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Hydridosilsesquioxane Modified Silica-Supported Platinum Nanoparticles

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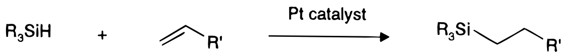
Platinum catalysts, such as chloroplatinic acid[1] and Karstedt's catalyst,[2] are frequently used to carry out hydrosilation reactions in which a hydrosilane (R_3SiH) adds across an alkene or alkyne function (Scheme 1).[3]

Scheme 1. Hydrosilation Reaction Catalyzed by Platinum.



In 1986, Lewis et al. provided evidence that platinum colloids[4] form during the hydrosilation reaction.[5] This work also showed the platinum colloids cause an acceleration of the hydrosilation reaction.[5,6] On the other hand, the platinum colloids that initially promote hydrosilation in high yields degenerate with time to give a catalytically inactive black precipitate.[7]

A variety of metal colloids have been prepared and characterized by prereacting platinum group metal compounds with hydrosilanes.[5,8,9] For example, the reaction between platinum metal compounds (i.e., $PtCl_2$, PtO_2, H_2PtCl_6, and Karstedt's catalyst) and dimethylethoxysilane, $Me_2(EtO)SiH$, gave rise to the evolution of hydrogen gas with a characteristic transition of solution color from colorless to yellow or orange within 2 h.[8a] Examination of the products by transmission electron microscopy (TEM) showed the presence of crystalline platinum particles having diameters which ranged from 1 to 5 nm. It has also been shown that the transition to the yellow colored solution during the hydrosilation reaction occurred simultaneously with the formation of platinum colloids having an average size of ca. 2 nm.[5] The chemical identity of the platinum

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(1) (a) Saam, J. C.; Speier, J. L. *J. Am. Chem. Soc.* **1958**, *80*, 4104. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(2) (a) Karstedt, B. D. U.S. Patent 3,775,452,1973. (b) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191. (c) Lewis, L. N.; Colborn, R. E.; Grade, H.; Bryant, Jr., G. L.; Sumpter, C.A.; Scott, R. A. *Organometallics* **1995**, *14*, 2202.

(3) (a) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *Organomet. Chem. Rev.* **1977**, *5*, 1. (b) Parshall, G. W., Ittel, S. D., *Homogeneous Catalysis;* John Wiley: New York, 1992; p, 39.

(4) Although the term "platinum colloids" was used by the Lewis group, we have used the general term "nanoparticles" to describe the platinum particles prepared in this work. See: Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693 for a detailed discussion on the distinctions and similarities between metal clusters and metal colloids and a complete review of the literature on platinum group metal colloids. The distinction between metal colloids and metal clusters has been discussed by Schmid (Schmid, G. *Endeavour* **1990**, *14*, 172) where the size of metal clusters was defined as being less than or equal to 10 nm. Using this definition, metal colloids would be considered to be greater than 10 nm.

(5) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7728.

(6) (a) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (b) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.

(7) The absence or depletion of oxygen in the hydrosilation reaction environment has been attributed to the darkening color of the platinum mixture over time. This color change reflects the formation of larger size colloids whose catalytic activity is reduced. It has been proposed that oxygen prevents irreversible platinum colloid (derived from Karstedt's catalyst) aggregation. See ref 6a.

(8) (a) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106. (b) Lewis, L. N.; Uriarte, R. J.; Lewis, N. *J. Catal.* **1991**, *127*, 67. (c) Lewis, L. N.; Lewis, N.; Uriarte, R. J. *Homogeneous Transition Metal Catalyzed Reactions*; Advances in Chemistry Series 230; American Chemical Society: Washington, DC, 1992; p 541.

