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Synthesis of Polysiloxane Stabilized Palladium Colloids and Evidence of Their Participation in Silaesterification Reactions

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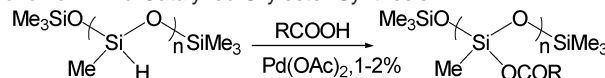
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Interest in the synthesis and properties of colloidal metal particles and metal clusters has grown constantly because of their unique properties. For noble metal colloids, especially catalytic applications are considered, because a unique combination of reactivity, stability, and selectivity is expected.^{1–3}

Various noble metal colloids stabilized by surfactants and solvents have been used for hydrogenation,^{4–6} Heck,⁷ and Suzuki⁸ coupling reactions. Even enantioselective hydrogenation reactions on noble metal colloids with chiral ligands have been performed.⁹ The controlled generation of Pd colloids is also promising for a number of other reactions, such as oxidative conversions and cyclizations.^{10–12} On the other hand, in the case of catalytic transformation involving silicon, only platinum-catalyzed hydrosilylation reactions are known to undergo the Si–C bond formation reaction via Pt colloid formation.¹³

Recently, we have described a novel route to biodegradable polysilylestere, via esterification of polyhydrosiloxanes in the presence of Pd(OAc)₂ (Scheme 1).^{14a}

Scheme 1. Pd-Catalyzed Silylester Synthesis



During these studies, the following observations led us to investigate this catalysis in detail: (i) When hydrosilanes were added to the reaction mixture containing catalytic amounts of Pd(OAc)₂, the color of the solution turned black accompanied by gas formation, presumably H₂. (ii) After the transformation was complete, a black precipitate was formed, and the solution became colorless. (iii) The black precipitate can be redispersed in the solution and was found catalytically active for silylesterification reactions, thus allowing recyclability.

On the basis of these elucidations, we decided to investigate the possibility that Pd colloids were formed during the catalysis and these particles were the active catalysts. In this communication, we present the first example of soluble polysiloxane network stabilized Pd colloids and unequivocal evidence of their participation in Pd(OAc)₂-catalyzed Si–H to Si–OCOR bond transformations.

In a Schlenk tube, Pd(OAc)₂ (0.004 g, 0.02 mmol) and acetic acid (0.06 mL, 1.00 mmol) were dissolved in 2.5 mL of benzene, and the mixture was examined by UV–visible spectroscopy. A peak at 400 nm indicative of Pd(OAc)₂ was observed (Figure 1a). Polymethylhydrosiloxane **1** (PMHS) (0.06 mL, 1 mmol, mw ≈ 2000, 33–35 Si–H units) was added, which was accompanied by generation of a gas, presumably H₂. After 5 min of addition of **1**, the Pd(OAc)₂ peak (400 nm) disappeared completely (Figure 1a), indicating the formation of a new catalytically active species.

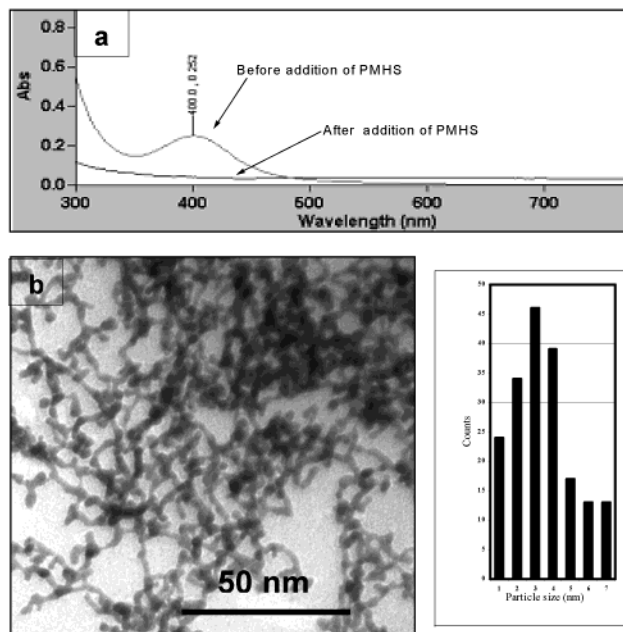


Figure 1. (a) UV–visible spectra of the reaction mixture; (b) TEM image and the particle size analysis of the Pd colloids obtained after the addition of starting materials (no staining was required).

One drop was deposited on Formvar/carbon coated grid and analyzed by transmission electron microscopy (TEM) (Figure 1b). As is evident from Figure 1b, Pd colloids were formed after the addition of PMHS and were stabilized by siloxane polymer network. Particle size analysis showed the average particle size of 6 nm with a standard deviation of 1 nm.

After completion of the catalysis, the precipitated black sticky solid was analyzed by scanning electron microscopy (SEM), IR, and multinuclear NMR techniques. Silicon moieties were present in the solid as evidenced by ²⁹Si NMR. The peaks at δ –36.15, –64.74, and –75.74 ppm correspond to a polymeric network containing Si–H, SiOCOR, and Si–OH moieties, respectively. The signal at δ –110.94 ppm indicates fully condensed network. FT-IR spectra also displayed characteristic signals associated with SiH and Si–O–Si bonds. SEM analysis (Figure 2) of this solid was also undertaken. Particles were found to be in the nanometer size regime (40–50 nm) and were stabilized by the polymeric network.

