the $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ ligand because the two double bonds are chemically equivalent. The downfield triplet resonance at 69.2 ppm ($J_{\text{Pt-C}} = 56$ Hz) was assigned to the methylene carbon of the $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$

Platinum Colloid Formation

The mechanism of the hydrosilylation reaction at the molecular level has been studied for many years (1–8), and several reviews have been devoted to the reaction (24–28). The Chalk-Harrod mechanism, developed during the 1960s, is the most often cited mechanism for hydrosilylation and is based on fundamental steps of organometallic chemistry (8); these include oxidative addition of a Si-H group to a metal-olefin complex, insertion steps and reductive elimination. However, a number of

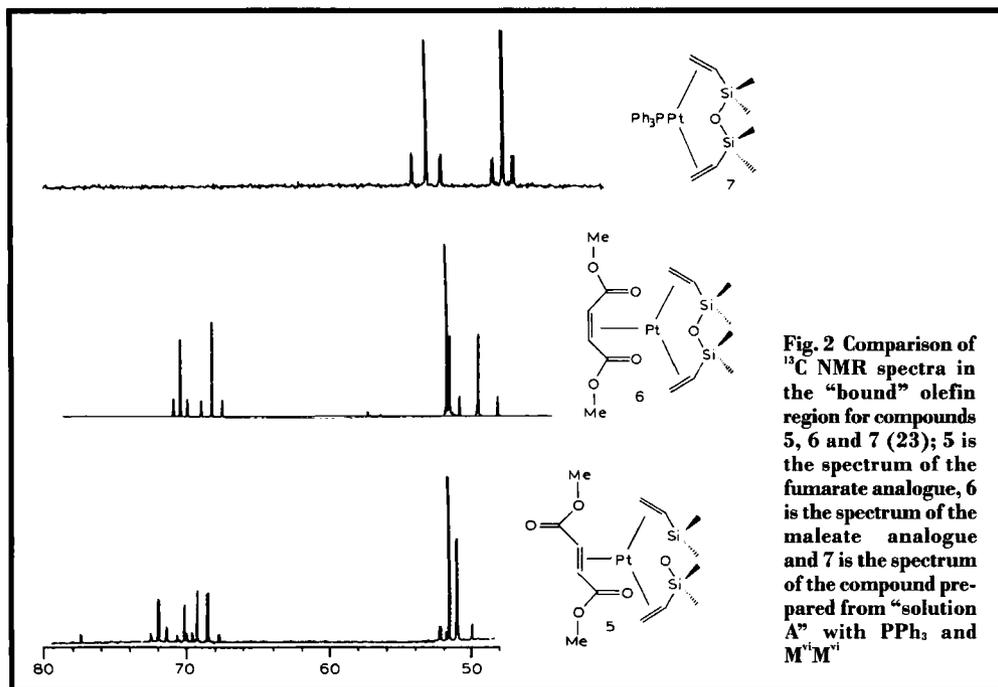


Fig. 2 Comparison of ^{13}C NMR spectra in the "bound" olefin region for compounds **5**, **6** and **7** (23); **5** is the spectrum of the fumarate analogue, **6** is the spectrum of the maleate analogue and **7** is the spectrum of the compound prepared from "solution A" with PPh_3 and $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$

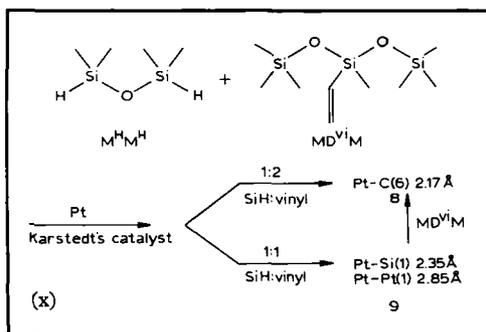
phenomena are not explained by the Chalk-Harrod mechanism and among these is the presence of an induction period (the time between the start of a chemical reaction and its observable occurrence), formation of coloured bodies and co-catalysis by oxygen.

