Enhanced stability of charged dendrimer-encapsulated Pd nanoparticles in ionic liquids†

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Highly stable dendrimer-encapsulated Pd nanoparticles in ionic liquids were prepared for the first time by using charged PAMAM dendrimers as templates, which could maintain hydrogenation efficiency for up to at least 12 recycles.

One of the characteristic features of dendrimers is the presence of nano-scaled internal cavities, which can host organic molecules[1] and metal nanoparticles for applications in many areas such as catalysis.[2,3] For instance, dendrimer-encapsulated nanoparticles (DENs) have been shown to be considerably active for hydrogenation[4–7] and carbon-coupling[4,5,8–10] reactions. By using partially quaternized poly(amidoamine) (PAMAM dendrimers) as templates, highly stable Pd and Pt nanoparticles encapsulated in dendrimers with monodispersion were possibly prepared in aqueous solution.[11] Crooks *et al.* reported that dendrimer-encapsulated Pd nanoparticles (Pd DENs) are effective for the reduction of olefins in aqueous,[6,7,10] organic,[5,12] and fluorous[5,13] solvents. Although there are intensive studies on the stability of DENs catalysts, much work is still needed to understand the dominant forces that stabilize the DENs catalysts, especially in ionic liquid (IL) media. The use of ILs as novel reaction media offers a convenient solution to both the solvent emission and the catalyst recycling problem.[14,15] Much of the recent studies suggested imidazolium ILs stabilize nanoparticles electrostatically and by coordination involving the imidazolium cations.[16] Dupont *et al.* reported that ILs are not only ideal for the generation of recyclable biphasic hydrogenation systems but also a suitable medium for the preparation and stabilization of transition-metal nanoparticles.[17] Recently, a combination of imidazolium functionalized ionic multi-walled CNT (IL-*f*-MWCNT)-supported nanoparticles with an IL was reported as a new recyclable IL-based catalytic system.[18] Herein, we investigate the underlying forces that stabilize Pd DENs in IL media and their biphasic catalytic performance of hydrogenation.

Preliminary experiments manifested that conventional ILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), had weak power to dissolve PAMAM dendrimers such as G4-OH. By contrast, a more polar IL, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C_2OHMIM][BF_4]), could dissolve PAMAM G4-OH well.[19] With PAMAM G4-OH as template and the molar ratio of PAMAM G4-OH to Pd at 2 : 40, the Pd DENs in [C_2OHMIM][BF_4] could be reused two times for the hydrogenation of styrene in high conversion (see Fig. 1S, ESI†). After the third run, however, the activity diminished upwards of 60% loss in styrene conversion due to the agglomeration of Pd DENs. It has been suggested that the repulsive electrostatic interactions between positively charged dendrimers play an important role in preventing agglomeration of metal nanoparticles in aqueous solution.[11] We reasoned that charged dendrimers could be stabilized in the same way in the IL [C_2OHMIM][BF_4]. Based on this consideration, we prepared low-generation dendrimers with negatively charged functional groups on their peripheries. The number of negatively charged groups could be adjusted by controlling the pH value of the solution. With this type of dendrimers as stabilizers, Pd nanoparticle catalysts prepared at the optimum pH catalyzed the hydrogenation of styrene up to six runs with the conversion of styrene $>90\%$ (see Fig. 2S, ESI†). It is obvious that the charges of dendrimers has a direct effect on preventing aggregation and hence stabilization of Pd nanoparticles. For example, the carboxylic-terminated G1.5-COOH dendrimer prepared by the saponification of corresponding G1.5-$COOCH_3$ were partially deprotonated at pH 3.6, forming dendrimer moieties with different charges (see Synthesis of PAMAM dendrimers and Fig. 6S-d in ESI†). These dendrimer molecules could be functioning as Pd nanoparticle stabilizers by using the neutral branches close to the Pd nanoparticles while the charged ones lie away from the Pd nanoparticles. When the catalysts dissolved in [C_2OHMIM][BF_4], they were stable enough due to the repulsive forces from like-charged particles. At lower pH, however, the number of charged branches decreased resulting in weak repulsive forces between like-sign charged Pd nanoparticles multidendrimer assemblies. By contrast, at higher pH, nearly all the branches of dendrimers were charged and the dendrimer molecules were hard to complex to the Pd nanoparticles because of strong repulsive forces between them. Consequently, the Pd nanoparticle catalyst was only well stabilized at an optimal pH. From the above results, we proposed a model for catalysis of Pd particles stabilized by this type of low-generation charged dendrimers (see Fig. 3S, ESI†).

