Dendrimer-Encapsulated Pd Nanoparticles as Fluorous Phase-Soluble Catalysts

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Here we describe the application of dendrimer-encapsulated Pd nanoparticles to fluorous biphasic catalysis.[1] Complexation of Pd/dendrimer composites with perfluorinated carboxylic acids renders the resulting nanocomposites preferentially soluble in fluorinated hydrocarbons. These new catalysts show high activity and selectivity for biphasic hydrogenation of alkenes and conjugated dienes. Moreover, the catalysts can easily be recovered and used for multiple reactions.

Reactions in biphasic fluorous/organic systems were suggested by Horvath and Rabai in 1994[2] to facilitate recovery and recycling of soluble catalysts. The general approach to biphasic catalysis is illustrated in Scheme 1.[3] The system consists of organic and fluorous layers. The catalyst is selectively soluble in the fluorous phase, while the reactants are preferentially soluble in the organic solvent. Stirring, sonicating, and/or heating of the mixture leads to formation of a fine emulsion and partial homogenization (with some solvents, complete homogenization is obtained at elevated temperatures), and the catalytic reaction proceeds at the interface between the two liquids. When the reaction is over, the liquid phases are separated, the product is isolated from the organic phase, and the catalyst-containing fluorous layer is recycled. Such easy separation and recycling are particularly attractive in terms of "green chemistry", and a number of fluorous phase-soluble catalysts have been reported in the literature, including some based on metal complexes.[4,5] Preparation of fluorous phase-soluble metal nanoparticles, however, has not previously been reported.

Catalytic properties of metal nanoparticles have been explored since the pioneering studies of Rampino and Nord in the early 1940s.[6] Over the past decade research in this area intensified,[7] because catalysis by nanoparticles is the most efficient type of heterogeneous catalysis. This is, of course, a consequence of the increase in total surface area with decreasing particle size. For example, 63% of Pd atoms in a 1.4-nm Pd particle are on the surface of the particle and thus available to perform a catalytic function. Apart from high efficiency, metal nanoparticles often show unique selectivity properties, which in some cases are superior to those of the bulk materials.[8]

An important drawback of colloidal catalysts is that they are difficult to separate from reaction mixtures and recycle. However, the fluorous-phase, biphasic strategy described here combines the high efficiency and selectivity of homogeneous catalysis with the ease of separation and recyclability of heterogeneous catalysis. Our approach is based on the synthesis of dendrimer-encapsulated metal nanoparticles.[9] To enhance solubility of the catalyst-carrying poly(amidoamine) (PAMAM) dendrimers in fluorous solvents,

Scheme 1
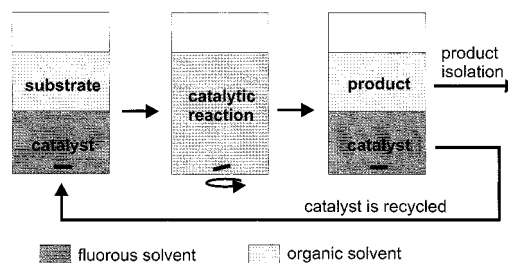
they were noncovalently modified with perfluoropolyethers.,[10,11] This was achieved by complexing the terminal dendrimer amine groups with the carboxylic end groups of the perfluoropolyethers.

Figure 1 shows a biphasic toluene/perfluoro-2-butyltetrahydrofuran (Fluoroinert FC-75) mixture containing dendrimer-encapsulated Pd nanoparticles complexed with poly(hexafluoropropylene oxide-*co*-difluoromethylene oxide) monocarboxylic acid, MW ∼550. The dark brown Pd/dendrimer catalyst resides exclusively in the fluorous phase. To the best of our knowledge, this is the first example of a stable solution of metal nanoparticles in fluorous solvents.

To probe the catalytic properties of this biphasic system, we performed hydrogenation of alkenes. Tetrahydrofuran and FC-75 were used as organic and fluorous solvents, respectively. The structures of the substrates used in these experiments and the corresponding turnover frequencies (TOFs) are shown in Table 1. The identity of the reaction products was confirmed by NMR after isolation,[12] and the TOFs were calculated from the rate of hydrogen uptake or the accumulation of product assessed by NMR. In some cases we calculated the TOF using both methods and found the results to be nearly identical. Interestingly, we found that addition of polar organic substrates to the reaction mixture often caused precipitation of the catalyst. This is likely due to competition between the substrate and the perfluorinated acid for the amine groups of the dendrimer. This problem was circumvented by using a large excess of the perfluorinated acid. We also note in passing that formation of a fine emulsion and vigorous stirring are critical for obtaining reproducible TOF values. The settling time for such emulsions depends on the substrate but ranges from a few seconds to 5 min.

The key result from this study is that the Pd/dendrimer nanocomposites are catalytically active in fluorous biphasic systems. Indeed, one catalyst was recycled 12 times, as shown in Scheme 1, without appreciable loss of catalytic activity. Despite significant mutual solubility of THF and FC-75, leaking of the catalyst into the organic phase was not observed within experimental error (∼1% of the total amount of catalyst).

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(1) The term "fluorous phase" refers to solutions prepared using perfluorinated organic solvents.

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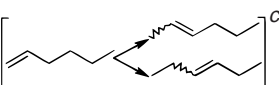(6) Rampino, L. D.; Nord, F. F. *J. Am. Chem. Soc.* **1941**, *63*, 2745.