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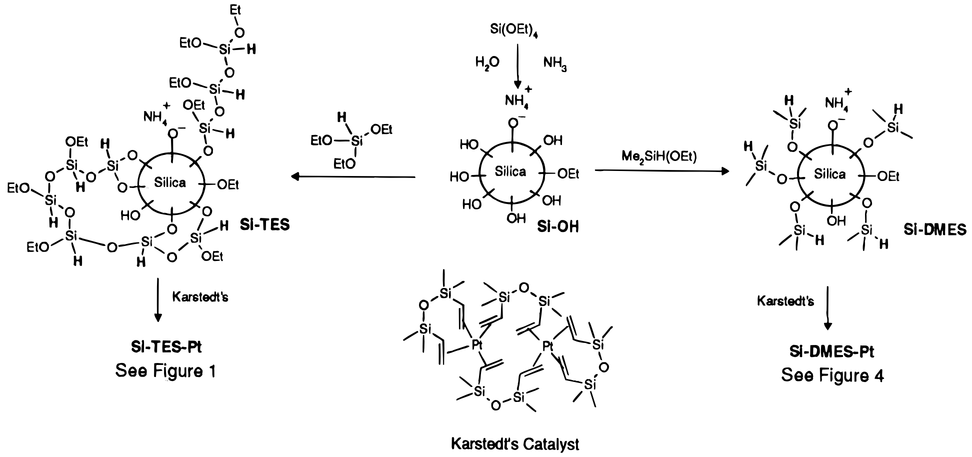
Scheme 2. Chemical Modification of Unmodified Silica, Si−OH, with Triethoxysilane (TES) To Give Si−TES and Dimethylethoxysilane (DMES) To Give Si−DMES[a]



[a] The surface reaction of Si−TES and Si−DMES with Karstedt's catalyst leads to Si−TES−Pt (see Figure 1) and Si−DMES−Pt (see Figure 4), respectively.

particles formed during reduction by hydrosilane reagents, as determined by X-ray analysis and EXAFS, suggests they are composed of platinum and organosilane fragments.[8,10,11]

This communication reports a simple method for the preparation of platinum nanoparticles supported on inorganic oxide materials,[12] particularly silica modified with SiH groups.[13,14] The supported platinum nanoparticles, derived by reacting Karstedt's catalyst with SiH modified silica, are catalytically active toward hydrosilation reactions and offer the advantage that the platinum does not aggregate to form an inactive precipitate. Thus, a single sample of the supported catalyst could be recycled to carry out more than one hydrosilation reaction.

Colloidal silica particles were prepared using the Stöber method[15] (Si−OH, Scheme 2), which is based on the hydrolysis and condensation of Si(OEt)$_4$ in an aqueous ethanol medium containing ammonia.[13,16] The mean hydrodynamic diameter of the particles in acetone, measured by DLS, was 179 nm with a standard deviation of the particle size distribution of 10%.

Si−OH was modified with HSi(OEt)$_3$ according to a previously reported published method to give Si−TES (Scheme 2).[13] From DLS measurements, Si−TES was found to have an increased hydrodynamic diameter of 192 nm indicating a 6 nm silsesquioxane layer on the silica surface. The electrophoretic mobility in acetone of Si−TES decreased, relative to the untreated particles, from -4.79×10^{-8} to -3.70×10^{-8} m^2 V^{-1} s^{-1} providing further evidence that the silica surface was coated with TES. The presence of SiH groups on Si−TES was confirmed by DRIFTS and ^{29}Si CP-MAS NMR spectroscopy.[17] The spectroscopic data of Si−TES revealed that the outer layer on the silica surface was composed of a cross-linked siloxane species bearing HSiO$_{3/2}$ units (Scheme 2) consistent with the structure reported for hydridosilsesquioxane gels.[18] The number of SiH groups per nm^2 was estimated to be 6−8 by titration with *N*-bromosuccinimide.[13]

The silica-supported platinum nanoparticles were prepared by the addition of Karstedt's catalyst (see Scheme 2) to Si−TES dispersed in THF.[19] The presence of platinum attached to Si−TES was confirmed by elemental analysis[20] and X-ray microanalysis using