It is known that metals can be encapsulated into the interior of higher-generation dendrimers.[2,5,20] Thus we speculate that the Pd nanoparticles might be stabilized by a single charged dendrimer as the generation of the dendrimer is increased. By

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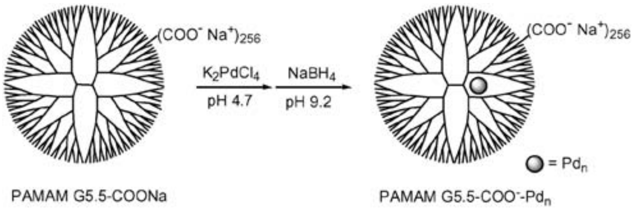

Scheme 1 Formation of carboxylate-terminated PAMAM G5.5-COO$^-$ encapsulated Pd nanoparticles (Pd DENs).

this way, metal nanoparticles encapsulated in the interior of higher generation dendrimers with charged functional groups on their peripheries will be very stable because of repulsive forces from like-sign particles and this type of DENs can be applied in IL biphasic systems for the recovery and recycling of DENs catalysts. We then carried out the template synthesis of carboxylate-terminated PAMAM G5.5-COO$^-$ encapsulated Pd nanoparticle catalysts (Scheme 1). The procedure used to prepare Pd DEN catalysts has been previously reported.[7] The total molar amount of Pd used for each hydrogenation reaction was maintained constant for all experiments, but the ratio of Pd to dendrimer was varied to yield Pd DENs having different sizes. Specifically, Pd DENs containing an average of 50, 100 and 150 Pd atoms (G5.5-COO$^-$-Pd$_n$, where n is the average number of atoms per particle) were synthesized.‡ Fig. 1 displays TEM images and particle size distributions of Pd nanoparticles encapsulated in G5.5-COO$^-$. The images indicated that these particles were well separated, which was a likely consequence of the high electrostatic charge on the host dendrimers, and that they were nearly monodisperse in size. The mean diameters, standard deviations (1σ) and calculated (in parentheses) diameters for the G5.5-COO$^-$-Pd$_{50}$, G5.5-COO$^-$-Pd$_{100}$ and G5.5-COO$^-$-Pd$_{150}$ were 1.9 ± 0.3 (1.2), 2.0 ± 0.3 (1.4), and 2.2 ± 0.2 (1.6) nm, respectively. Note that all these measured sizes were significantly larger than expected using the equation $n = 4\pi r^3/3V_g$ where n is the number of Pd atoms, r is the nanoparticle radius and V_g is the volume of one Pd atom (15 Å^3).[7] However, the results were consistent with those for Pd DENs prepared within hydroxyl-terminated PAMAM dendrimers such as G4-OH.[6]

