# Hydrosilation Reactions Catalyzed by Supported Bimetallic Colloids

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*Received June 26, 1996*⊗

The preparation and catalytic properties of bimetallic colloids consisting of a ligand-stabilized Pt shell on Au or Pd cores supported by alumina are described. The aim of this work is to study the influence of the electronegativity of the colloidal core metals on the activity and selectivity of the surface Pt in hydrosilation reactions. Au is more electronegative and Pd is more electropositive than Pt. Results are compared to controls in which the hydrosilation reaction is catalyzed by colloids made of pure Pt which are also stabilized with the same ligands and supported by alumina. The reaction of HMTS with 1-octene to form bis(trimethylsiloxy)octamethylsilane (BTOMS) was selected to serve as an example of a typical hydrosilation reaction. The synthesis of the bimetallic colloids was accomplished by the seed-growth mechanism. The inner core consisting of Au (diameter = 18 nm) or Pd (diameter = 20 nm) was generated by the reduction of $HAuCl_4$ or $H_2PdCl_4$, respectively, by sodium citrate. The Pt outer shell was then grown on the core metals by the reduction of $H_2PtCl_6$ with hydroxylammonium chloride. The thickness of the Pt shell depended on the molar concentration of $H_2PtCl_6$. Colloidal Pt of undefined morphology is used in industrial processes which require temperatures as high as 120 °C and a 25% excess of the olefin in order to obtain quantitative yields of BTOMS. The hydrosilation process however became more efficient if Pt colloids of 9 nm diameter (Pt9) or bimetallic Au/Pt18/27 colloids (diameter Au core = 18 nm, thickness of Pt shell = 4.5 nm) were used. The first number indicates the diameter of the inner core metal and the second number indicates the total diameter of the bimetallic particle. Both types of colloids were stabilized by $p$-$H_2NC_6H_4SO_3Na$ (sodium sulfanilate) ligands. These colloid catalysts operated best at 60 °C and without a need for excess 1-octene. The yield of BTOMS is 92−93% after 24 h reaction time. The hydrosilation process was improved remarkably if bimetallic colloids made of Pd/Pt20/27 catalysts are used. A BTOMS yield of 90% was reached after only 4−6 h and became greater than 96% after a 24 h reaction period. In addition, ca. 1% of byproducts were formed and only 0.2% of the HMTS was left unreacted. Lifetime testing of the heterogenized colloids, especially of the optimal Pd/Pt system, indicated that catalytic activity was constant over at least six cycles. The results presented in this paper clearly prove that catalysts consisting of layered metals also demonstrate significantly enhanced activity resulting from mutual interaction of the component metals.

## Introduction

Hydrosilation reactions represent one of the most important routes in silicon polymer synthesis.[1] Complexes of transition metals containing Co, Ni, Pd, and Pt were thought to act as homogeneous catalysts in hydrosilation. However, it has been shown that these complexes serve only to form precursors of the true catalysts, which are in fact metal colloids formed from these complexes during the course of an induction period.[1−4] Reaction mechanisms formulated to describe homogeneous hydrosilation, for example those developed by Chalk and Harrod,[5] cannot be valid unless the homogeneous character of the reaction is guaranteed. Several groups have determined that the catalytic process is heterogeneous and proceeds with metal colloids rather than molecular complexes.[6−10] Among the transition metals, colloids made of Pt were shown to be the most effective catalysts in the hydrosilation process.[11,12]

The formation of metal colloids from molecular complexes in the induction period has disadvantages which are avoided by the direct use of prefabricated colloids. First of all, the size of prefabricated colloids can be strictly controlled, a condition not possible from metal complexes. Second, the complete hydrosilation process can be performed heterogeneously. A third advantage, and the purpose of this work, is the ability to enhance the catalytic properties of a known metal by forming it as a bimetallic species. In this case, as opposed to an alloying method, the active metal catalyst exists as a spherical shell over a core made of another metal and the catalytic area is increased. The use of these prefabricated colloids in catalysis offer another significant advantage. Because the metal colloids are stabilized (complexed) by simple ligands, they can be isolated and handled much like any “normal” chemical compound.[13−19]

The catalytic ability of bimetallic colloids which are basically alloys has been studied extensively. Layered bimetallic colloids

