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Water-soluble platinum and palladium nanoparticles modified with thiolated β-cyclodextrin†

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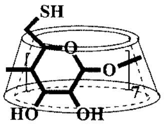
Pt and Pd nanoparticles can be modified with surface-attached cyclodextrin receptors leading to water-soluble materials that exhibit catalytic activity for the hydrogenation of allylamine.

The modification of metal[1] and semiconductor[2] nanoparticles with organic monolayers has become a very fruitful and active field of research in modern chemistry. An attractive aspect of recent developments in this area is that the final materials may exhibit combined properties from their inorganic nuclei and their organic surfaces. Our group is particularly interested in the modification of metal nanoparticles (metal clusters or colloids) with organic monolayers prepared with suitable, synthetic molecular hosts. We have recently reported several examples illustrating the use of cyclodextrins (CDs) for the modification of gold colloidal[3] or cluster[4] particles. In this report, we demonstrate the surface attachment of CDs to platinum and palladium nanoparticles that catalyze the hydrogenation of allylamine. As opposed to classical Pt and Pd catalytic materials, these novel nanocomposites are soluble in aqueous media and can be easily recovered by precipitation with ethanol.

Ulman and coworkers have recently reported the preparation of platinum nanoparticles protected with alkanethiol monolayers.[5] Inspired by this report, we decided to adapt our published procedure for the preparation of CD-modified gold clusters[4] to the synthesis of Pt and Pd nanoparticles derivatized with chemisorbed CD hosts. To this end, solutions of $PtCl_4^{2-}$ or $PdCl_4^{2-}$ sodium salts in DMSO–H_2O were readily reduced with BH_4^- in the presence of *per*-6-thio-β-cyclodextrin[6] (HS-β-CD, see structure below), leading to the isolation of dark precipitates.‡ These materials show FTIR spectra which are very similar to that exhibited by free HS-β-CD, indicating the presence of the thiolated CD in the dark solids (ESI, Fig. S1†). Furthermore, close inspection of these IR spectra reveals that the weak S–H stretching peak at *ca.* 2560 cm^{-1}, which is clearly visible in the spectrum of free HS-β-CD, disappears in the spectrum of the dark precipitates collected from the reduced Pt and Pd complex solutions. This is consistent with the anticipated conversion of the H–S bonds in HS-β-CD to metal–thiolate bonds as the CD host chemisorbs on the surface of the metal nanoparticles.[3b] ^{1}H NMR spectroscopy also provides experimental evidence that supports the presence of HS-β-CD in the dark precipitates. However, the proton resonances from the CD receptors appear as broad peaks, a result of their relative proximity to the metal particles.[4,7] These spectroscopic features must result from the presence of HS-β-CD molecules attached to the metal nanoparticles, since any free HS-β-CD molecules were washed away before spectroscopic analysis.‡



HS-β-CD

TEM measurements recorded on the precipitates collected from the reduction of the Pt (or Pd) complex in the presence of HS-β-CD verified that these solids materials are composed of metal particles with dimensions in the nanometer range. Typical TEM images are shown in Fig. 1 and histograms showing the particle size distributions (obtained from individual measurements on at least 100 particles) are given as ESI (Fig. S2).† The average diameters were 14.1 ± 2.2 and 15.6 ± 1.3 nm for the Pt and Pd particles, respectively. Both the Pt and Pd nanoparticles exhibit limited polydispersity and their sizes fall clearly into the colloidal particle domain.

All these results clearly indicate that the derivatization of the Pt and Pd nanoparticles with surface-attached, thiolated β-CD receptors proceeds smoothly, yielding reasonably monodisperse, CD-modified Pt (or Pd) colloidal particles. Unlike modification with alkanethiols,[5] which passivates the particle surfaces and renders them catalytically inactive, we anticipated that these CD-covered Pt (and Pd) nanoparticles will exhibit catalytic activity. Therefore, in order to substantiate this hypothesis, we selected the hydrogenation of allylamine as a

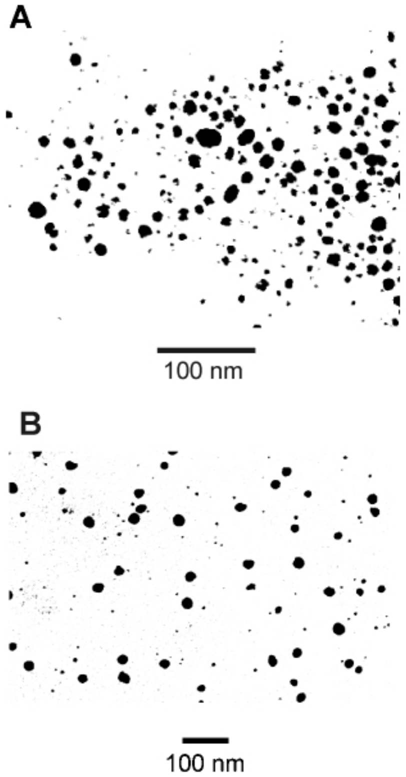


Fig. 1 TEM images of (a) CD-modified Pt nanoparticles and (b) CD-modified Pd nanoparticles.