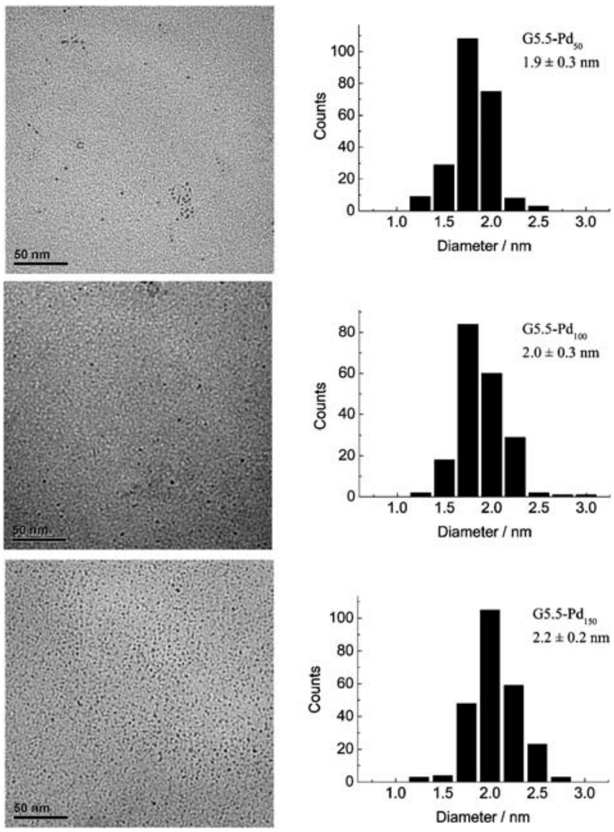

Fig. 1 TEM micrographs and particle-size histograms of G5.5-COO$^-$-Pd$_n$ DENs.

To further clarify the properties of G5.5-COO$^-$-Pd$_n$, their electrophoretic mobilities were measured using the capillary electrophoresis (CE) (see Fig. 5S, ESI†). The pH value of sample solutions was adjusted to 9.18 to ensure complete ionization of the dendrimer carboxyl groups. Compared with the electropherogram for G5.5-COO$^-$ with a mobility peak at 3.3 cm^2 V^{-1} s^{-1} × 10^{-4}, a new peak for the G5.5-COO$^-$-Pd$_n$ samples appeared at lower mobility value. If a simple charge/(mass)$^{2/3}$ calculation was performed,[21] the G5.5-COO$^-$ sample should be expected to have a higher theoretical electrophoretic mobility (based on formal charge) than G5.5-COO$^-$-Pd$_n$. We then reasoned that the new peaks at mobility of 2.6, 2.4 and 2.3 cm^2 V^{-1} s^{-1} × 10^{-4} corresponded to G5.5-COO$^-$-Pd$_{50}$, G5.5-COO$^-$-Pd$_{100}$ and G5.5-COO$^-$-Pd$_{150}$, respectively. The more Pd particles embedded in the interior of G5.5-COO$^-$, the lower the mobility the G5.5-COO$^-$-Pd$_n$. Since slab-gel electrophoresis offers high resolving power, it is extremely useful and applicable to naturally monodispersed molecules such as proteins or DNA. Proteins and DNA exhibit bands on electrophoresis gels whereas most abiotic polymers that have very broad mass distributions exhibit smears.[21] By referring to the results in literature,[21,22] we can reason that a singlet in the electropherogram represents monodispersity while a multiplet represents multidispersity. The singlet CE peaks of G5.5-COO$^-$-Pd$_n$ suggest the monodispersed characteristics of G5.5-COO$^-$-Pd$_n$. In addition, the results indicated that there were free G5.5-COO$^-$ molecules in the reduced samples, which can explain the fact that the measured particle sizes (HRTEM) for G5.5-COO$^-$-Pd$_n$ are significantly larger than expected. The CE observations provided additional strong evidence that Pd nanoparticles reside in the dendrimer interior. To our knowledge, this is the first published report on the use of capillary electrophoresis as a characterization technique for DENs.

The catalytic behavior and the recyclability of these G5.5-COO$^-$-Pd$_n$ in [C$_2$OHMIM][BF$_4$] were then performed using the hydrogenation of styrene as a probe reaction.§ After each catalytic reaction, no apparent agglomeration occurred and the separation of IL layer and products was accomplished simply by decantation. It can be seen from Fig. 2 that the G5.5-COO$^-$-Pd$_n$ in [C$_2$OHMIM][BF$_4$] maintained their efficiency for up to at least 12 recycles. The TEM images of the G5.5-COO$^-$-Pd$_{150}$ before and after 12 catalytic runs were similar, with an average particle size after 12 cycles of 2.2 ± 0.3 nm (see Fig. 4S, ESI†). The results implied that the G5.5-COO$^-$-Pd$_n$ were very stable in IL media. Presumably, the charges on the periphery of carboxylate-terminated PAMAM dendrimer play an important role in the stability of G5.5-COO$^-$-Pd$_n$ in the IL. Also, adopting an IL with adequate polarity as the reaction medium might be undoubtedly necessary.