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

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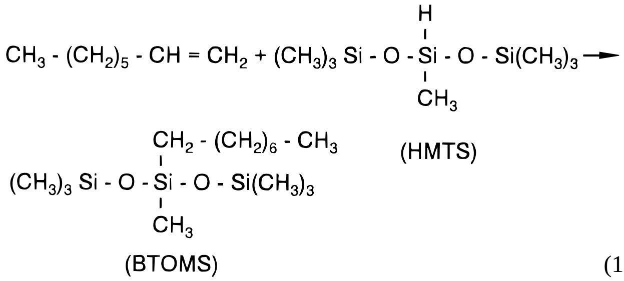
S0020-1669(96)00762-8 CCC: $14.00

have only recently been used by us, and we have demonstrated a considerable increase in activity over that of the monometallic species.[20] We have also shown that the ligand molecules of the heterogeneous bimetallic colloid have a definitive influence on selectivity during the process.[21] These findings have prompted us to continue to study the behavior of bimetallic colloids in catalysis, specifically that of hydrosilation.

Pt is known to be the most active metal in hydrosilation catalysis. We created bimetallic colloids with Pt shells surrounding cores consisting of Au or Pd. The purpose was to study the electronic influence of a metal more electronegative than Pt, namely Au, and of a metal more electropositive than Pt, namely Pd, on the activity and selectivity during hydrosilation. The hydrosilation of 1-octene by HMTS into BTOMS is shown in eq 1. This reaction is used as a standard for the study of catalysis in hydrosilation reactions. Because side reactions, also catalyzed by Pt, include the isomerization of 1-octene into less reactive octenes, an excess of the olefin (ca. 25%) is added in industrial processes to ensure the quantitative consumption of the silane. Because separation is expensive, isomers of the olefin as well as the unreacted educts remain part of the reaction mixture. This process is also energy intensive as temperatures near 120 °C are needed when Pt is used as a "homogeneous" catalyst.[22]



$$CH_3-(CH_2)_5-CH=CH_2+(CH_3)_3Si-O-\overset{H}{\underset{CH_3}{Si}}-O-Si(CH_3)_3 \longrightarrow (CH_3)_3Si-O-\overset{CH_2-(CH_2)_6-CH_3}{\underset{CH_3}{Si}}-O-Si(CH_3)_3 \qquad (1)$$

## Experimental Section

**General Procedures.** The synthesis of ligand-stabilized Au and Au/Pt colloids was accomplished according to the procedures described in refs 13 and 16. Transmission electron microscopy (TEM) was performed with JEOL JEM-200 CX (Cambridge) and a Philips CM 200 FEG (Essen) instruments. A DANI 8520 gas chromatograph linked to a Shimadzu C-R5A integrator was used for gas chromatographic analysis. The gas chromatograph was equipped with PONA capillary columns (cross-linked methyl silicon gum, film thickness equal to $0.5 \times 10^{-3}$ mm) with dimensions of 50 × 0.2 mm.

In order to successfully synthesize the metal colloids, the following precautionary measures were taken. First of all, glassware was treated with boiling aqua regia and washed carefully with deionized water. Any contact with organic materials such as grease or gum was avoided. The water used for the synthesis demonstrated a conductivity of less than 0.5 $\mu$S. The determination of the "Si−H" value was performed in an apparatus containing a jar charged with a specific amount of reaction mixture. A solution consisting of 5% $NaOC_4H_9$ (from 1.2 g of Na in 98.9 g of *n*-butanol) was added dropwise into the reaction mixture via a dropping funnel. Equivalent amounts of hydrogen gas, which indicate the amounts of nonreacted silane, were collected in a gas burette.