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(9) For other related studies reporting the reduction of metal salts using hydrosilanes, see: (a) Anderson, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 5083. (b) Keinan, E.; Greenspoon, N. *J. Am. Chem. Soc.* **1986**, *108*, 7314. (c) Tour, J. M.; Pendalwar, S. L.; Cooper, J. P. *Chem. Mater.* **1990**, *2*, 647. (d) Tour, J. M.; Cooper, J. P.; Pendalwar, S. L. *J. Org. Chem.* **1990**, *55*, 3452. (e) Tour, J. M.; Pendalwar, S. L. *Tetrahedron Lett.* **1990**, *31*, 4719. (f) Nadkarni, D. V.; Fry, J. L. *J. Chem. Soc., Chem. Commun.* **1993**, 997. (g) Kini, A. D.; Nadkarni, D. V.; Fry, J. L. *Tetrahedron Lett.* **1994**, *35*, 1507. (h) Fry, J. L.; Nadkarni, D. V. U.S. Patent 5,281,440, 1994. (i) Reed-Mundell, J. J.; Nadkarni, D. V.; Junz, Jr., J. M.; Fry, C. W.; Fry, J. L. *Chem. Mater.* **1995**, *7*, 1655.

(10) The Lewis group has characterized the products formed during hydrosilation reactions. See: Lewis, L. N.; Stein, J.; Smith, K. A.; Messmer, R. P.; Legrand, D. G.; Scott, R. A. Recent Mechanism Studies on Hydrosilylation. *Progress in Organosilicon Chemistry*; Chojnowski, J., Marciniec, B., Eds.; Gordon and Breach: Basel, 1995; pp 263−285.

(11) The term "platinum nanoparticles" used throughout this paper should not be regarded as meaning they are composed only of bulk platinum metal. Although we do not know the specific chemical identity of the supported metal species, work by the Lewis group (see ref 10) suggests the platinum species formed during the hydrosilation reaction contains both platinum and silicon.

(12) Marzán, L. Liz; Philipse, A. P. *Colloids Surf.* **1994**, *90*, 95.

(13) Ketelson, H. A.; Brook, M. A.; Pelton, R. *Chem. Mater.* **1995**, *7*, 1376.

(14) For other SiH modification procedures reported using silica gel as the substrate see: (a) Bräuer, L.; Gruber, H.; Greber, G. *Angew. Makromol. Chem.* **1990**, *180*, 209. (b) Sandoval, J. E.; Pesek, J. J. *Anal. Chem.* **1989**, *61*, 2067. (c) Sandoval, J. E.; Pesek, J. J. U.S. Patent 5,017,540, 1991. (d) Le Déoré, C.; Révillon, A.; Hamaide, T.; Guyot, A. *Polymer* **1993**, *34*, 3048. (e) See also ref 9g−i.

(15) Stöber, W. F.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(16) Ketelson, H. A.; Brook, M. A.; Pelton, R. *Polym. Adv. Tech.* **1995**, *6*, 335.

(17) ^{29}Si CP-MAS δ (ppm) −75.2, −84.6, −101.9, −110.8. IR, cm^{-1}: 2251 s. Elemental analysis: 4.12% C, 1.45% H, 43.88% Si.

(18) (a) Pauthe, M.; Phalippou, J.; Corriu, R.; Leclercq, D.; Vioux, A. *J. Non-Cryst. Solids* **1989**, *113*, 21. (b) Belot, V.; Corriu, R.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1991**, *3*, 127. (c) Tour, J. M.; Kafka, C. M. *Adv. Mater.* **1993**, *5*, 47. (d) Soraru, G. D.; D'Andrea, G.; Campostrini, R.; Babonneau, F. *J. Mater. Chem.* **1995**, *5*, 1363.

(19) To a suspension of Si−TES (0.1 g) dispersed in THF (10 mL) was added Karstedt's catalyst (0.15 g, 3.1 mg of Pt) under an open atmosphere which after heating for 8 h at 60 °C yielded a translucent yellow dispersion. The product, Si−TES−Pt, was cleaned with THF using four centrifugation/redispersion and sonication cycles.

(20) Elemental analysis performed by Guelph Chemical Laboratories, Guelph, Ont., Canada showed 3.78% C, 1.27% H, 40.14% Si, 0.53% Pt.