In the 1980s Lewis and co-workers proposed a mechanism based on the intermediacy of platinum colloids (13, 14, 25, 26), which had been observed via transmission electron microscopic (TEM) analysis of reaction solutions following platinum-catalysed hydrosilylation (27).

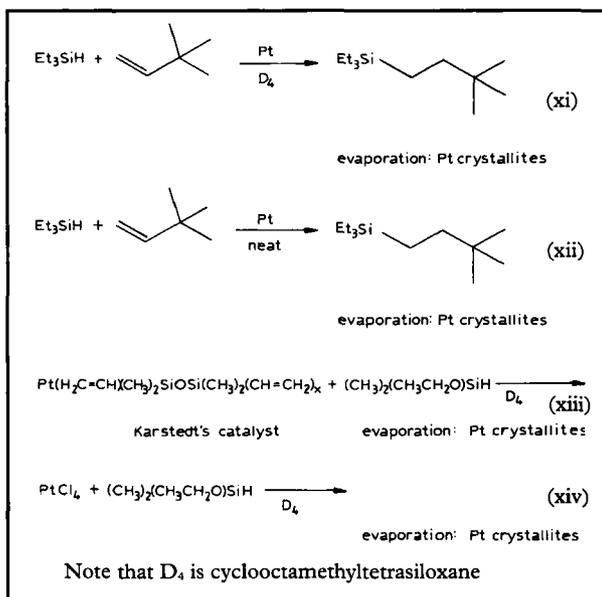
Reaction solutions from a platinum-catalysed hydrosilylation reaction were originally analysed by first evaporating the reaction solutions and then recording the TEM images (12–14, 22–25). TEM analysis showed, in some cases, that colloidal platinum had formed after the hydrosilylation reaction. More recently, Pt EXAFS of reaction solutions from hydrosilylation reactions has shown that the type of platinum species formed in solution at the end of a reaction depends on:

- the ratio of Si-H to vinyl used (21), and
- the nature of the olefin (hydrocarbon or silicon-vinyl).

The two types of platinum end products observed are illustrated in Equation (x) where



8 was the species formed at high vinyl concentrations and **9** was the platinum product formed when the concentration of Si-H was greater than,



or equal to, that of vinyl. Compound **8** was the designation used for platinum species containing only Pt-C bonds (at a typical Pt-C:olefin distance of around 2.17 Å and with a co-ordination number, number in parentheses, of six). Compound **9** was the species that contained both Pt-Pt and Pt-Si single bonds as determined by EXAFS.

Platinum species **9** could be converted to **8** in the presence of excess olefin (if the olefin was a silicon-vinyl compound, that is, if more $\text{MD}^{\text{vi}}\text{M}$ was added). Compound **8** was formed when silicon-olefin was the olefin source, that is $\text{MD}^{\text{vi}}\text{M}$.

However, if a Si-H compound was reacted with an olefinic hydrocarbon, such as hexene, which does not contain silicon-vinyl, then **9** was formed regardless of the stoichiometry of olefin and Si-H. Similarly, with neo-hexene (3,3-dimethyl-1-hexene) platinum reaction product **9** is formed from the platinum-catalysed hydrosilylation reaction between neo-hexene and a number of different Si-H compounds, even if the concentration of Si-H:neo-hexene is 1:2.

The reactions in Equations (xi) to (xiv), (where (xi) and (xii) describe the platinum catalysed hydrosilylation of triethylsilane with neo-hexene), all give dark-coloured solutions. TEM analyses of the reaction products from these