**Synthesis of Pt9 Colloids Stabilized by *p*-$H_2NC_6H_4SO_3Na$.** A 1.600 mL sample of deionized water was heated to boiling in a 2 L beaker. Then 12 mL of a 1.4% w/w solution of $H_2PtCl_6$ (6.6 g of Pt $L^{-1}$) were then added with stirring followed by addition of 80 mL of a 1% w/w trisodium citrate solution (10 g of $Na_3$-citrate·$2H_2O$ $L^{-1}$). After 4 h of boiling, a black dispersion containing 80 mg of colloidal Pt was formed. The colloids were stabilized by addition of 0.5 g of *p*-$H_2NC_6H_4SO_3Na·2H_2O$ which was added after cooling to room temperature. The colloids were isolated by evaporating the water at a temperature of 60 °C under vacuum (water jet pump) until agglomeration of the colloids was detected. This precipitate was then separated by centrifugation at 5000 rpm. The colloid fraction was then washed with 2−5 mL of deionized water. The centrifugation was repeated but the colloids were now washed in 2−5 mL of ethanol. The stabilized colloid precipitate should demonstrate a metallic sheen.

**Synthesis of Pd/Pt20/27 Colloids Stabilized by *p*-$H_2NC_6H_4SO_3Na$.** The seed colloids of Pd were generated per the procedure of Turkevich from $H_2PdCl_4$ and trisodium citrate.[23] A 15 mL sample of 0.37 M $H_2PdCl_4$ solution and 60 mL of 0.68 M trisodium citrate solution were added to 3000 mL of deionized water in a 4 L beaker and heated to boiling. After 24 h, a dark brown dispersion consisting of 20 nm Pd colloids was formed. After cooling to room temperature, the reaction mixture was diluted to 8 L. Then 1.5 L of $H_2PtCl_6$ (from 3.92 mmol Pt and 20.0 mmol hydroxylammonium chloride) were added over the course of 10 h. After this was stirred for 24 h at room temperature, 0.5 g of *p*-$H_2NC_6H_4SO_3Na·2H_2O$ were added. The colloids were purified by centrifugation as given above for Pt.

**Synthesis of Au/Pt18/27 Colloids Stabilized by *p*-$H_2NC_6H_4SO_3Na$.** The synthesis of ligand-stabilized Au/Pt colloids has been described by us in 1991.[16]

**Preparation of the Catalysts.** The corresponding ligand-stabilized colloid precipitate was dispersed in 1 L of deionized water. Enough $Al_2O_3$ substrate was added to result in a mixture that was 0.25% w/w in terms of colloid/substrate. The mixture was stirred until the solution became colorless. After filtration, the catalyst was dried under vacuum at room temperature and was ready for use.

**Hydrosilation Reactions.** Equimolar amounts of HMTS and 1-octene together with the catalyst were mixed in a 50 mL 3-necked flask equipped with a reflux condenser and a contact thermometer. The mixture was then heated to the desired reaction temperature (120 or 60 °C) and kept constant until completion. The progress of the reaction was monitored by gas chromatography to determine the Si−H values. The Si−H level indicates the amount of unreacted silane and was registered by means of volumetric measurement of gaseous hydrogen which is evolved from the reaction of the silane with sodium butanolate. Then 1 g of catalysts was used to react with 67.5 mmol of HMTS and equivalent amounts or a 25% excess of 1-octene. In order to control the effect of other possible catalytic influences, test reactions without metal colloids were also conducted at 120 °C.

## Results and Discussion

**(a) The Catalysts.** The layered structure of Au/Pt and Au/Pd colloids was detected by us by means of HRTEM (high resolution transmission electron microscopy) and confirmed by EDX (energy dispersive x-ray) analysis.[16] In the case of Au/Pd, the outer Pd shell was homogeneous and resembled a uniform spherical shell surrounding the spherical Au core. This was not the case for the Au/Pt particles. The Au/Pt colloids consisted of the same Au core but were not surrounded by a uniform contiguous layer of Pt. The Au was covered with Pt particles of ca. 5 nm in diameter which were probably formed in a separate nucleation process and then adsorbed onto the surface of the Au. This phenomenon may be due to the broad miscibility gap of Au and Pt between 2 and 85 wt.-% Au in mixtures.[24] HRTEM analysis of the pure Pt colloid catalysts showed an average particle size of 9 ± 2.3 nm. In addition, all colloids were characterized by elementary analyses. As ligand-stabilized colloids cannot be regarded as stoichimetrically well-defined molecules, analytical data can only inform on average