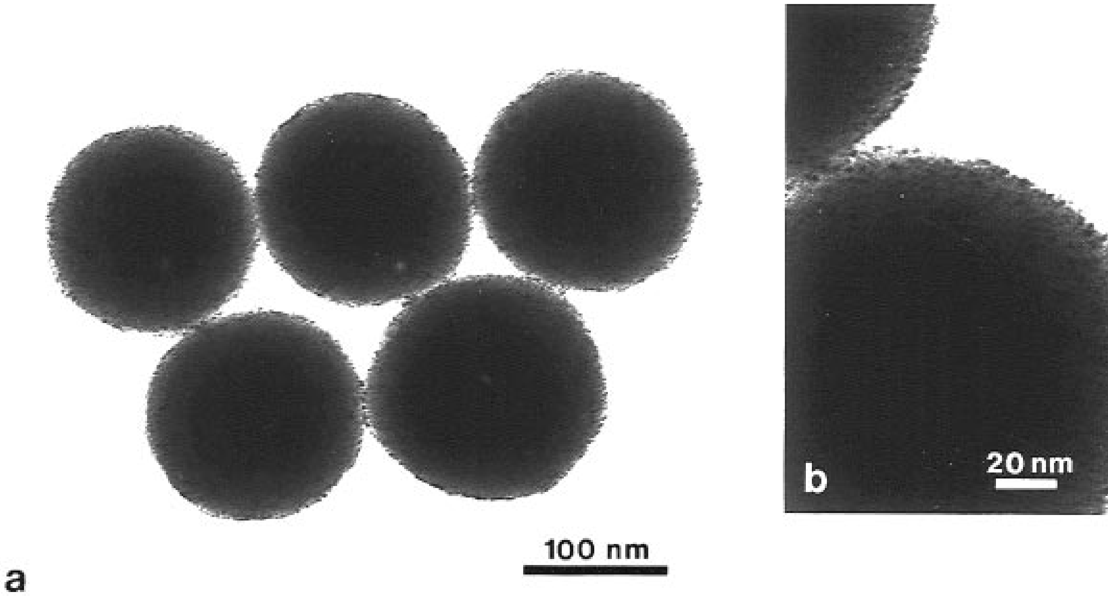

Figure 1. (a) TEM micrograph of silica-supported platinum nanoparticles (Si−TES−Pt). The average diameter of the supported platinum nanoparticles was 2 nm. (b) Higher magnification of Si−TES−Pt.

transmission electron microscopy (TEM).[21] A typical TEM micrograph is shown in Figure 1a in which platinum nanoparticles are observed to be uniformly distributed and attached to the silica surface. Figure 1b (higher magnification) shows the platinum nanoparticles are well separated from one another. The diameters of at least 100 supported platinum nanoparticles were measured to give an average diameter of 2 nm. Thin sections of the platinum−silica samples,[22] probed by X-ray microanalysis, showed no platinum signals in the silica core indicating most or all of the platinum resided on the silica surface.

The supported platinum nanoparticles were also imaged after silver staining; the platinum nanoparticles served as catalysts and nucleation sites for the reduction of silver ions (silver lactate) to metallic silver in the presence of hydroquinone (Figure 2).[23−25] As shown in Figure 2, the metallic silver precipitates grew selectively from the platinum nanoparticles. The electroless deposition of metals including copper, nickel, and palladium on substrates has previously been shown to occur when metal colloids such as gold, palladium, and platinum are used as catalysts.[26,27]

The role of the SiH functional groups was illustrated by the following experiments: (i) no supported platinum on silica was observed when Si−OH dispersions were treated with Karstedt's catalyst; (ii) the addition of preformed platinum nanoparticles[28] to Si−TES did not lead to platinum on the silica surface as confirmed by X-ray microanalysis.

