

Preparation of Dendritic Carbosilane-supported Palladium Catalyst and Its Catalytic Activity in Hydrogenation of Organic Compounds

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Abstract: The preparation of palladium complex from PdCl₂•2H₂O and carbosilane dendrimers with peripheral aminopropyl groups was described. The compound obtained was characterized by IR, ¹H NMR, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectrometric (ICP-AES) spectroscopy respectively. The metal complex was employed as catalyst in hydrogenation of organic compounds. The high activity of the complex was probably due to the formation of the coordinatively unsaturated palladium.

Keywords: Dendrimer, complex, catalysis.

A great deal of interest has been shown in the field of dendrimer during the past decade¹⁻¹⁰. Among the main potential applications of dendrimer, catalysis stands as one of the most promising applications, because dendrimers offer a unique opportunity to combine the advantages of homogeneous and heterogeneous catalysis¹¹. It is possible to change the structure, size, and solubility of dendrimers and metallodendrimers at will¹². It has been demonstrated that this metallodendritic catalyst is possible to remove from the reaction medium after reaction.

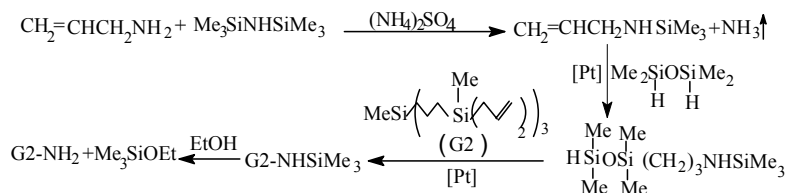
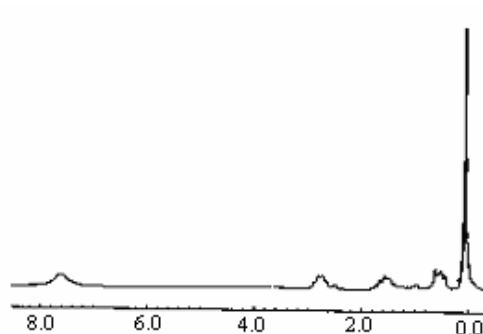
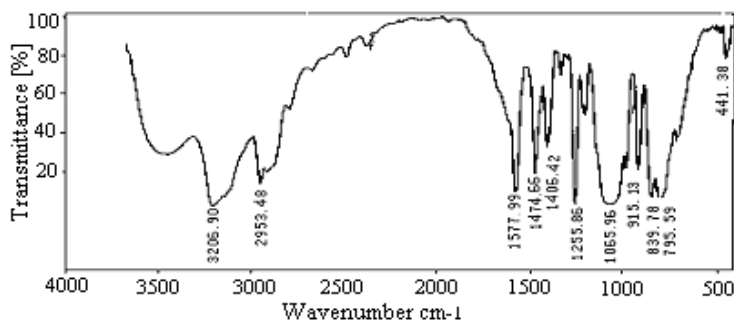
In previous report, we detailed a novel synthetic methodology for the production of metallodendrimer catalysts, *via* a procedure involving attachment of aminopropyl to the carbosilane dendrimer periphery. The resulting dendrimer ligands were transmetalated affording catalytic units of Pt complex¹³. In this paper, we have prepared another dendritic carbosilane-supported Pd complex and further explored its catalytic activity in the hydrogenation of organic compounds.

Results and Discussion

Recently, we reported the synthesis of carbosilane dendrimer functionalized with aminopropyl group (**Scheme 1**), and this system could be converted into metallodendrimer¹³.

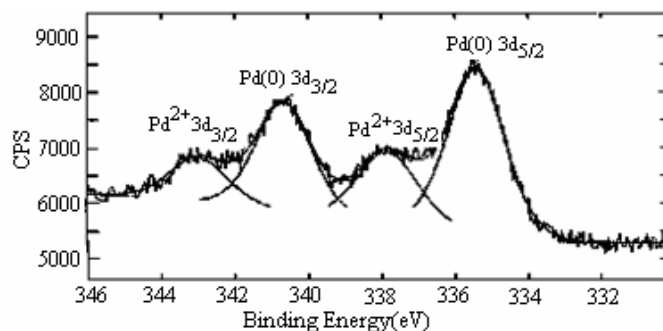
The number of amino group of the carbosilane dendrimer could be calculated by titration with perchloric acid in acetic acid: RNH₂+HClO₄→RNH₃⁺ClO₄⁻.

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Scheme 1 Synthesis of carbosilane dendrimers functionalized with aminopropyl group**Figure 1** ^1H NMR spectrum of palladium dendritic carbosilane in DMSO-d₆**Figure 2** Infrared spectrum of palladium dendritic carbosilane

We extended the earlier studies and prepared a novel palladium catalyst containing carbosilane dendrimer with the N→PdCl fragments attached to the dendritic backbone. The palladium derivative was obtained by a one-step reaction. Treatment of the carbosilane dendrimers functionalized with aminopropyl groups with PdCl₂·2H₂O in refluxing ethanol for 5 h afforded a brown powder after filtration.