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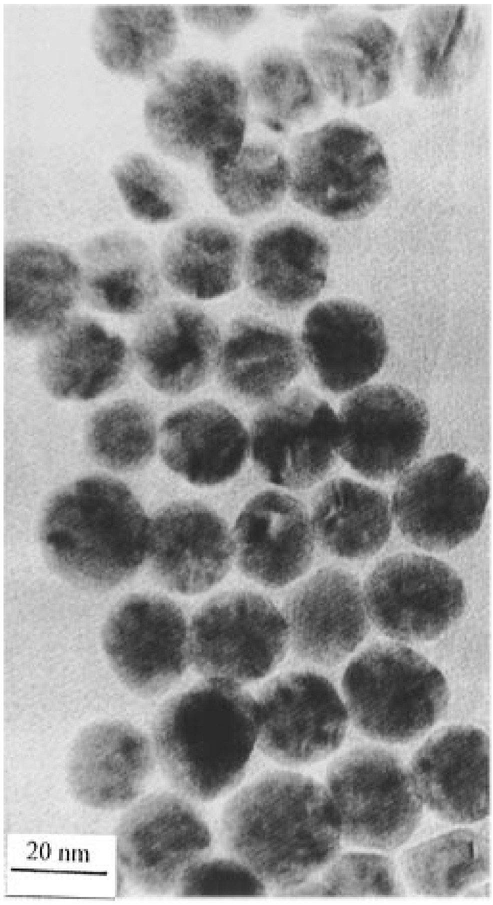

**Figure 1.** Transmission electron microscopic image of ~ 20 nm palladium colloids.

compositions. The purified solid colloids described in this paper consist of ca. 95% metal and 5% ligands.

The morphology of the Pd/Pt colloids differed significantly from that of the Au/Pt colloids. Although both bimetallic colloids were formed essentially by the same seed-growth procedure[25] (see Experimental Section), a relatively uniform Pt shell was formed on the Pd nanometal core. The amount of $H_2PtCl_6$ added to the Pd colloid dispersion determined the thickness of the Pt shell and the resulting diameter was easy to calculate.[20] Figure 1 shows a HRTEM image of 20 ± 3 nm Pd colloids stabilized with sodium sulfanilate ligands. As one can see, the size distribution is relatively small. A Pt layer equal to 3.5 nm in thickness was added to the Pd metal cores, resulting in an overall diameter of 27 nm, and are shown in Figure 2. It is evident that the smooth Pd nanometal cores are covered with a darker Pt layer which is not uniform but varies in thickness (illustrated by the alternating of light and dark areas). A magnification of the regions discussed is shown in Figure 3.

As one discusses layered bimetallic particles, the question of migration processes may arise. Several papers deal with this phenomenon; however, migration has been shown to happen in the topmost atomic layers.[26,27] The interface of the two different metals in the colloids discussed in this paper is far below the surface. As has been demonstrated on Au/Pd colloids, remarkable mixing of the two metals can be observed at temperatures far above those applied here.[28]

As stated before, stabilization of the bimetallic colloids made them easy to handle. With Pt as the surface metal, we found that sodium sulfanilate was the most effective ligand. The $Al_2O_3$, doped with 0.25 wt. % of a specific colloid, served as the supporting material for the ligand-stabilized metal and bimetallic colloid catalysts. TEM images of the colloids on the support before and after the catalysis prove their stability in size. Hydrosilation reactions were catalyzed by monometallic systems consisting of Pd20 and Pt9 (both stabilized by sodium sulfanilate) and Au18 (stabilized by $P[C_6H_4SO_3Na]_3$). The bimetallic colloid systems were all stabilized by sodium sulfanilate and consisted of Au/Pt18/36, Au/Pt18/27, and Pd/Pt20/27.