To show that the method used to support the platinum nanoparticles was not an artifact of the Stöber silica surface, crystalline alumina was modified using TES and Karstedt's catalyst under the same conditions used for Si-TES-Pt.[29] TEM analysis of the cleaned alumina product (Figure 3) demonstrated that platinum nanoparticles having an average diameter of 3 nm were uniformly distributed on the SiH-modified alumina support. A few larger particles, 4−5 nm in diameter, were also observed as shown in Figure 3.

While the presence of SiH groups is necessary for the formation of the supported platinum nanoparticles, they do not control the platinum nanoparticle size. Rather, the control of size appears to be provided by the hydridosilsesquioxane structure (on the Si−TES surface). To demonstrate this, identical Si−OH was modified with a silane $EtOSiHMe_2$ (DMES), which cannot form a network structure but rather binds with a

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(21) A JEOL 1200 EX TEM (80 kV) was used to examine and image all specimens. For TEM imaging of the silica particles in whole, a drop of the colloidal dispersion was put on a 200 mesh nickel grid with a support film and air-dried.

(22) Slices of the silica particles, approximately 50 nm thick, were prepared by embedding the particles in epoxy resin and sectioning with an ultramicrotome.

(23) The silver enhancement experiments were carried out as follows. The whole mount particles were prepared as described above. The developer consisted of citrate buffer (5 parts of 2.3 M citric acid (BDH) and 2 parts of 1.6 M sodium citrate (BDH)) at pH 3.6, 17% gum arabic (Fluka), 0.6% hydroquinone (BDH), and 0.35% silver lactate (lactic acid, silver salt (Sigma)). A grid was incubated in the developer at room temperature for 15 min followed by incubation in Kodak rapid fix (diluted 1:4 with water) for 4 min at room temperature. Both incubation steps were performed in the dark. The grid was thoroughly washed with water before examining in the electron microscope.

(24) (a) James, T. H. *J. Am. Chem. Soc.* **1939**, *61*, 648. (b) Danscher, G.; Norgaard, J. R. *J. Histochem. Cytochem.* **1981**, *29*, 531. (c) Danscher, G.; Norgaard, J. R. *J. Histochem. Cytochem.* **1983**, *31*, 1394.

(25) Using the procedure described in ref 23, there was no detection by TEM analysis of silver growth directly from the silica surfaces bearing only SiH groups. We note, however, that silver reduction (as evidenced by the formation of a black-brown precipitate) occurred during the addition of aqueous silver lactate to Si−TES. Examination of Si−TES samples by TEM, after being mixed with the silver solution for 30 min, showed that the silver was only dispersed in the interstitial spaces. See ref 9i for a method which is claimed to deposit ultrathin layers of silver on silica gel modified with SiH groups.

(26) Niederprum, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *14*, 614.

(27) Hamilton, J. F.; Baetzold, R. C. *Science* **1979**, *205*, 1213.

(28) Karstedt's catalyst (0.1 g, 0.82 mM Pt) was added to a THF solution (5 mL) containing triethoxysilane (0.2 mL, 1.1 mmol). Hydrogen gas evolution was immediately observed after adding the platinum catalyst to the solution, which became yellow after 15 min of stirring. The particle size distribution was narrow with a mean diameter of 2 ± 1 nm based on TEM analysis by measuring 400 particles prepared on a carbon film.

(29) Aluminium oxide powder (0.2 g, Johnson Matthey, <1 μm, α 99.99%) was dispersed into 75 mL of acetone (99.5 wt %) by sonication and triethoxysilane (2.8 mL, 15 mmol) was added under a nitrogen atmosphere. The dispersion was refluxed under a positive nitrogen pressure for 36 h. ^{29}Si CP-MAS δ (ppm): −75, −85, −102. After washing the alumina three times with THF using centrifugation/redispersion cycles, the modified alumina was dispersed in THF (10 mL) to which Karstedt's catalyst (0.16 g, 3.2 mg of Pt) was added.