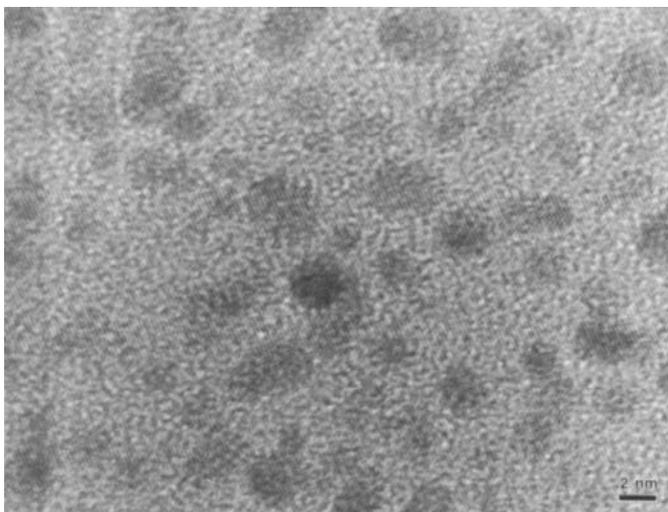


Fig. 3 Transmission electron micrograph of the platinum colloids formed by evaporation of the reaction product between $(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{O})\text{SiH}$ and Karstedt's catalyst solution, $(\text{Pt}(\text{CH}_2)_2(\text{H}_2\text{C}=\text{CH})\text{SiOSi}(\text{CH}=\text{CH}_2)(\text{CH}_3)_2)_x$, Equation (xiii). The dark spots are platinum crystallites which reveal diffraction fringes corresponding to the platinum (111) lattice spacing

solutions after evaporation all show that platinum crystallites were present.

A representative TEM, from Equation (xiii), is shown in Figure 3; here individual crystallites can be seen, displaying diffraction fringes with spacing which matches that for the (111) plane in crystalline platinum. The diffraction pattern also could be indexed to that of platinum. Finally, energy dispersive X-ray spectroscopy of the spots confirmed that they were composed of platinum.

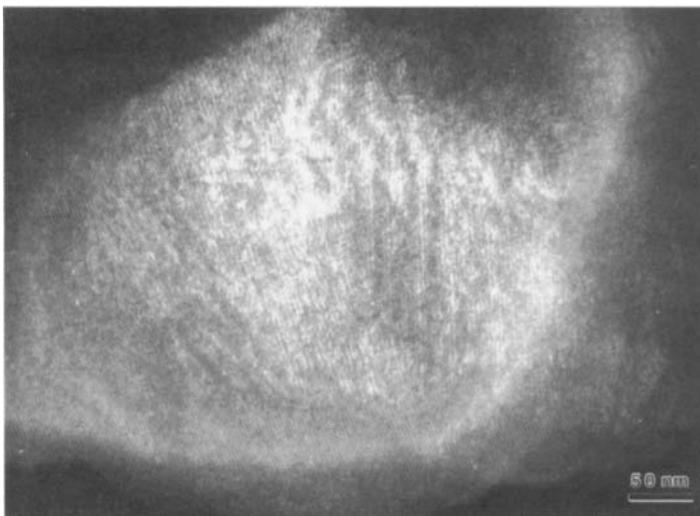
In the reactions shown in Equations (xi) and (xii), *in situ* studies showed that platinum of type 9 (from Equation (x)) formed in the reactions with neo-hexene. On evaporation, the type 9 platinum composition is converted to platinum crystallites. The effect of dilution with D₂ or

of running the reaction without solvent was examined together with the effect on platinum crystallite size. Reactions between dimethyl-ethoxysilane and either Karstedt's catalyst (Equation (xiii)) or PtCl_4 (Equation (xiv) (12)) were carried out under conditions where previous reports had shown that colloids formed. The Table shows the results of a statistical analysis of the particle sizes of the platinum crystallites formed from the reactions in Equations (xi) to (xiv).

The particle size of the crystallites may have been affected by the platinum concentration; it can be seen in the Table that the larger particles from Equation (xiv) are produced from a higher platinum concentration. The particles formed from Equations (xi) and (xiii) were

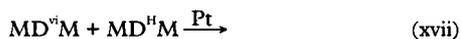
Statistics on Particle Sizes of Platinum Crystallites Formed in Equations (xi) to (xiv)					
		Number average			
Equation	Pt concentration, mg ml ⁻¹	Mean, Å	Minimum, Å	Maximum, Å	Standard deviation
(xi)	0.29	24.4	16	36.1	3.6
(xii)	0.3	17.3	10.3	26.4	2.9
(xiii)	0.3	22.6	9.6	33.3	3.6
(xiv)	0.46	30.4	17.6	46.9	5.4

Fig. 4 Transmission electron darkfield image of the evaporated solution from Equation (xvii). Note the presence of moiré diffraction fringes due to slight misalignments of the thin crystalline sheets making up the material



similar in size and larger than those from Equation (xii). Equation (xii) did not use D, diluent.