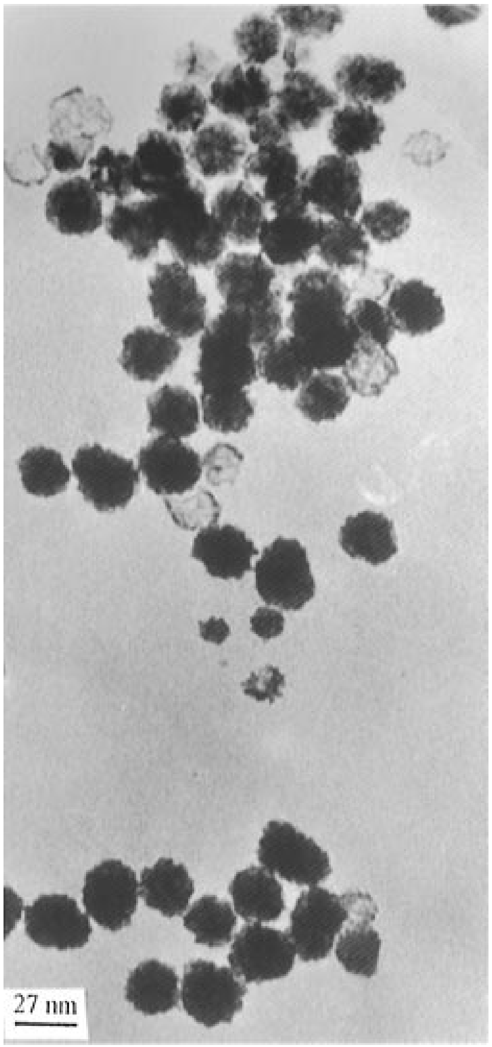

**Figure 2.** Transmission electron microscopy of an assembly of bimetallic palladium−platinum colloids. The 20 nm Pd core is coated by darker looking Pt of an average thickness of 3.5 nm, resulting in ca. 27 nm particles (Pd/Pt 20/27).

**(b) Au/Pt Catalysts.** The first experiments with the Au/Pt catalytic system were conducted under the industrial conditions mentioned earlier (120 °C and 25% excess of olefin).[22] The initial reaction rate following 6 h of hydrosilation converted 50% of the HMTS into BTOMS. After 3 days, 93% of the reactant was converted into BTOMS. Unfortunately, the catalyst was more or less deactivated after just one hydrosilation cycle. Because of this apparent deactivation, the reaction temperature was decreased to 60 °C and the HMTS/1-octene ratio was decreased to 1:1. The results are shown in Figure 4. From Figure 4 it can be concluded that ca. 90% of BTOMS is formed

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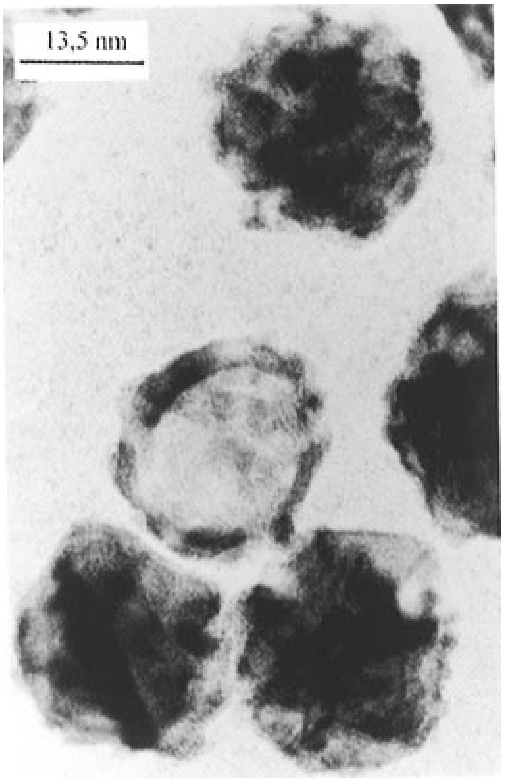

**Figure 3.** Magnified TEM images of Pd/Pt 20/27 colloids. Lighter and darker areas indicate irregular Pt coating.

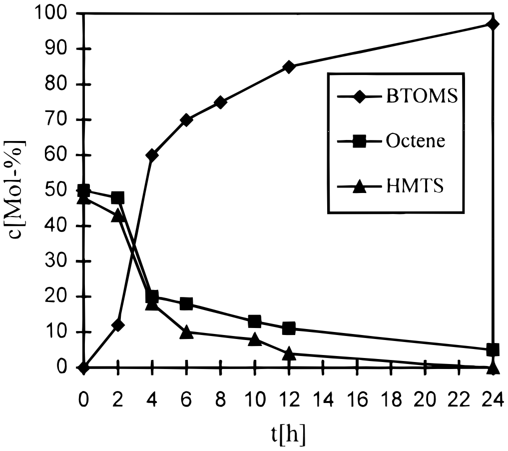

**Figure 4.** Hydrosilylation of 1-octene by heptamethyltrisiloxane (HMTS) (molar ratio 1:1) to bis(trimethylsiloxy)octylmethylsilane (BTOMS) at 60 °C using Au/Pt 18/36 on $Al_2O_3$ as catalyst.