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† Electronic supplementary information (ESI) available: Fig. S1 (FTIR spectra) and S2 (size distribution histograms). See http://www.rsc.org/suppdata/cc/b0/b002423f/

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Table 1 Percentage conversion from allylamine (1.8 mmol) to propylamine under 1.0 atm H_2(g) at room temperature in D_2O solution (2.0 mL)

Catalyst	Amount/mg	*t*/h	Conversion (%)
CD-mod. Pt	10	6	> 95
CD-mod. Pd	10	6	100
None	—	6	0
CD-mod. Pt	5	1	10
CD-mod. Pd	5	1	30

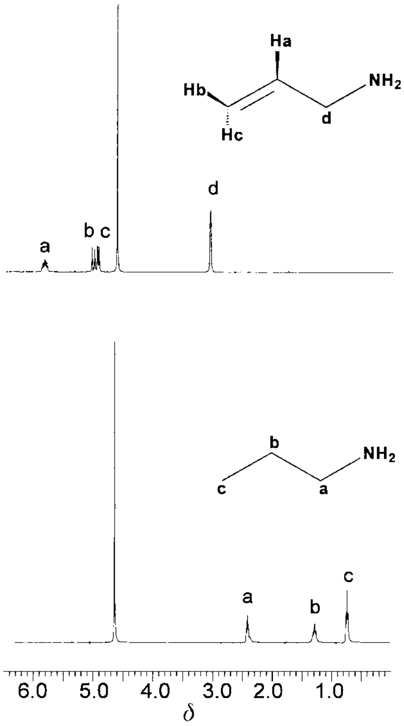

Fig. 2 ^{1}H NMR spectra of a 0.9 M solution of allylamine in D_2O containing 10 mg of CD-modified Pd colloids before (top) and after (bottom) 6 h of exposure to an H_2(g) atmosphere at 760 mm Hg.

straightforward test reaction. Our experimental results clearly verified the activity of these nanoparticles as 'homogeneous' catalysts[8] (Table 1). Under the surveyed reaction conditions,‡ both CD-modified Pt and Pd colloids catalyzed the hydrogenation of allylamine to propylamine. In a set of experiments, using 10 mg of each catalyst and 6 h reaction time, the surface modified Pt and Pd colloids achieved full conversion. In a second series of experiments, using 5 mg of each catalyst and a shorter reaction time of 1 h, the CD-modified Pd nanoparticles were more efficient than the CD-modified Pt nanoparticles. As an illustrative example, Fig. 2 shows the ^{1}H NMR spectra recorded before and after 6 h of hydrogenation catalyzed by 10 mg of the CD-modified Pd nanoparticles. We should note here that both types of CD-modified metal nanoparticles were soluble in the reaction medium and could be easily recovered at the end of the reaction by precipitation with ethanol.

In conclusion, we have demonstrated that the surface modified Pt and Pd colloidal particles reported in this work are active catalysts for the hydrogenation of allylamine in aqueous solution. These novel materials may find applications in 'green chemistry' and, perhaps, lead to 'selective' catalytic activity,[9] modulated by the molecular recognition properties of the surface-attached hosts. We are currently working towards this important goal.

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Notes and references

‡ *Preparation of modified metal colloids*: a DMSO–H_2O (1 : 4 v/v) solvent mixture was used to dissolve the metal complex. A sample of 0.125 mmol of Na_2PtCl_4 (or Na_2PdCl_4) was dissolved in 20 mL of the solvent mixture and placed in a 100 mL round bottom flask under vigorous stirring. Another 20 mL aliquot of solvent containing 12.5 mg (0.0096 mmol) of HS-β-CD and 75.5 mg (40 mmol) of $NaBH_4$ was prepared and carefully homogenized. The latter solution was added through an addition funnel to the metal complex solution, while maintaining the stirring rate. The reaction mixture was allowed to run its course overnight. After this, 10–15 mL of absolute ethanol was added to precipitate the metal particles. The dark precipitate was collected by centrifugation and washed several times, first with DMSO to remove free HS-β-CD and then with ethanol to remove the DMSO. Complete removal of the thiolated cyclodextrin was verified by thin layer chromatography (TLC). Once this was achieved, the sample was dried under vacuum at 60 °C during 24 h. The resulting dried powder was submitted for characterization by spectroscopic analysis or transmission electron microscopy (TEM) and used in the catalytic experiments.

Catalytic experiments: the CD-modified Pd and Pt colloids prepared in this work were tested for catalytic activity under identical reaction conditions. A solution of a measured amount of the catalyst in 2 mL of D_2O was stirred in a 5 mL peak-shaped flask and saturated with hydrogen gas for 10 min. Allylamine (136 μL, 1.8 mmol) was added with a microsyringe and a ^{1}H NMR spectrum was recorded just prior to the hydrogenation reaction. The flask was then sealed with a rubber septum under a hydrogen atmosphere (760 mm Hg) and left for the selected reaction time. At the end of this time, another ^{1}H NMR spectrum was recorded to monitor the extent of conversion from allylamine to propylamine.

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8 The term *homogeneous* catalyst is usually reserved for molecular species. We use this term liberally in order to emphasize the soluble character of these Pt and Pd nanoparticles. These systems lie along the borderline between homogeneous and heterogeneous catalysts as a natural reflection of their colloidal character.

9 For a recent example of novel Pt- and Pd-based catalysts that exhibit some degree of selectivity, see: M. Zhao and R. M. Crooks, *Angew. Chem., Int. Ed.*, 1999, **38**, 364.