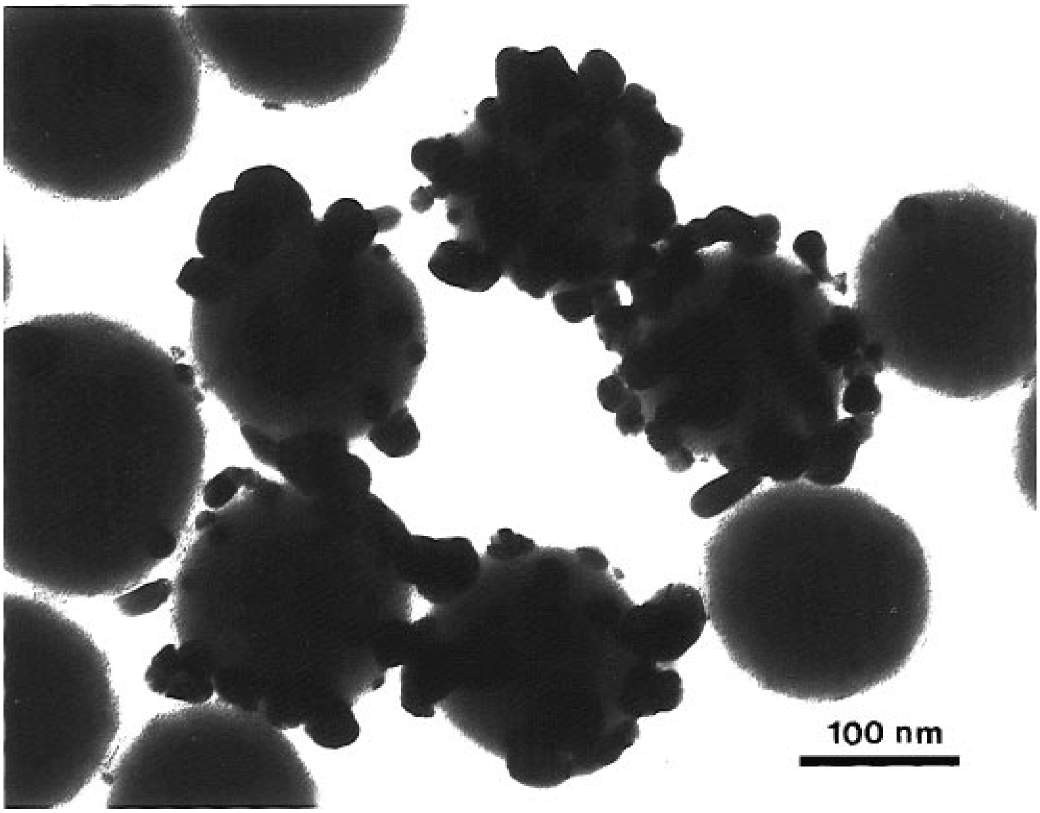

Figure 2. TEM micrograph of silica-supported platinum nanoparticles (Si–TES–Pt) after applying the silver enhancement method to the particles.[23–25]