after a 24 h period with less than 1% of byproducts. It should also be pointed out that, again from Figure 4, an induction period was detected. We hypothesize that the reasons for this induction period is the time necessary to remove oxygen from the colloid surfaces, which is always present after preparing in the presence of air. The projected lifetime of the catalyst can be deduced from Figure 5. After four cycles, the activity was reduced to about 70% of the original value.

The same catalyst but with a thinner coating of Pt (Au/Pt18/27) demonstrated improved properties. Under identical conditions, the yield of BTOMS was ca. 92% after 24 h reaction period, and after six cycles, the activity remained unchanged. These results are shown in Figure 6. The results of the Au/Pt18/27-catalyzed reactions are summarized in Table 1. For the remaining experiments, the reaction results are summarized in tables showing the concentration of components as a function of time.

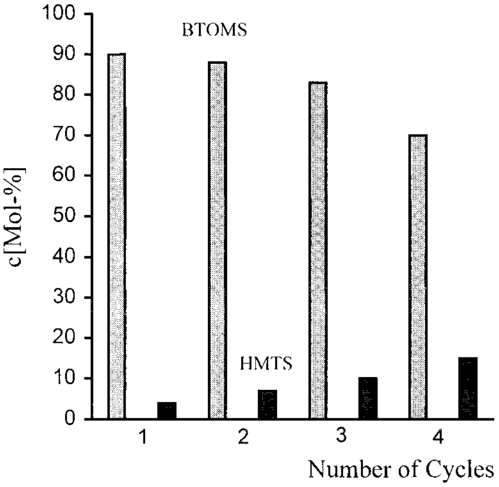

**Figure 5.** Stability of the Au/Pt 18/36 catalyst during BTOMS formation at 60 °C. After 4 cycles the yield of BTOMS is reduced from 90% to ca. 70%.

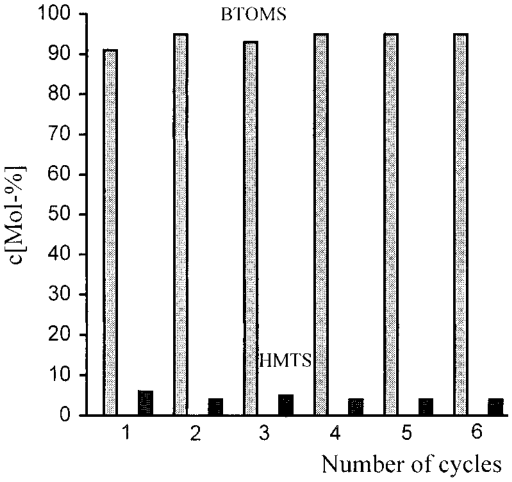

**Figure 6.** Stability of the Au/Pt 18/27 catalyst at 60 °C. After six cycles the activity is practically the same as at the beginning.

**Table 1.** Formation of BTOMS from HMTS and 1-Octene (1:1) with Dependence on Time with Au/Pt 18/27 on $Al_2O_3$ at 60 °C

| time (h) | BTOMS (mol %) | byproducts (mol %) | HMTS (mol %) |
|---|---|---|---|
| 2 | 19.8 | 0.4 | 20.8 |
| 6 | 78.7 | 1.3 | 7.7 |
| 12 | 81.5 | 1.7 | 5.4 |
| 24 | 91.5 | 3.0 | 1.5 |

**Table 2.** Formation of BTOMS from HMTS and 1-Octene (1:1) with Dependence on Time with Pd/Pt 20/27 on $Al_2O_3$ at 60 °C

| time (h) | BTOMS (mol %) | byproducts (mol %) | HMTS (mol %) |
|---|---|---|---|
| 2 | 63.9 | 1.5 | 13.5 |
| 4 | 89.4 | 1.5 | 3.0 |
| 6 | 93.5 | 1.4 | 1.0 |
| 12 | 95.8 | 1.4 | 0.8 |
| 24 | 96.3 | 1.2 | 0.2 |