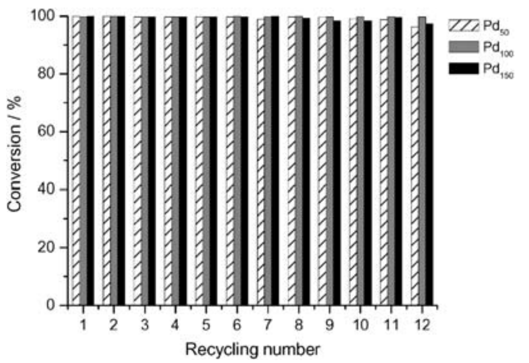

Fig. 2 Catalyst recycling in the hydrogenation of styrene by G5.5-COO^--Pd_n in [C_2OHMIM][BF_4] at 323 K and 0.5 MPa of H_2 for 180 min (molar ratio of styrene to Pd = 500).

In summary, we have found for the first time that the charges on the periphery brought about the enhanced stability of DENs in ILs. The negatively charged PAMAM G5.5-COO^--Pd_n in [C_2OHMIM][BF_4] maintained their hydrogenation efficiency for up to at least 12 recycles. Characteristic studies by TEM and CE provided strong evidences that Pd nanoparticles resided in the dendrimer interior before and after the catalytic runs. Like charged dendrimers, natural enzymes are also charged macromolecules. The knowledge gained in this study might be applied to practical applications for enzyme recycling in IL biphasic systems. Such research is currently underway and progress will be published in due course.

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Notes and references

‡ *General procedure* for the preparation of Pd nanoparticle catalysts: For preparation of higher generation dendrimer encapsulated Pd nanoparticles (Pd DENs), dendrimer aqueous solution (G5.5-COO^-, 0.1 μmol; G4-OH, 0.5-3 μmol) was added to 1.0 mL of 0.1 mol L^{-1} acetate buffer solution, and was purged with Ar for 0.5 h. Then, 5 μmol of K_2PdCl_4 was added. The mixture was stirred at room temperature for about 1 h followed by dialysis overnight. The Pd complex was reduced with 2 mg of $NaBH_4$ in 0.5 mL of water. 1.0 mL of [C_2OHMIM][BF_4] was added and the mixture was then evaporated in vacuum at 323 K for >3 h.

For preparation of low-generation dendrimer stabilized Pd nanoparticle catalysts, carboxylate-terminated G1.5-COO^- aqueous solution (8 μmol) was added to 1.0 mL of deionized water, and was neutralized by 0.1 mol L^{-1} HNO_3 to about pH 7. K_2PdCl_4 solution (5 μmol) was added and the pH value of the mixture was adjusted to the desired value. The mixture was stirred at room temperature for about 1 h followed by reduction with 2 mg of $NaBH_4$ in 0.5 mL of water. 1.0 mL of [C_2OHMIM][BF_4] was added and the mixture was then evaporated in vacuum at 323 K for >3 h.

§ *Typical procedure* of catalytic hydrogenation: The catalyst solution and 0.50 mL of styrene were introduced into a stainless steel autoclave. The autoclave was flushed three times consecutively with high purity hydrogen. The autoclave was then filled with hydrogen to the desired pressure. The reaction mixture was stirred at 800 rpm at 323 K for the required time. The reaction was quenched by putting the reactor in an ice/water bath. The reactants in the upper layer and the catalyst in the lower layer were separated by decantation. The organic phase was analyzed with a gas chromatograph equipped with an FID and a capillary column (SE-30, 30 m × 0.32 mm × 0.25 μm). The residual reactant mixture in the IL phase was removed in vacuum at 323 K for >1 h. The new cycle was restarted by addition of fresh substrate. This process was repeated 11 times.

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