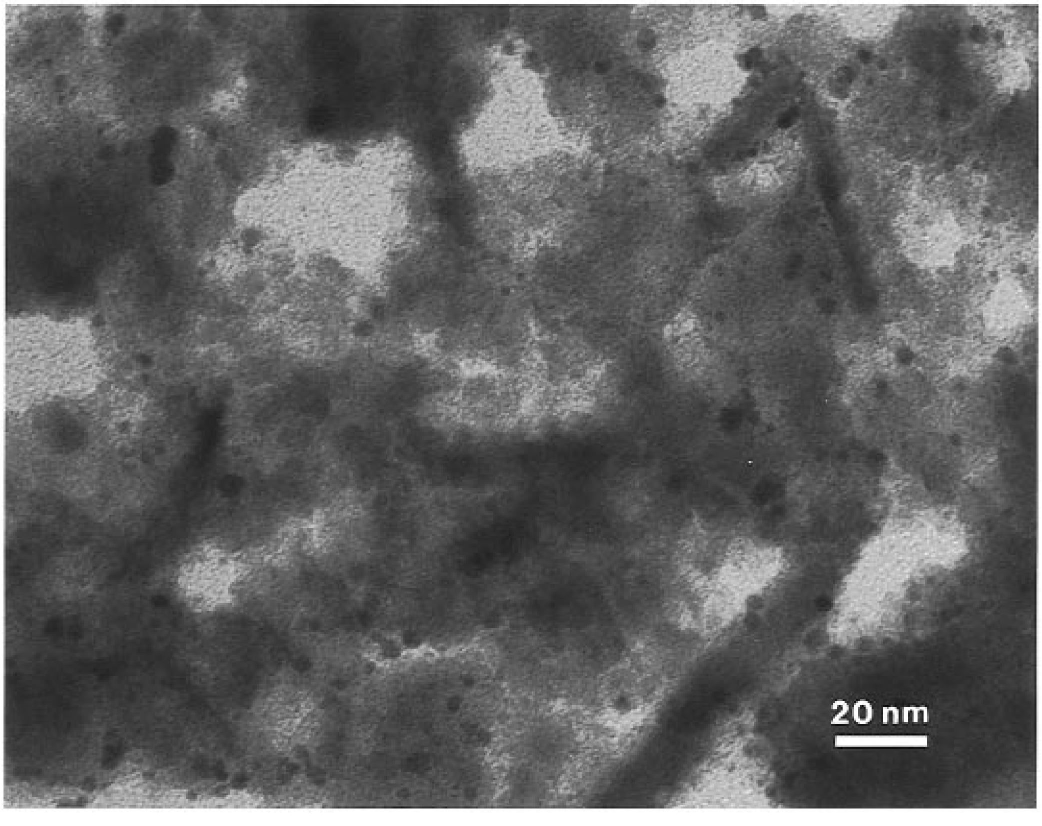

Figure 3. TEM micrograph of alumina particles modified with TES which have been treated with Karstedt's catalyst.

surface monolayer or less to give Si–DMES (Scheme 2).[13] Subsequent reaction of Si–DMES with Karstedt's catalyst led to the formation of platinum aggregates (see Figure 4) on the silica surface.

The catalytic properties of Si–TES–Pt (Figure 1) were demonstrated by using them in a hydrosilation reaction with phenylacetylene and bis(trimethylsiloxy)-methylsilane to give *E*-$PhCH{=}CHSiMe(OSiMe_3)_2$ and $H_2C{=}CHPh(SiMe(OSiMe_3)_2)$.[30,31] A single catalyst sample was effective in three consecutive reactions with no indication of poisoning. Furthermore, TEM examination of Si–TES–Pt following three hydrosilation