**(c) Pd/Pt Catalysts.** The use of Pd, an electropositive metal with respect to Pt, instead of Au, leads to a remarkable improvement of catalytic properties. Pd/Pt20/27 bimetallic colloid catalysts accelerated the conversion of HMTS into BTOMS dramatically. After only a 4 h reaction period, an 89% yield of BTOMS was achieved. After a 24 h reaction period, the yield was ca. 96% with only ca. 1% byproducts. Results are listed in Table 2. Lifetime testing demonstrated results that were similar to the Au/Pt18/27 colloid system shown in Figure 6.

**Table 3.** Formation of BTOMS from HMTS and 1-Octene (1:1) with Dependence on Time with Pt9 on $Al_2O_3$ at 60 °C

| time (h) | BTOMS (mol %) | byproducts (mol %) | HMTS (mol %) |
|---|---|---|---|
| 2 | 15.7 | 0.5 | 37.8 |
| 4 | 47.8 | 0.4 | 20.6 |
| 6 | 63.7 | 1.7 | 15.6 |
| 12 | 80.2 | 1.6 | 8.4 |
| 24 | 93.1 | 1.6 | 0.6 |

**(d) Pt Catalysts.** The catalytic metal in all of our bimetallic species was Pt, and therefore, colloids made of pure Pt were used as controls in this experiment. The activity of ligand-stabilized Pt9 on $Al_2O_3$ was comparable to that of the Au/Pt species. Results are summarized in Table 3. After 4 h of reaction, just ca. 48% BTOMS is formed. The 90% mark was only reached after a 24 h reaction period. The lifetime of the pure Pt colloid was very good and can be seen in Figure 7. The activity was fairly constant over six cycles of hydrosilation. Neither Pd20 nor Au18 demonstrated any catalytic activity of the hydrosilation reaction. Increasing the temperature to 120 °C from 60 °C did not induce catalytic activity of colloids made of pure Au or Pd.

## Summary and Conclusions

The combination of Pt, the most active catalyst for hydrosilation reactions, with Au in the form of a bimetallic layered colloid with Pt on the surface did not improve catalytic properties over that exhibited by colloids made of pure Pt. If Pd was used as the core metal, the surface Pt undergoes a remarkable positive shift in activity without any decrease of selectivity. Lifetime testing of Pd/Pt catalysts also indicated that the activity is stable over at least six cycles of hydrosilation under 60 °C conditions.

Recently we have shown that the combination of Au and Pd in layered colloids both lead to a considerable improvement of catalytic activity and selectivity in the semihydrogenation of 2-hexyne into *cis*-2-hexene.[20] In the experiment described here, only the Pt-coated Pd catalysts showed significant improvement in activity and selectivity. The two experiments show once again that the activities of potential catalysts cannot be easily predicted.

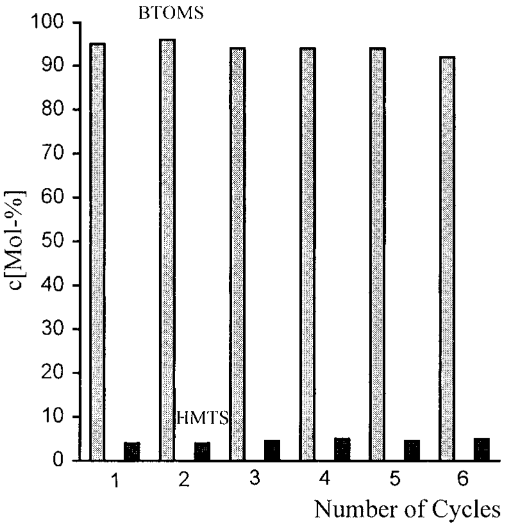

**Figure 7.** Stability of the Pt9 catalyst at 60 °C. The activity is constant over six cycles.

In order to elucidate the electronic situation in bimetallic systems combined with a third component, namely the alumina supporting material, we have started investigations on the molecular level by techniques such as scanning tunneling microscopy (STM). This seems to be the only means of clarifying the “black-box” of heterogeneous catalysis.

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