

## Selective Hydrogenation by Pd Nanoparticles Embedded in Polyelectrolyte Multilayers

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This communication describes the catalytic properties of nanoparticles embedded in multilayer polyelectrolyte films. The polyelectrolytes limit aggregation of the metal nanoparticles and also impart catalytic selectivity by restricting access to active sites. Size-based selectivity in hydrogenation of small alcohols reaches values as high as 24. Additionally, relative to a commercial palladium-on-alumina catalyst, the nanoparticle/polyelectrolyte system suppresses isomerization of allyl alcohol and 1-penten-3-ol during hydrogenation.

Metal nanoparticles are attractive for catalysis because their large surface area-to-volume ratio allows effective utilization of expensive metals.<sup>1,2</sup> Moreover, variation of nanoparticle size sometimes allows control over catalytic activity.<sup>3</sup> Unfortunately, however, aggregation of naked nanoparticles often prohibits tailoring of particle size.<sup>4</sup> To overcome this problem, catalytic nanoparticles have been immobilized on solid supports (e.g., carbon, metal oxides, and zeolites) or stabilized by capping with ligands ranging from small organic molecules to large polymers.<sup>5–7</sup> Recently, novel systems such as dendrimers,<sup>8</sup> block copolymer nanospheres,<sup>9</sup> and cross-linked lyotropic liquid crystals<sup>10</sup> were employed to encapsulate metal nanoparticles.

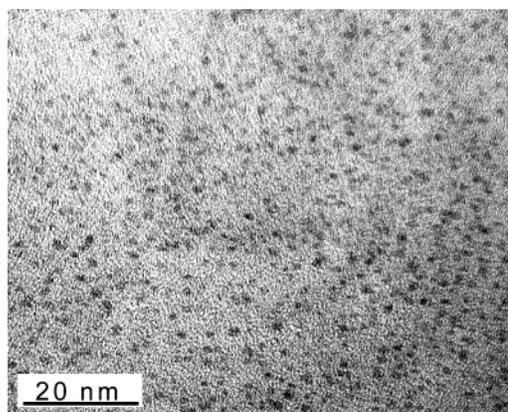
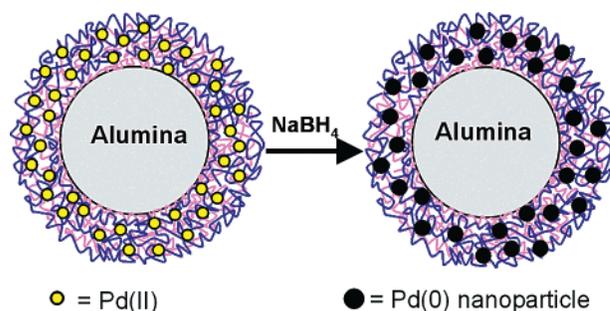
Multilayer polyelectrolyte films (MPFs) are especially attractive for encapsulating metal nanoparticles because their layer-by-layer deposition is both convenient and versatile.<sup>11–20</sup> Nearly any highly charged material can be used in alternating polyelectrolyte deposition, and careful selection of constituent polyelectrolytes should allow controlled access to nanoparticles embedded in MPFs. Using hydrogenation as an initial example, we demonstrate in this communication that MPFs are indeed capable of mediating selective catalysis by encapsulated nanoparticles.

Our preparation of nanoparticle catalysts in MPFs begins with alternating adsorption of poly(acrylic acid) (PAA) and polyethylenimine–Pd(II) complex (PEI–Pd(II)) on 150- $\mu\text{m}$  diameter alumina particles. Subsequent reduction of Pd(II) by  $\text{NaBH}_4$  yields catalytic Pd nanoparticles embedded in MPFs (Scheme 1). The alumina particles are small enough that they can be suspended in solution by vigorous stirring, but large enough so that simple filtration allows catalyst recovery.

We and others previously reported the synthesis of a variety of nanoparticles by reduction of metal ions in MPFs.<sup>16–18,21</sup> Catalysis of many organic reactions specifically requires Pd nanoparticles, and the TEM image in Figure 1 confirms that Pd nanoparticles can be produced by reduction of Pd(II) ions in PAA/PEI films. The particles have diameters of 1–3 nm and are well distributed throughout the film.

To show that encapsulation of Pd nanoparticles in polyelectrolyte films can result in selective catalysis, we hydrogenated a series of unsaturated alcohols using PAA/PEI–Pd(0) films on alumina particles as well as a commercial Pd-on-alumina catalyst. Table 1 summarizes the turnover frequencies (TOFs) for aqueous hydrogenation of allyl alcohol (1), 1-penten-3-ol (2), and 3-methyl-1-

**Scheme 1.** Formation of Nanoparticles in MPFs



**Figure 1.** TEM image of 3.5 bilayers of PAA/PEI–Pd(0) on a carbon-coated copper grid.

**Table 1.** Turnover Frequencies (TOFs) for Hydrogenation of Structurally Related Unsaturated Alcohols by Several Pd Catalysts

Substrate	TOF (moles hydrogenated per mol Pd per h)				
	5% Pd on alumina	3.5-bilayer PAA/PEI–Pd(0) <sup>a</sup>	3.5-bilayer PAA/PEI–Pd(0) <sup>b</sup>	7 bilayers <sup>c</sup>	Coated 5% Pd on alumina <sup>d</sup>
1	1300±150	727±128	435±64	141±20	33±5
2	1500±120	278±23	94±7	65±8	15±3
3	1500±100	60±15	23±4	6±1	7±1

