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Tetraglyme-mediated synthesis of Pd nanoparticles for dehydrogenation of ammonia borane†

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Palladium nanoparticles (PdNPs) were conveniently prepared in tetraglyme (TG) solution using a variety of palladium precursors. At 140 °C, TG promoted Pd₃(OAc)₆ to produce irregular shaped PdNPs with an average size of 4 nm. When these PdNPs were re-dispersed in TG and used for the dehydrogenation of ammonia borane (AB) at 85 °C, remarkably enhanced catalytic performance was achieved to release 2.3 equiv. of H₂ in 1 h.

The development of chemical hydrogen storage materials for vehicular applications has been a long haul.¹ Among the materials that have been examined, NH₃·BH₃ (AB) has been considered a potential candidate due to its high hydrogen storage capacity of 19.6 wt%.² To meet the material-based gravimetric target set by the USDOE for 2015, 9 mat. wt%,³ the development of high performance dehydrogenation catalysts of AB is indispensable. First, many homogeneous catalysts⁴ have been developed to meet the DOE target, because they are known to be convenient and effective in extracting hydrogen from AB. However, despite their wellunderstood and superb activities, homogeneous catalysts were not stable during AB dehydrogenation and lost their initial activities by forming insoluble metal particles.⁵ Also, they suffer from various pertinent problems such as catalyst recovery from spent fuels and the sacrifice of the storage capacity due to the excessive use of solvents.⁶ If further research is successful in finding new catalyst systems that provide practical rates and gravimetric and volumetric storage capacities, it will likely be necessary to 'heterogenize' these catalysts in order to develop a controllable hydrogen generation system.⁷ Because of the advantages of heterogeneous catalysis, current research has been directed toward the development of heterogeneous catalysts possessing high activity. It should be noted that heterogeneous catalysis on AB hydrolysis has been reported by Xu et al.,⁸ Ramachandran and Gagare,⁹ and Jagirdar et al.,¹⁰

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which utilized noble or basic metals such as Pd, Rh, Ru, Cu, Ni, and Co. The hydrolysis of AB in the presence of a heterogeneous catalyst can provide up to three equivalents of hydrogen per mole of AB at room temperature at satisfactory

rates. In the first report of metal-catalyzed amine-borane dehydrogenation, Roberts and coworkers heated a solid mixture of Pd on charcoal and t-BuMeHNBH₃ at 120 °C to give the aminoborane, t-BuMeNBH₂, which was converted to the cyclic dimer.¹¹ Manners et al. also demonstrated that heterogeneous Rh(0) colloids (1.5 mol%) activated AB releasing 2 equiv. of H₂ to form borazine in tetraglyme at 45 $^{\circ}$ C in 72 h.⁵ Sneddon et al. investigated the dehydrogenation of AB in ionic liquids such as bmimCl, including the use of heterogeneous catalysts. The use of 0.5 mol% Pd/C resulted in a modest increase in the reaction rate; a loss of 4.6 wt% H2 after 2.5 h at 85 °C was observed.¹² Özkar et al. recently reported that in situ-generated palladium(0) nanoclusters, stabilized by oleylamine, are highly active heterogeneous catalysts in the dehydrogenation of AB at room temperature.¹³ In addition, Burrell et al. reported on the dehydrogenation of AB assisted by heterogeneous catalysts in diglyme at 70 °C, where Pt-, Pd-, and RuNPs demonstrated catalytic activity towards the dehydrogenation of AB, with the strongest catalytic activity being observed for the PtNPs. In this case, 1.5 equiv. of H₂ was extracted within 30 min and close to 2 equiv. of H₂ after 6 h.^{6b} However, several issues still greatly influence the catalytic release of H₂ from AB; for instance, the reaction rates and maximum quantity of H₂ still need to be further increased.

During the homogeneous catalysis of AB dehydrogenation by palladium precursors,^{4f} we observed that tetraglyme (TG) used as the AB solvent¹² functioned as a multifunctional reagent for the formation of Pd nanoparticles (PdNPs). It was found that the TG-mediated route not only produced sizecontrolled PdNPs, but also stabilized them against conglomeration without the need for additional stabilizers. Thus, we present a facile synthesis of TG-mediated PdNPs in the absence of any extra reducing agent or capping agent.

Among the various palladium precursors that were tried, $Pd_3(OAc)_6$ (1) showed the best TG solubility and therefore was used for the synthesis of the NPs (see the experimental section).¹⁴ At room temperature, 1 was quantitatively converted to PdNPs by multiple actions of TG: reduction followed by stabilization.

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Fig. 1 (A) UV-Vis absorbance spectra for **1** dissolved in TG at 25 °C after (a) 0 min, (b) 10 min, and (c) 20 min. (B) PdNP kinetic profile for AB dehydrogenation at 85 °C and HRTEM images of the catalyst, PdNPs (inset). *Reaction conditions*: 0.123 g AB, 0.03 g TG, and 2 mol% PdNPs (0.008 g) at 85 °C.

