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Catalytic Pd Nanoparticles Synthesized Using a Lyotropic Liquid Crystal Polymer Template

Julia H. Ding and Douglas L. Gin*

Department of Chemistry, University of California,
Berkeley, California 94720-1460

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Stabilized clusters and colloids of noble metals such as Pd with nanometer-scale dimensions are of particular interest as catalysts for organic and inorganic reactions.[1] It is well-known that the per-atom catalytic efficiency of metal clusters and colloids often increases as the cluster size decreases. However, the probability of cluster aggregation also increases as particle size is reduced.[2] To prevent aggregation, metal nanoparticles are often synthesized in the presence of stabilizers which adsorb to the particle surface, prevent agglomeration, and help control particle size.[3] For example, catalytically active Pd nanoparticles have been successfully synthesized in the presence of ligands,[4] functionalized polymers,[5] and surfactants.[6] One of the caveats with stabilizers is that strong adsorption to the nanoparticle active sites may diminish catalytic activity.[3] An alternative method for generating stabilized metal nanoparticles involves synthesizing them in or on nanoporous supports, which help define particle size and serve to immobilize the resulting particles. For example, Pd nanoparticles have been synthesized on carbon[7] and metal oxide supports,[8] on layered clays,[9] and in zeolite cages.[10] More recently, templates such as dendrimers,[3] block copolymer micelles,[11] and mesoporous sieves[12] have been used as the support material. Herein, we present a new strategy for synthesizing Pd nanoparticles with both good stability and catalytic activity by using a cross-linked lyotropic liquid crystal (LLC) assembly as an organic template. Initial studies on the resulting Pd-loaded materials show high product selectivity in the hydrogenation of benzaldehyde and high catalytic activity in the Heck olefination of aryl halides.

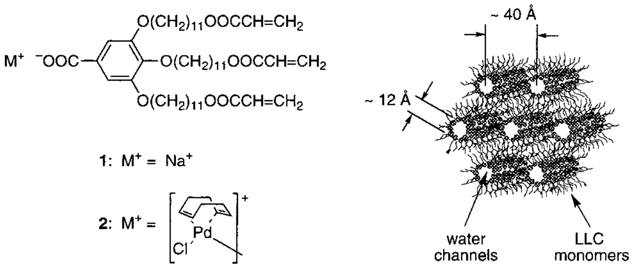

Figure 1. The structure of LLC monomers, **1** and **2**, and the inverted hexagonal phase.

Recently, we developed a method for generating nanoporous polymer networks by cross-linking amphiphilic monomers such as **1** in the inverted hexagonal LLC phase with retention of phase microstructure (Figure 1).[13] Since these cross-linked networks have close-packed cylindrical channels with essentially monodisperse diameters, it was thought that they might make ideal templates for the formation of catalytically active Pd nanoparticles to afford a new type of size-selective heterogeneous catalyst. In addition, the ionic headgroups in the walls of the nanochannels might also serve to modulate or modify the reactivity and/or selectivity of the nanoparticles formed inside. In an initial effort to put Pd into the nanochannels, a Pd(II) salt of **1** was synthesized via ion exchange with dichloro(1,5-cyclooctadiene)palladium(II) in acetonitrile.[14] Although the resulting monomer (**2**) formed the inverted hexagonal phase with 10 wt % water and 2 wt % photoinitiator (2-hydroxy-2-methylpropiophenone), UV irradiation did not result in a cross-linked matrix. Instead, reduction of the Pd(II) to Pd(0) by the generated radicals occurred,[15] accompanied by the loss of order in the material. Attempts to cross-link the LLC monomer using an excess of photoinitiator relative to Pd(II) were also unsuccessful.

To incorporate Pd atoms into the LLC polymer template, ion exchange was performed on the cross-linked inverted hexagonal phase of sodium salt **1** rather than trying to polymerize **2** directly. Up to 95% exchange of Pd(II) for Na^+ was achieved by stirring the powdered polymer of **1** with a 0.026 M acetonitrile solution of dichloro(1,5-cyclooctadiene)palladium(II), as assessed by elemental analysis. The resulting pale

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(14) The structure of **2** was deduced from ^1H NMR analysis, which revealed a stoichiometric amount of 1,5-cyclooctadiene in the compound. See Supporting Information for details.

(15) UV irradiation (365 nm, 1600 $\mu W/cm^2$) of an inverted hexagonal phase of **2** without added photoinitiator did not generate black Pd(0) particles.