When hydrosilylation reactions were run with silicon-vinyl substrates, for example Equation (x) where platinum of type 8 is formed, TEM analyses of the resulting evaporated solutions were different from those obtained from Equations (xi) to (xiv). Note that all of these reactions were carried out in neat solutions and it is not known if the absence of diluent contributed to the observed TEM. TEM of evaporated solutions from Equations (xv) to (xviii) showed the complete absence of the platinum crystallites seen in Figure 3.



A darkfield TEM micrograph, prototypical for the evaporated solution from Equations (xv) to (xviii) is shown in Figure 4. Energy dispersive X-ray spectroscopy confirmed the presence of platinum. However, the diffraction pattern did not match that of metallic platinum

or any platinum compound in the powder diffraction file. Electron diffraction analysis indicated the presence of a crystalline material which had formed in very thin crystalline sheets that were slightly misaligned with respect to one another. The moiré diffraction fringes due to this misalignment are clearly visible in the micrograph.

Evaporation of the product solution from the reaction between $PtCl_4$ and a siloxane-like Si-H source, M_3T^H , tris(trimethylsiloxy)silane $(Me_3SiO)_3SiH$, gave a TEM similar to Figure 3, while evaporation of the product solution from the reaction between $PtCl_4$, M_3T^H and M_3T^{vi} gave a TEM similar to Figure 4. Further studies are underway to determine the structure of platinum species present during hydrosilylation under the various conditions discussed here. The species in Figure 4 may be explained by these analyses (29).

Summary and Conclusions

Hydrosilylation is widely used industrially for the preparation of monomers with silicon-carbon bonds and for producing crosslinked polymers.

Highly active, silicone-soluble platinum catalysts can be prepared by the reaction of chloroplatinic acid with vinyl-silicon containing compounds. The vinyl-silicon compounds, such as

divinyltetramethyldisiloxane ($M^{vi}M^{vi}$) reduce platinum(IV), in chloroplatinic acid, to platinum(0) with the concurrent conversion of the silicon-vinyl group to a silicon-oxygen group. A typical platinum catalyst is Karstedt's catalyst, $Pt_x(M^{vi}M^{vi})_y$.

Inhibitors are widely used in industry to control the platinum-mediated addition reaction of curable systems. The addition of inhibitors prevents hydrosilylation (crosslinking) at low temperature while permitting rapid reaction at elevated temperature. Commonly used inhibitors include those with electron deficient double bonds, such as maleates and fumarates. Dimethyl maleate reacts with Karstedt's catalyst to make a complex containing a chelating $M^{vi}M^{vi}$ group and a maleate ligand.

Previous studies reported that formation of platinum colloids was a key step in hydrosilylation. It is now clear that colloid formation occurs as an end stage of the reaction. EXAFS analy-

sis has shown that molecular compounds are present during hydrosilylation. Colloidal platinum is observed by TEM after evaporation of solutions from several reactions which involve platinum, a Si-H compound and either poorly co-ordinating olefins or no olefin. However, in some cases where silicon-vinyl-containing species were present, the reaction product between platinum and a Si-H-containing compound did not give colloidal platinum species; and TEM analysis showed that the crystalline material present was not metallic platinum crystallites.

Further work is in progress to identify the structures of platinum intermediates formed during hydrosilylation and industry continues to search for more highly active catalysts and more effective inhibitors.

Acknowledgements

I would like to thank Jim Grande for performing the statistical analysis from the TEM images.