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(11) Preparation of Pd nanoparticles encapsulated within the interior of amine-terminated, fourth-generation PAMAM dendrimer was described in ref 10. An aqueous solution of dendrimer-encapsulated nanocomposites, which contained 10 μmol of Pd and 1 μmol of dendrimer, was purified by dialysis, concentrated to 1 mL by rotorary evaporation, and mixed with 20 mL of an ethanolic solution of poly(hexafluoropropylene oxide-*co*-difluoromethylene oxide) monocarboxylic acid (300 mg, MW 550, Aldrich Chemical Co., Milwaukee, WI). This mixture was evaporated and the product found to be selectively soluble in fluorous solvents. That the brown color resulting from the presence of the nanoparticles was found to reside exclusively within the fluorous phase and that no agglomeration of Pd was observed serve to confirm the presence of the Pd particles within the dendritic hosts. Interestingly, perfluoroalkanoic acids $CF_3(CF_2)_n$COOH ($n = 11, 17$) failed to solubilize Pd/dendrimer composites in fluorinated solvents.

(12) In the biphasic system, ∼95% of polar (e.g., vinyl acetate) and ∼85% of nonpolar (e.g., hexene) substrates/products are contained in the organic phase. Product assays were performed on combined organic fractions following extraction of the fluorous phase with pure THF.

Figure 1. Two-phase system consisting of (top phase) toluene and (bottom phase) perfluoro-2-butyltetrahydrofuran (Fluoroinert FC-75). The dark color (brown) in the bottom phase indicates that the dendrimer-encapsulated Pd nanoparticles, complexed with poly(hexafluoropropylene oxide-*co*-difluoromethylene oxide) monocarboxylic acid, are selectively extracted into the fluorous phase. No detectable color was observed in the organic phase.

Table 1. Substrate Structures and Turnover Frequencies Obtained for Hydrogenation in the Fluorous Biphasic System Described in the Text

substrate	TOF [mol H$_2$ (mol Pd)$^{-1}$ h^{-1}]	
	in biphasic mixture,[a]	with polymer-bound Pd(0) particles[e]
(allyl ether structure)	400	565
(methyl acrylate structure)	50	820[b]
(vinyl acetate structure)	10	
(cyclohexene structure)	3	122
(1,5-hexadiene/hexenes structure)[c]	20	165
(1,5-cyclooctadiene structure)	40[d]	884

[a] The substrate (10 mmol) was dissolved in THF (10 mL) and mixed with FC-75 (5 mL) containing 1.5 g of acid-terminated perfluoropolyether and the catalyst (10 μmol of Pd). The mixture was connected to a hydrogen buret and stirred vigorously. Hydrogenation was performed at room temperature and atmospheric pressure. Results are the average of at least two runs with independently prepared batches of catalyst; results obtained with different batches of catalysts were reproducible to within ~30%. [b] Butyl acrylate. [c] 1-Hexene was used as the starting material. After 15 h the reaction mixture contained *n*-hexane and 1-hexene:2-hexenes:3-hexenes in a 1:10:1 ratio. [d] Product is a mixture of cyclooctene (ca. 99%) and cyclooctane. [e] From ref 14.

These new catalysts can be used for hydrogenation of a range of unsaturated compounds, and also for isomerization of terminal alkenes (Table 1). The reaction selectivity resembles that of colloidal, rather than bulk, Pd catalysts. For instance, Hirai and co-workers found that colloidal Pd can selectively hydrogenate 1,3-cyclooctadiene to cyclooctene (yield 99.9%), while conventional Pd/C catalysts are only moderately selective (ca. 83%).[13] The unoptimized dendrimer-encapsulated catalysts yield a 99% conversion of 1,3-cyclooctadiene to cyclooctene (Table 1).

Some conclusions can be drawn by comparing the TOF values obtained using biphasic catalysis with literature data for the same reactions catalyzed by a polymer-supported Pd(0) catalyst (Table 1).[14] High values of TOFs for both catalysts are consistent with the presence of nanoparticles. The selectivity pattern exhibited by the two types of catalysts is somewhat different. The range of TOF numbers for biphasic catalysis is far greater than that for conventional polymer catalysis, which suggests the possibility of selectively hydrogenating one substrate in the presence of another. We believe that this added selectivity arises mainly from the polar nanoenvironment within the dendrimer interior in which the catalytic reactions occur. For example, the data in Table 1 indicate that more polar substrates undergo catalytic conversion faster in the biphasic system. Taking into account that the dendrimer interior is hydrophilic, one could reason that polar substrates would partition in the dendrimer interior more easily, which would promote encounters between the substrate and the surface of the catalyst. As we have previously shown, selectivity can also be influenced by the size of the substrate: for a given polarity, smaller substrates more easily penetrate the sterically crowded dendrimer surface.[9] Finally, solubility of the substrate in the fluorous phase can also affect the catalytic selectivity.

To summarize, we have described preparation of fluorous phase-soluble dendrimer-encapsulated Pd nanoparticles. The method is very general and could be applied to virtually any type of inorganic material that can be sequestered within a dendrimer interior. Moreover, the entire reaction sequence is carried out using commercially available materials, and no covalent dendrimer modification is required. The Pd/dendrimer catalysts are quite active for alkene hydrogenation. We also showed that the selectivity pattern exhibited by these new catalysts is enhanced by the local dielectric environment within the dendrimer.[15] Perhaps most importantly, however, the methodology is very simple to implement and the catalysts are easy to separate from the product and recycle. Taken together, these factors suggest that these materials are promising candidates for selective, environmentally friendly catalysis applications.

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