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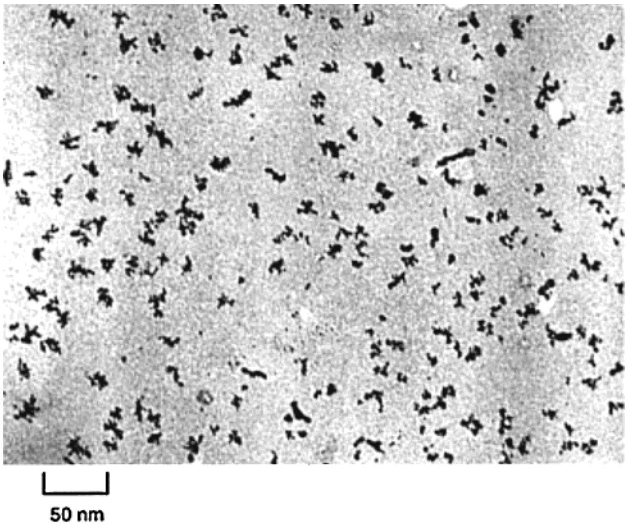

Figure 2. TEM photograph of the Pd nanoparticle composite after H_2 reduction.

yellow Pd(II)−LLC polymer maintains the inverted hexagonal structure, as confirmed by X-ray diffraction (d_{100}, 34.6 Å; d_{110}, 20.0 Å; d_{200}, 17.3 Å). To generate catalytically active Pd(0) particles in the matrix, the Pd(II)−LLC polymer was reduced with hydrogen gas to afford a shiny black material containing up to 8.35 wt % total Pd. Powder X-ray diffraction of the resulting material revealed that the order in the system disappeared upon reduction of the Pd(II) ions in the channels. Transmission electron microscopy (TEM) showed that roughly spherical 4−7 nm diameter Pd particles are formed in the polymer matrix in a largely random spatial arrangement (Figure 2). Since the diameter of the channels in the LLC matrix is only on the order of 1.5−2 nm,[13] the formation of Pd particles larger than this value indicates that nanoparticle aggregation accompanies collapse of the ordered channel structure.

The loss of order upon Pd nanoparticle formation can be rationalized in two ways if one assumes that the LLC network is highly cross-linked at the tail ends of the assembled monomers, but the remainder of the system near the headgroups has some mobility and must rely on the noncovalent interactions of the ionic headgroups with the hydrophilic solvent to maintain the phase-segregated structure. First, the rapid growth and expansion of the Pd nanoparticles inside the nanochannels may cause the more fluid region of the LLC network near the headgroups to disorder. This would allow particle size to exceed the channel diameter until particle growth becomes physically stifled upon reaching the heavily cross-linked tail end region of the polymer. Second, the formation of less hydrophilic headgroups in the channels upon Pd reduction may also contribute to the loss of order in the system. The $(COO)_2Pd$ groups lining the hydrophilic channels are converted to Pd(0) particles and COOH groups upon H_2 reduction. The fact that the parent acid of **1** does not display any amphiphilic behavior in water (only its salts do), suggests that the weakly acidic COOH moiety does not self-ionize sufficiently in water to act as a good headgroup for formation of LLC phases. Thus, the in situ formation of COOH groups would mean the loss of the crucial ionic headgroup−solvent interactions needed to maintain the phase-segregated structure. Control experiments involving acidification of the cross-linked inverted hexagonal phase of **1** also resulted in the loss of order (as determined by X-ray diffraction). This behavior is consistent with the cross-linked LLC assembly having some mobility near the headgroups, and that good ionic groups at the organic−water interface are essential for maintaining the ordered structure even in the polymer.[16]

Although the cross-linked LLC composite loses its initial order upon Pd(0) formation, it still exhibits excellent catalytic activity for the hydrogenation of benzaldehyde and for Heck coupling. In the catalytic hydrogenation of benzaldehyde with heterogeneous Pd catalysts, partial reduction to generate benzyl alcohol exclusively is difficult to obtain, since full reduction to toluene typically occurs. For example, 10% Pd on carbon (Aldrich) reduces benzaldehyde completely to toluene in 50 min. However, our Pd nanoparticle material shows high selectivity for conversion to the benzyl alcohol intermediate under the same conditions. A 98% yield of benzyl alcohol from benzaldehyde was observed with our catalyst in 3 h. This increase in product selectivity and commensurate decrease in overall reactivity is most likely due to partial deactivation of the Pd nanoparticles via surface interactions with the carboxylate groups in the polymer.

Our motivation for studying the Heck reaction with our Pd nanoparticle composite arises from (1) the importance of the Heck reaction in organic synthesis, and (2) the limited number of heterogeneous Heck catalysts available. Although heterogeneous Pd catalysts such as Pd/C, Pd/Al_2O_3, $Pd/BaSO_4$, and Pd/SiO_2 have been applied to Heck reactions, they often suffer from several drawbacks, such as low turnover number (TON) and limited lifetimes.[11] Nanostructured Pd clusters, such as colloidal Pd[6] and Pd-grafted MCM-41,[12] have recently shown more promising activity for heterogeneous catalysis of the Heck reaction. To assess the catalytic activity of our Pd nanoparticle composite, the coupling of activated and nonactivated aryl halides with *n*-butyl acrylate or styrene was used as a test platform (Scheme 1).[17] In comparison to colloidal Pd[6]- and Pd-grafted MCM-41,[12] the composite exhibited comparable or better catalytic activity for the olefination of activated aryl halides, but at significantly lower reaction temperatures (Table 1). For example, quantitative coupling of 4-bromonitrobenzene and styrene was achieved after only 2 h at 80 °C using 0.087 mol % composite based on Pd content (Table 1). In contrast, Pd-grafted MCM-41 requires 8 h and reaction temperatures in the 120 °C range to achieve similar yields and rates with 0.1 mol % catalyst.[12] Turnover numbers (TON) as high as 1149