References

- 1 B. Marciniak, J. Gulinski, W. Urbaniak and Z. W. Kornetka, in "Comprehensive Handbook on Hydrosilylation", ed. B. Marciniak, Pergamon, Oxford, 1992
- 2 V. B. Pukhnarevich, E. Lukevics, L. I. Kopylova and M. G. Voronkov, "Perspectives of Hydrosilylation", Institute of Organic Synthesis, Riga, Latvia, 1992
- 3 I. Ojima, in "The Chemistry of Organic Silicon Compounds", Vol. 2, eds. S. Patai and Z. Rappaport, Wiley Interscience, New York, 1989, Chapter 25, pp. 1479-1526
- 4 D. A. Armitage, in "Comprehensive Organometallic Chemistry", Vol. 2, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, pp. 117-120
- 5 J. L. Speier, "Advances in Organometallic Chemistry", Vol. 17, eds. F. G. A. Stone and R. West, Academic Press, New York, 1979, pp. 407-447
- 6 E. Lukevics, Z. V. Belyakova, M. G. Pomeransteva and M. G. Voronkov, *J. Organomet. Chem. Libr.*, 1977, 5, 1
- 7 C. Eaborn and R. W. Bott, in "The Bond to Carbon", ed. A. G. MacDiarmid, Marcel Dekker, New York, 1968
- 8 J. F. Harrod and A. J. Chalk, in "Organic Synthesis via Metal Carbonyls", Vol. 2, eds. I. Wender and P. Pino, Wiley, New York, 1977, pp. 673-703
- 9 W. Noll, "Chemistry and Technology of Silicones," Academic Press, New York, 1968
- 10 J. Rich, J. Cella, L. N. Lewis, S. Rubinsztajn, J. Stein, N. Singh and J. Wengrovius, in "Kirk-Othmer: Encyclopedia of Chemical Technology," Wiley, New York, 1997
- 11 J. Stein, L. N. Lewis, K. A. Smith and K. X. Lettko, *J. Inorg. Organomet. Polym.*, 1991, 1, 325
- 12 L. N. Lewis and N. Lewis, *Chem. Mater.*, 1989, 1, 106
- 13 L. N. Lewis and R. J. Uriarte, *Organometallics*, 1990, 9, 621
- 14 L. N. Lewis, N. Lewis and R. J. Uriarte, in "Homogeneous Transition Metal Catalyzed Reactions," Adv. Chem. Ser. 230, eds. W. R. Moser and D. W. Slocum, American Chemical Society, Washington, D.C., 1992, p. 541
- 15 B. D. Karstedt, *U.S. Patent* 3,775,452; 1973
- 16 G. Chandra, P. Y. Lo, P. B. Hitchcock and M. F. Lappert, *Organometallics*, 1987, 6, 191
- 17 P. B. Hitchcock, M. F. Lappert and N. J. W. Warhurst, *Angew. Chem., Int. Ed. Engl.*, 1991, 30, 438
- 18 D. N. Willing, *U.S. Patent* 3,419,593; 1968
- 19 B. A. Ashby and F. J. Modic, *U.S. Patent* 4,288,345; 1981
- 20 L. N. Lewis, R. E. Colborn, H. Grade, G. L. Bryant, C. A. Sumpter and R. A. Scott, *Organometallics*, 1995, 14, 2202
- 21 L. N. Lewis, C. A. Sumpter and M. Davis, *J. Inorg. Organomet. Polym.*, 1995, 5, 377, and references therein
- 22 L. N. Lewis, C. A. Sumpter and J. Stein, *J. Inorg. Organomet. Polym.*, 1996, 6, 123
- 23 L. N. Lewis, J. Stein, R. E. Colborn, Y. Gao and J. Dong, *J. Organomet. Chem.*, 1996, 521, 221

- 24 L. N. Lewis, J. Stein, K. A. Smith, R. P. Messmer, D. G. LeGrand and R. A. Scott, in "Progress in Organosilicon Chemistry," eds. B. Marciniak and J. Chojnowski, Gordon & Breach, Amsterdam, 1995, p. 263
- 25 L. N. Lewis and N. Lewis, *J. Am. Chem. Soc.*, 1986, **108**, 7228
- 26 L. N. Lewis, *J. Am. Chem. Soc.*, 1990, **112**, 5998
- 27 L. N. Lewis, R. J. Uriarte and N. Lewis, *J. Mol. Catal.*, 1991, **66**, 105
- 28 L. N. Lewis, R. J. Uriarte and N. Lewis, *J. Catal.*, 1991, **127**, 67
- 29 J. Stein, L. N. Lewis and Y. Gao, manuscript in preparation