<sup>a</sup> Hydrogenation carried out in deionized water. <sup>b</sup> Hydrogenation carried out in methanol–water (4:1 v/v). <sup>c</sup> Two bilayers of PAA/PEI–Pd(0) capped with five bilayers of PAA/PEI. <sup>d</sup> 3.5 bilayers of PAA/PEI deposited on 5% Pd on alumina.

penten-3-ol (3), which differ only in the substituents at the  $\alpha$ -carbon of the double bond. On “naked” 5% Pd-on-alumina catalyst (column 2), the reaction rates for 1, 2, and 3 are very close ( $1/2 \approx 1/3 \approx$

0.87), showing that the presence of additional alkyl groups at the  $\alpha$ -carbon does not have a significant effect on reactivity. However, for alumina coated with [PAA/PEI-Pd(0)]<sub>3</sub>PAA (3.5 bilayers of film, Table 1, column 3), the initial rate for hydrogenation of **1** is 3- and 12-fold faster than that for **2** and **3**, respectively. To further improve selectivity, we capped two bilayers of PAA/PEI-Pd(0) with five bilayers of PAA/PEI (without any Pd). With the capping layers, selectivity for **1** over **3** increases to 24 (Table 1, column 5). The presence of the capping layers decreases the hydrogenation rate for all of the alcohols, but hydrogenation of **3** is most attenuated. This likely results from very slow diffusion of **3** through the film (see below).

We also carried out the hydrogenation in a 4:1 methanol-water mixture because hydrogen and the unsaturated alcohols (particularly **2** and **3**) are more soluble in organic solvents than in water. The rate of hydrogenation of **1** is 40% lower in 80% methanol than in pure water, but selectivities are 60–80% higher (Table 1, column 4). The increased selectivity and decreased rate probably result from less swelling of the film in the methanol-water mixture. These selectivities are, in general, about 2–3-fold higher than those reported for dendrimer-encapsulated Pd nanoparticles, suggesting that the polyelectrolyte films provide highly restricted access to catalytic sites of nanoparticles.<sup>22</sup>

In practical applications of selective catalysts, such as minimizing the number of purification steps involved in organic reactions, one substrate must be hydrogenated in the presence of several impurities.<sup>23</sup> In an equimolar mixture of **1** and **2**, use of the commercial 5% Pd-on-alumina catalyst results in almost no selectivity between these substrates. However, when using the 3.5-bilayer PAA/PEI-Pd(0)-on-alumina catalyst, the conversion of **2** is only 46% when **1** is 93% converted. Selective conversion is more dramatic for the hydrogenation of a mixture of **1** and **3**, where the conversion of **3** is 14% when that of **1** is 91%. However, because the rate of hydrogenation is first-order with respect to alcohol concentration, the rate of hydrogenation of **1** decreases at high conversions, and thus it may be difficult to achieve 99% conversion of **1** with minimal conversion of other substrates. (In noncompetitive reactions, decreasing the initial concentration of allyl alcohol by a factor of 10 gave a 7-fold decrease in TOF, suggesting a reaction order of 0.85.)

To understand the mechanism behind selective hydrogenation by encapsulated nanoparticles, we examined substrate diffusion through an alumina membrane (0.02- $\mu$ m pore size) coated with seven PAA/PEI bilayers.<sup>24</sup> The ratio of the transport rate through the membrane for **1/2** was about 4, and that for **1/3** was 15. The transport experiments suggest that differential rates of transport to the Pd nanoparticles may account for selectivities. First-order reaction rates are also consistent with diffusion-limited kinetics. We hypothesize that both diffusion through PAA/PEI films and access to Pd nanoparticles rely on specific paths through the polyelectrolyte matrix. Larger substrate molecules may have fewer paths available to them, and thus they diffuse more slowly through membranes and to active sites. In addition to size issues, the greater hydrophobicity of the larger alcohols may also limit their access to hydrophilic transport pathways.

Coating of the commercial catalyst with 3.5 bilayers of PAA/PEI resulted in a selectivity of 5 for hydrogenation of **1/3** along with a  $\sim$ 40-fold reduction in the rate of hydrogenation of **1**. (Table 1, column 6). These results are consistent with diffusion-based

selectivity, but they suggest that there are differences in transport pathways to the commercial catalyst and the embedded nanoparticles.

Substrate isomerization is a common but unwanted process in hydrogenation, and in some cases, this side reaction is even dominant over hydrogenation.<sup>25</sup> Minimization of isomerization is thus desirable to improve the yield of hydrogenation reactions. Hydrogenation of **1** with polyelectrolyte-encapsulated Pd nanoparticles produces 60% less acetone than does hydrogenation with the commercial Pd catalyst at similar yields. Similar decreases in isomerization were observed with substrate **2**.

In conclusion, layer-by-layer deposition of PAA and PEI-Pd(II) on alumina and subsequent reduction of Pd<sup>2+</sup> is a versatile method for synthesizing immobilized Pd catalysts. The polyelectrolyte matrix stabilizes the particles, introduces selectivity, and significantly decreases unwanted isomerization. Further exploitation of the versatility of polyelectrolyte films should increase selectivity in hydrogenation as well as other reactions.

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**Supporting Information Available:** Procedures for hydrogenation reactions, synthesis of nanoparticle-containing MPFs, TEM, and determination of the amount of Pd in different catalysts as well as SEM images of commercial and nanoparticle-based catalysts (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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