After product isolation, the remaining sticky solid was washed with benzene, and the same catalysis was repeated again. A black solution was obtained after addition of the reactants. Catalysis was continued until total conversion to silylester, indicating that the presence of silicon network stabilization facilitates the redispersion of catalytically active Pd particles.

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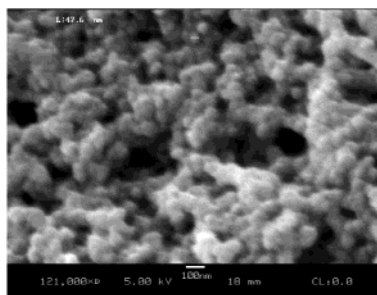


Figure 2. SEM image of the gummy solid obtained after the catalysis.

Table 1. Comparison of the Catalytic Activity

acid	silane	Pd colloids	2% Pd(OAc) ₂	yield
CH ₃ COOH	2	rt, 5 h	rt, 8 h	95%
CH ₃ COOH	1	70 °C, 12 h	70 °C, 3.5 h	95%
C ₆ H ₅ COOH	2	70 °C, 6 h	70 °C, 6 h	95%
C ₆ H ₅ COOH	1	70 °C, 24 h	70 °C, 24 h	85%

To further probe the identity of the “real catalyst”, poisoning experiments using mercury, as well as added ligand (PPh₃), were performed.¹⁵ A standard reaction mixture was prepared, and after addition of the polysiloxane (i.e., after generation of Pd colloids), 2.5 equiv of Hg was added to the reaction mixture. After 30 min, the reaction mixture became completely clear and was examined by NMR and TEM. Only 15–20% of the expected product was formed. If the catalysis was continued for an even further 24 h, there was no increase in the silyl ester formation. Under identical reaction conditions, the quantitative conversion to corresponding silyl ester takes place after 3.5–4 h.

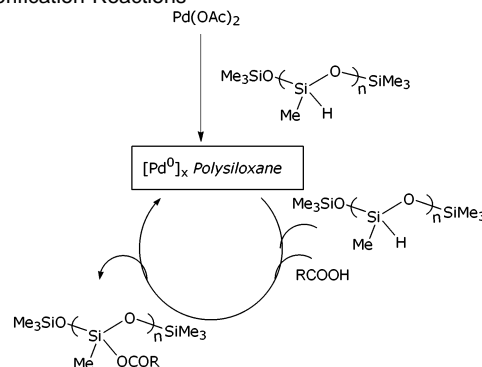
When the silyl esterification was carried out in the presence of PPh₃ (3:1 PPh₃:Pd(OAc)₂), no reaction took place under standard conditions even after 18 h. If PPh₃ was added after the generation of the Pd colloids, only 25% conversion of reactants to product was obtained after 24 h of reaction.

Catalyst poisoning tests along with UV, TEM, and catalyst isolation (evacuation to dryness) and then reuse experiments firmly establish that Pd colloids are the real catalysts in the present system. On the basis of this evidence, it seems plausible that the silicones play the role of intermediate host stabilizing agents.

We also investigated the independent generation of Pd siloxane networked particles by reacting **1** (0.06 mL, 1 mmol) with Pd(OAc)₂ (0.09 g, 0.4 mmol) in 20 mL of benzene. After 2 h of stirring at room temperature, the obtained black precipitate was filtered and washed with an excess of benzene. SEM showed similar particle size distribution, and ²⁹Si displayed peaks at the same positions as in the case of the solid obtained from catalytic reactions. This powder was used as catalyst for silyl esterification reactions of polymer **1** and its monomeric model siloxane 1,1,1,3,5,5,5-heptamethyl trisiloxane **2**. Under identical reaction conditions and molar ratios, independently generated Pd colloids showed similar catalytic efficiency as in the case of previous experiments (see Table 1).

Our mechanistic proposal is presented in Scheme 2. The first step in the catalysis is hydrosilane induced reduction of Pd(OAc)₂ to colloidal Pd particles, and their stabilization by hydrosilane polymer matrix. Stabilized Pd colloids undergo the oxidative-addition and reductive-elimination sequence with Si–H and COOH bonds to produce silyl esters.^{14b}

Scheme 2. Mechanistic Proposal for the Pd Colloid-Catalyzed Silyl esterification Reactions



After total consumption of Si–H and COOH bonds, these particles precipitate out along with silicon matrix. When these particles are recharged with Si–H and acid containing moieties, they redisperse and again undergo the oxidative-addition, reductive-elimination sequence. The presence of the soluble polysiloxane matrix (which is not fully condensed in the form of silica) allows for particle redispersion, hence making them recyclable.

In conclusion, we have successfully demonstrated Pd particle stabilization by polysiloxane network and their active role as a recyclable catalyst in the silyl esterification reactions. We are further examining the catalytic efficiency of polysiloxane stabilized Pd colloids for industrially important conversions.

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Supporting Information Available: Experimental details, TEM images (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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