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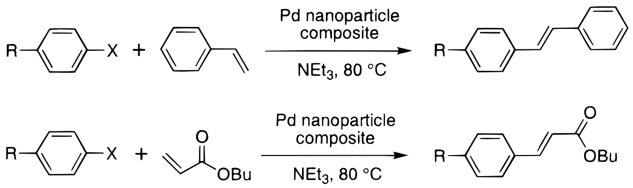
(16) Similar loss of order was observed when the cross-linked LLC phase of the Cd(II) of another carboxylate monomer was exposed to H_2S, forming CdS nanoparticles and COOH groups in situ. See: Gray, D. H.; Gin, D. L. *Chem. Mater.* **1998**, *10*, 1827.

(17) General procedure for Heck catalysis studies: To a 75-mL sealed tube were added aryl halide (0.90 mmol), styrene (1.16 mmol) or *n*-butyl acrylate (1.16 mmol), triethylamine (1.25 mmol), *n*-dodecane (10.0 μL), nitrosobenzene (2.0 mg), dimethylformamide (10.0 mL), and Pd nanoparticle composite (1.0 mg, 0.00078 mmol Pd based on wt content). The reaction mixtures were heated to 80 °C (or 110 °C for one sample) and monitored by gas chromatography using the added *n*-dodecane as an internal standard. The coupling products were purified by passage through a plug of silica gel and identified by ^1H and ^{13}C NMR spectroscopy.

Scheme 1



R	H	H	NO_2	OMe	COMe
X	Br	Cl	Br	Br	Br

Table 1. Results of the Heck Coupling of Activiated and Nonactivated Vinyl Halides with Styrene and *n*-Butyl Acrylate Using the Pd Nanoparticle Composite as a Heterogeneous Catalyst

vinyl substrate	aryl halide	mol % Pd cat.	T (°C)	t (h)	yield (%)	TON	E/Z ratio
styrene	C_6H_5Br	0.087	80	8	54	621	12/1
styrene	C_6H_5Cl	0.087	110	24	<5		
styrene	4-$BrC_6H_4NO_2$	0.087	80	2	100	1149	27/1
styrene	4-$BrC_6H_4NO_2$	0.087, reused	80	20	91	1046	
styrene	4-$BrC_6H_4COCH_3$	0.087	80	2	96	1103	21/1
styrene	4-$BrC_6H_4COCH_3$	0.087, reused	80	2	96	1100	21/1
styrene	4-BrC_6H_4OMe	0.087	80	2	17	195	
n-butyl acrylate	C_6H_5Br	0.087	80	48	21	241	5.6/1
acrylate	4-$BrC_6H_4NO_2$	0.087	80	2	100	1149	166/1

were observed for our Pd nanoparticle composite, and this high catalytic activity was preserved even after two recycles. This result suggests that for Heck olefination, the deactivating effect of the template matrix on nanoparticle activity is less severe in our case than when mesoporous silica is used as the template. Unfortunately, only moderate conversions for the coupling of nonactivated aryl halides with styrene or *n*-butyl acrylate were observed with our system, similar to that observed using colloidal Pd[6]- and Pd-grafted MCM-41[12] as catalysts. The lower isolated yields for the coupling of nonactivated aryl halides such as bromobenzene with styrene (54%) can be partially attributed to thermal polymerization of some of the styrene substrate over the course of the reaction.[18] If based on the amount of aryl halide consumed, a yield of 96% was achieved for the coupling of bromobenzene and styrene.

In summary, we have developed a LLC template-based synthesis of catalytic Pd nanoparticles. A new type of Pd nanoparticle composite was prepared by ion exchanging Pd(II) into the ionic channels of the cross-linked inverted hexagonal phase and subsequently reducing the Pd(II) to Pd(0) with H_2. The resulting composite contains Pd particles ranging from 4 to 7 nm in diameter and exhibits high catalytic activity with respect to hydrogenation and Heck coupling. Although this new template approach was initially demonstrated with Pd, the concept can be applied to other transition metals or lanthanides to produce nanostructured metal ion composites and nanoparticles. For example, irreversible near-quantitative ion exchange of Cu(II) and Zn(II) into cross-linked inverted hexagonal phases of **1** has already been achieved using this technique. We are currently investigating the metal binding properties of the nanostructured organic matrices, as well as the properties of the metal clusters subsequently formed inside.

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Supporting Information Available: Experimental procedures for the synthesis, polymerization, and Pd(II) exchange of **1**; the subsequent reduction of the cross-linked Pd(II)-LLC composite; and the catalytic hydrogenation of benzaldehyde with the catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Polystyrene oligomers were isolated from precipitation of these reaction mixtures.