New Platinum-Based Lean NO_x Conversion Strategy

The introduction of increasingly stringent environmental legislation brings benefits to our quality of life, and presents challenges to catalytic chemists, who are required to develop novel solutions to enable the new legislation to be met. Within the automotive area, new legislative limits to exhaust pollutants mean that it will soon be necessary for the catalytic converters on diesel vehicles to additionally remove significant concentrations of nitrogen oxides, NO_x, from the exhaust feed, besides the oxidation functions for carbon monoxide, CO, and hydrocarbon which they already perform.

Diesel engines are extremely fuel-efficient. This is achieved by ensuring that combustion occurs under highly oxidising conditions, and results in a strongly oxidising gas feed which needs to be treated using a catalytic converter. Under such highly oxidising conditions the oxidation of the unburnt hydrocarbons to CO₂ and H₂O and of the CO to CO₂ is relatively straightforward. However, reducing NO_x to N₂ under such conditions is very difficult.

The major breakthrough in automotive NO_x control under very oxidising conditions was reported simultaneously by the Held group in Germany (1) and by the Iwamoto group in Japan (2). These workers independently showed that significant quantities of NO_x could be reduced to N₂ under highly oxidising conditions using a catalyst of copper incorporated into ZSM-5 zeolite. Others have characterised the mechanistic aspects of the reaction over Cu/ZSM-5 (for example (3)), and have shown that the major role of the copper is to oxidise NO to NO₂. This subsequently reacts with hydrocarbon-derived species activated by the surface of the zeolite.

The copper catalyst can only be used at relatively high temperature (350–550°C), and it is not particularly stable. The conversion of NO to NO₂ over copper is poor at the low temperature end of this range, so its performance here is nowhere near as good as that of platinum. At high temperature the NO to NO₂ reaction becomes limited by thermodynamics and both copper and platinum catalysts then become equivalent in their NO oxidation performance.

Now, Iwamoto has used the mechanistic

information/approach to develop a highly efficient NO_x conversion catalyst system capable of operating at low temperatures (4). The strategy uses two separate catalysts – one to oxidise the NO into NO₂ and the other to reduce this NO₂ into N₂. Iwamoto has shown that platinum incorporated into ZSM-5 zeolite is a highly efficient NO oxidation catalyst and this catalyst is used to perform the first step in the conversion process. The second step is carried out using indium incorporated into ZSM-5 zeolite. Since there is only a small amount of unburnt hydrocarbon in the exhaust stream of a diesel vehicle, additional hydrocarbon needs to be injected to provide the reductant to achieve significant NO_x conversions.

Position of Hydrocarbon Injection

Platinum is an excellent oxidation catalyst, which means that if the hydrocarbon were injected in front of the platinum catalyst, substantial quantities would be converted over the platinum, thereby lowering the hydrocarbon concentration reaching the indium catalyst. Iwamoto proposes that this additional hydrocarbon injection should instead occur between the two catalysts: that is, after the platinum catalyst and before the indium catalyst, thus ensuring that the indium reduction catalyst sees enough hydrocarbon to effect the reduction of the NO₂ generated over the platinum catalyst.

This approach is the latest in the long line of platinum-based strategies developed to remove NO_x under highly oxidising conditions. Within industry and academia, platinum-based work is continuing to advance the technology further to ensure that future environmental legislation can be met.

A. P. WALKER

References

- 1 W. Held, A. König, T. Richter and L. Puppe, SAE Paper 900496, 1990
- 2 M. Iwamoto, Proc. Catalytic Technology for Removal of Nitrogen Monoxide, Tokyo, 1990, 17
- 3 G. P. Ansell, A. F. Diwell, S. E. Golunski, J. W. Hayes, R. R. Rajaram, T. J. Truex and A. P. Walker, *Appl. Catal. B: Environ.*, 1993, **2**, 81
- 4 M. Iwamoto, A. M. Hernandez and T. Zengyo, *Chem. Commun.*, 1997, (1), 37