The UV-Vis spectral changes shown in Fig. 1A(a) and (b) indicate discernible PdNP formation. Within 10 min, the 400 nm peak assigned to 1 disappeared and a new plasmonic band appeared. This corresponds to the darkening of the solution, indicating colloidal PdNP formation. After 20 min, the production of PdNPs was complete, according to the plasmonic visible spectra, which tailed out at 700 nm (Fig. 1A(c)). In the inset of Fig. 1B, the high-resolution transmission electron microscopy (HRTEM) images of the PdNPs (2) prepared at 25 °C demonstrate that the Pd atoms are clustered and have an average diameter of 6.4 nm. The result suggests the possibility that commercial TG samples contain small amounts of hydroxy-containing impurities, some of which significantly influence nanoparticle growth (see Fig. S2 (ESI†) for details).

It was noted that the further size control of the resulting NPs might be possible by varying the temperature, because TG has a high boiling point. Fig. 2A presents the HRTEM images of the PdNP samples prepared at various temperatures and their average particle sizes. The thermal reaction of 1 in a TG solution was conducted separately at temperatures of 25 (2), 50 (3), 80 (4), 110 (5), 140 (6), 170 (7), 220 (8), and 270 $^{\circ}$ C (9) for 3 h. The graph in Fig. 2B shows the variation in



Fig. 2 (A) HRTEM images of PdNPs prepared at (2) 25 °C, (3) 50 °C, (4) 80 °C, (5) 110 °C, (6) 140 °C, (7) 170 °C, (8) 220 °C, and (9) 270 °C, scale bar = 4 nm (B). Average particle size of PdNPs prepared at different temperatures. (C) AB dehydrogenation kinetic profiles exhibited by 2–9.

the average PdNP particle size with temperature. We found that increasing the reaction temperature decreased the particle size and size distribution.

The HRTEM images show that the PdNPs formed at temperatures below 80 °C, however, are polydispersed, within a size range of 4 to 8 nm (Fig. 2A(2)-(4)). Above 140 °C (Fig. 2A(6)-(8)), burst nucleation consumed most of the precursors, leading to the formation of smaller PdNPs and a relatively narrow size distribution. However, heating above 270 °C (the boiling point of TG) decreased the binding of TG to the surfaces of the PdNPs. Consequently, larger particles with increased polydispersion were observed (Fig. 2A(9)). Fig. 2C plots the amount of H₂ generated from AB as a function of the reaction time at 85 °C. The 4.2 nm PdNPs (6) prepared at 140 °C exhibited improved catalytic activity compared to the 5.3-6.5 nm ones prepared at temperatures below 110 °C. Dramatic increases in the rate of H₂ release with these PdNPs (6) for both the first and second equiv. of H₂ were observed with the release of 1.5 equiv. of H₂ in 5 min and 2.3 equiv. of H₂ in 1 h at 85 °C, respectively. The optimum AB/TG in the semi-solid state consists of 0.123 g of AB and 0.03 g of TG with 2 mol% PdNPs (0.008 g) (see the ESI⁺ for details).

The catalytic activity of the PdNPs (6) was compared with that of a commercial Pd on carbon (Pd/C) and Pd black. The catalytic activity demonstrated by the PdNPs produced in this study was much higher than that of Pd/C or Pd black. Following the well-established nanoparticle synthesis protocol, we prepared "dodecanethiol-capped PdNPs"¹⁵ and "oleylamine-capped PdNPs"¹⁶ using dodecanethiol and oleylamine, respectively. Of the three types of PdNPs screened under the described AB dehydrogenation conditions, the TG-mediated PdNPs gave the best dehydrogenation performance. A comparison of the catalytic activities of the three types of PdNPs for AB dehydrogenation is shown in Fig. 3. The excellent performance of the TG-mediated PdNPs is attributed to the high cleanliness¹⁷ of the surface of the PdNPs and their capability of dispersion in the TG solvent.

Our method is convenient, requiring only a single chemical reagent for the synthesis of the PdNPs. We believe that the broad size distribution and irregular shape come from the weak interaction between the palladium metals and TG. Even given the larger size-distribution of the PdNPs, the easy removal of TG in our case¹⁷ granted them higher catalytic activity than the smaller size-distributed ones prepared from strongly bound surfactants. It has been suggested that the



Fig. 3 Comparison of catalytic activities for AB dehydrogenation: PdNPs (6), dodecanethiol-capped PdNPs (DT-PdNPs), oleylaminecapped PdNPs (OA-PdNPs), 10% Pd/C, and Pd black.

catalytic activity is dependent on the number of low coordination number sites available on the surface of the nanoparticles, and irregular PdNPs bear more of these sites than flatter and more faceted ones.¹⁸ If these low coordination number corner and/or edge positions are implicated as active sites for AB dehydrogenation, then their relatively higher occurrence in the PdNPs generated in this study could account for their superior catalytic performance.

During the course of the reactions, the activity of the PdNPs was observed to decrease. After catalytic dehydrogenation, a visible layer appeared to coat the catalyst. This coating was removed by simple immersion in methanol and the PdNPs retrieved from the solvent exhibited close to their original catalytic activity, which was sustainable up to the tenth cycle without any discernible catalytic loss (Table S1, ESI⁺). ¹¹B NMR analysis of the spent fuels in TG indicated the initial formation (after 5 min) of cyclic intermediates, as identified by Sneddon¹² and Shaw et al.¹⁹ (Fig S6, ESI[†]). Further dehydrogenation (after an additional interval of 25 min) confirmed the simultaneous decay of these signals and the formation of borazine and polyborazylene. LANL recently reported that one form of the spent AB fuel, polyborazylene, can be regenerated efficiently in a one-pot process by the addition of hydrazine and ammonia as appropriate digesting and reducing agents.20

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