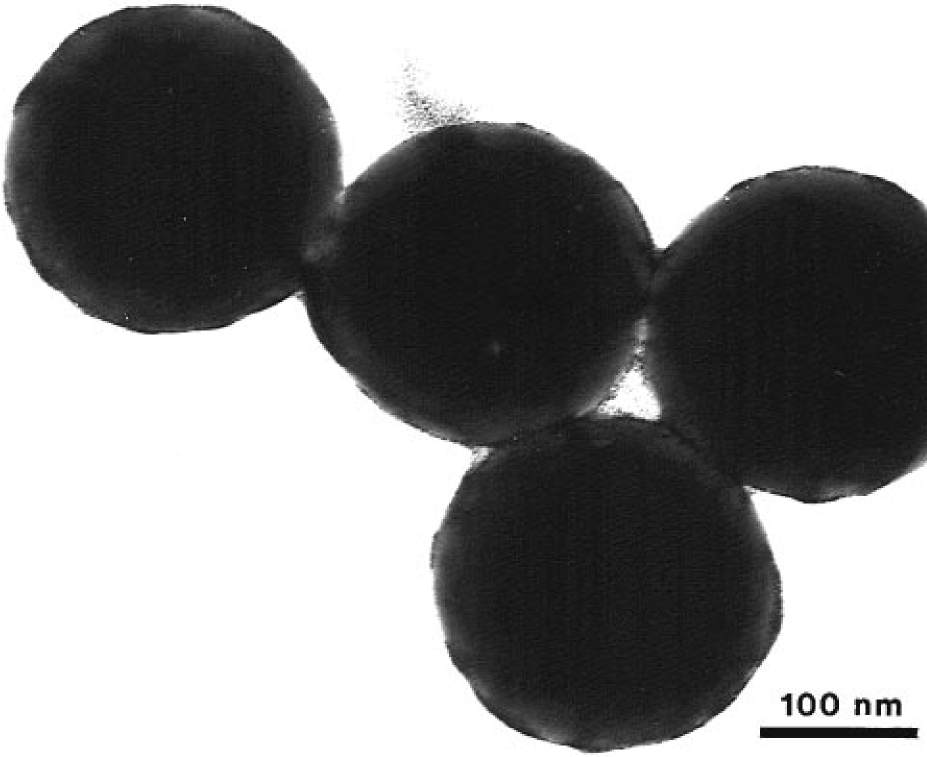

Figure 4. TEM micrograph of Si−DMES particles which have been treated with Karstedt's catalyst (i.e., Si-DMES-Pt).

reactions showed no indication of platinum agglomeration. This behavior is in marked contrast to Karstedt's catalyst which initially promotes hydrosilation in high yields but quickly degenerates into almost completely inactive metal aggregates.

In summary, we have demonstrated that SiH groups grafted to silica can be used to prepare supported nanosized platinum particles that are catalytically active toward hydrosilation reactions. We speculate that the hydridosilsequioxane network structure constrains the growth of the particles and prevents their aggregation.

The method described herein to prepare supported platinum particles may prove to be an attractive system to study the actual catalytic species involved in the hydrosilation reaction. The focus of future work will be to extend the preparation procedure to other metal compounds and to elucidate the structure of the platinum species and the platinum particle growth mechanism[32] in the presence of hydridosilsesquioxane-modified silica.

Acknowledgment. The financial support of the Natural Sciences and Engineering Council of Canada is greatly appreciated. The authors gratefully acknowledge Dr. Glen Facey (Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada) for performing the ^{29}Si CP-MAS NMR measurements on the hydridosilsequioxane-modified silica samples.

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(30) A typical experiment: To a solution consisting of bis(trimethylsiloxy)methylsilane (4.9 g, 22 mmol) and phenylacetylene (2.3 g, 22 mmol) was added Si−TES−Pt (0.3 g) dispersed in THF (5 mL). After heating at 60 °C for 8 h, the solids were removed by centrifugation and the supernatant was analyzed by ^{1}H NMR spectroscopy. The solids were washed three times with THF using centrifugation/redispersion cycles before use in a subsequent hydrosilation reaction.

(31) ^{1}H NMR analysis of the hydrosilation product mixture showed 61% of the E isomer, $PhCH{=}CHSiMe(OSiMe_3)_2$, obtained from the β addition, and 39% of the α product, $Ph(SiMe(OMe_3)_2)C{=}CH_2$. This was verified from the ratios of the vinyl signal areas obtained by integration of their respective ^{1}H NMR signals. β (*E*-isomer): ^{1}H NMR ($CDCl_3$) δ (ppm) 0.12 (s, 3H), 0.17 (s, 18H), 6.25 (d, 1H, $J = 19$ Hz), 6.95 (d, 1H, $J = 19$ Hz), 7.2−7.4 (m, 5H). α isomer: ^{1}H NMR ($CDCl_3$) δ (ppm) 0.05 (s, 3H), 0.19 (s, 18H), 5.69 (d, 1H, $J = 3$ Hz), 5.90 (d, 1H, $J = 3$ Hz), 7.2−7.4 (m, 5H).

(32) Whitesides and co-workers have studied the platinum-catalyzed reaction of dialkyl(diolefin)platinum(II) complexes with dihydrogen in the presence of glass beads coated with Pt(0). McCarthy, T. J.; Shih, Y.-S.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4649. More recently, work has appeared which describes in detail the mechanism of formation of Ir sols which may be generally applicable to the formation of metal nanoparticles. Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335.