The palladium dendritic carbosilane was characterized by IR, ^1H NMR, XPS and ICP-AES spectroscopy. Direct evidence for palladium carbosilane was provided by ^1H NMR spectrum of the complex, which displayed a low-field shift (δ 7.40-7.80 ppm). And in the infrared spectrum, the absorption bands of secondary amine salt (3207 cm⁻¹ and 1578 cm⁻¹) appeared. The measurement of the content of Pd with ICP-AES gave 4.90%. ^1H NMR and IR spectra of the palladium dendritic carbosilane were shown in **Figure 1** and **Figure 2**.

Figure 3 XPS spectrum of palladium dendritic carbosilane

The binding energies of the palladium $3d_{3/2}$, $3d_{5/2}$ were determined for this dendrimer complex with X-ray photoelectron spectroscopy (XPS). The complex has slightly lower Pd (3d) binding energies than PdCl_2 and the Cl(2p) binding energy is similar to that of PdCl_2 . The XPS spectra showed that the valence state of the metal ion was Pd(II). Pd(0) could also be detected simultaneously, indicating that the complex exists as expected. XPS spectrum of the palladium dendritic carbosilane was shown in **Figure 3**.

Some representative rates of initial hydrogen uptake for hydrogenation of organic compounds at 30°C under an atmospheric hydrogen pressure are given in **Table 1**.

The reaction showed an induction period of about 3 minutes without pretreatment of the catalyst with hydrogen. This dendrimer complex was an effective catalyst for the reduction of the C=C bond and carbonyl group. The rate was greatly affected by change of the solvent; nonalcoholic solvents, such as THF, acetone, toluene, *iso*-PrOH and *n*-butanamine necessitated the use of high pressure of hydrogen. In comparison with monomeric-analog $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$, this dendrimer catalyst was more active for hydrogenation. The rate of styrene hydrogenation in ethanol was twenty times faster than that of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ under the same Pd concentration. Other notable difference was that the monomeric catalyst produced palladium plating during the reaction.

The remarkable increase in activity of this dendrimer-supported catalyst may be mainly due to the formation of coordinatively unsaturated palladium. The dendrimer catalyst can be reused without loss in activity. The details of the catalyst nature and hydrogenation mechanism are under investigation.

Table 1 Hydrogenation rates of organic compounds ^a

Substrate	Initial Rate (mL/min)
Styrene	2.25
1-Hexene	0.50
Allyl alcohol	0.077
Acetophenone	1.1
Benzaldehyde	0.91
Benzophenone	0.066

a. Using dendrimer-Pd complex 0.023 mmol, 0.05 mol substrate, 1 atm of hydrogen at 30°C in [15-(volume of substrate)] mL of ethanol.

Experimental

General all sensitive, organometallic manipulations were performed under a dry and deoxygenated nitrogen atmosphere. All solvents were carefully dried and distilled *prior to use*. The reagents that were purchased commercially were used without further purification. The starting material G2-NH₂ was prepared according to literature procedure. XPS spectra were recorded on ESCALab 220i-XL electron spectrometer. ¹H NMR spectrum was recorded on a JEOL FX-90Q instrument. IR spectrum was recorded on a Nicolet 10sx FT-IR instrument. ICP-AES was done on IRIS-advantage (Thermo Electron, Boston, U. S.) instrument.

Preparation of periphery palladium carbosilane dendrimers: Into a 100 mL flask were added 1.10 g of G2-NH₂ (2.8 mmol as aminopropyl groups), 0.30 g of PdCl₂•2H₂O and 20 mL of anhydrous EtOH, the reaction mixture was refluxed for 5 h, a brown suspension was obtained, then the solid was isolated by centrifugation, and dried in vacuum to give a brown solid (0.84 g, 60% yield). ¹H NMR(DMSO-d₆, δ ppm) -0.10-0.10(m, Si-CH₃), 0.40-0.70(m, Si-CH₂CH₂-), 1.30-1.70(m, Si-CH₂CH₂CH₂Si-), 2.60-2.90(m, -CH₂NH-), 7.40-7.80(m, Pd←NH<). IR(cm⁻¹, neat): 3448(m), 3207(m, -CH₂NH-), 2953(m), 1578(s, Pd←NH<), 1475(s, -CH₂-NH-), 1256(s, Si-(CH₃)₃), 1066(m, Si-O-Si), 839(s), 795(s).

Hydrogenation of organic compounds with the palladium carbosilane dendrimer: The dendrimer complex and the solvent were added to a 50 mL reaction flask and the hydrogen pressure was set near 1 atm.; The substrate were added at stirring and the volume of hydrogen uptake at constant pressure was measured.

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